

Piezoelectric nitride nanowires for energy harvesting and pressure sensing

Lu Lu

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UNIVERSITE PARIS-SACLAY



Nanofils piézoélectriques de nitrure pour la récupération d'énergie et la détection de pression

Piezoelectric nitride nanowires for energy harvesting and pressure sensing

Thèse de doctorat de l'Université Paris-Saclay Préparée à l'Université Paris-Sud

École doctorale n°575 Physique-et-ingénierie: électrons, photons, sciences du vivant (EOBE) Spécialité de doctorat: Electronique et optoélectronique, nano-etmicrotechnologies

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Mme Lu LU

Composition du Jury :

M Elie Lefeuvre	
Professeur, Université Paris-Sud	Président
M Guilhem Larrieu	
Chargé de recherche, LAAS CNRS	Rapporteur
Mme Guylaine Poulin-Vittrant	
Chargé de recherche, Université de Tours	Rapporteur
M Joël Eymery	
Directeur de recherche, CEA INAC	Examinateur
Mme Olga Boyko	
Maître de conférences, Sorbonne Université	Examinateur
Mme Maria Tchernycheva	
Directeur de recherche, Université Paris-Sud	Directeur de thèse
M Francois H. Julien	
Directeur de recherche, Université Paris-Sud	Co-Directeur de thèse
Mme Noëlle Gogneau	
Chargé de recherche, C2N CNRS	Invité
M Pascal Chretien	
Ingénieur de recherche, GEEPS	Invité

Thèse de doctorat



Titre : Nanofils piézoélectriques de nitrure pour la récupération d'énergie et la détection de pression

Mots clés : piézogénérateur, nitrure, nanofil, GaN, semiconducteurs piézoélectriques

Résumé : Ce travail de thèse se focalise sur l'étude de piézogénérateur à base de nanofils de GaN. L'objectif principal est de développer des nouveaux dispositifs pour la conversion d'énergie mécanique en énergie électrique pour la récupération d'énergie et la détection de déformations transitoires. Le région active des dispositifs développés consiste en des nanofils ou microfils de GaN encapsulé dans une couche polymère. Les nanofils sont synthétisés par épitaxie par jet moléculaire (EJM) tandis que les microfils sont synthétisés par épitaxie en phase vapeur aux organométalliques (EPVOM).

Trois architectures de dispositifs sont explorées: basées sur une matrice rigide, une matrice flexible, et sur un dispositif entièrement flexible. Deux dispositifs d'excitation mécanique, développés et mis en place pour les besoins de la thèse, sont utilisés pour caractériser les dispositifs piézogénérateurs. En particulier, un mode d'excitation cyclique discontinue (tapping) et un mode d'excitation cyclique continue sont utilisés pour explorer les performances électriques des piezogénérateurs dans une large bande de fréquence (de 1 Hz à 3 kHz). Basé sur ces observations expérimentales, une synthèse complète du comportement des transitoires de tension aux bornes des piézogénérateurs lorsqu'ils sont soumis à différentes déformations est faite. Un désign basé sur une diode Schottky aux sommets des nanofils et différents designs capacitifs sont comparés et leurs circuits électriques équivalents sont proposés. Les mécanismes de fonctionnement des piézogénérateurs ont été validés par des observations expérimentales.

Enfin, un processus pour fabriquer des piézogénérateurs et des capteurs entièrement flexibles a été développé et ces derniers ont été caractérisés. En particulier, la fabrication d'un dispositif flexible composé d'une matrice de pixel actif a été démontrée.

Pour le piézogénérateur rigide à base de nanofils synthétisés par EJM, la plus haute densité de puissance moyenne mesurée atteint 22.1 mW/cm³. Pour les piézogénérateurs flexibles à base de microfils synthétisés par EPVOM, la plus haute densité de puissance moyenne mesurée atteint 16.5 μ W/cm³. Le dispositif flexible montre une bonne sensibilité aux vibrations de faible amplitude et répond de façon stable à un tapotement avec le doigt. Une énergie moyenne d'environ 100 pJ peut être délivrée par ce dernier lorsqu'il est soumis à une déformation cyclique par le tapotement d'un doigt.

Title : Piezoelectric nitride nanowires for energy harvesting and pressure sensing

Keywords : piezogenerator, nitride, nanowire, piezoelectric semiconductors

Abstract : This PhD work focuses on the study of GaN nanowire-based piezogenerating devices. The main objective is to develop novel devices for mechanical-to-electrical energy conversion for energy harvesting and for detection of transient deformations. The active material of the developed devices consists of a polymer-embedded nanowire membranes containing either molecular beam epitaxy (MBE) grown GaN nanowires or metal-organic chemical vapor deposition (MOCVD) grown GaN microwires.

Three device architectures are explored, namely a piezogenerator with a rigid matrix, with a flexible matrix and a fully flexible device. Two home-made mechanical excitation set-ups are used to characterize the generators. In particular, tapping mode and continuous compression deformations are applied to explore the devices' electrical performance in a large frequency range (from 1 Hz to 3 kHz). Based on these extensive experimental investigations, a panoramic summary of the generator transient behavior under various deformation conditions are made. A Schottky diode design and different versions of capacitive design for the piezogeneration are compared, and their equivalent electrical circuits are proposed. The piezogenerators' working mechanisms are further validated by experimental investigations.

Finally, a process to fabricate fully flexible generators and sensors is developed and these flexible devices are extensively characterized. In particular, a flexible device composed of a matrix of active pixels is demonstrated.

For the MBE nanowire-based piezogenerators on a rigid substrate, the best recorded average power output density reaches 22.1 mW/cm³. For the MOCVD microwire based flexible generators, the best recorded average power output density attains 16.5 μ W/cm³. The flexible devices show a good sensitivity to ambient vibrations and respond stably to finger tapping deformations. An average energy of about 100 pJ can be delivered by the flexible device under one finger tapping gesture.

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Preface

Ambient energy harvesting (also known as energy scavenging) has attracted much attention in recent years. Contrary to traditional batteries, which have to be recharged or replaced after a certain time of usage, ambient energy harvesters can deliver energy as long as the power source is present around. This character of a harvester can be of great interest in terms of medical in-vivo devices requiring a power supply. Indeed, it is difficult and also risky to replace human-body embedded electronic devices, such as a pace-maker, due to battery exhaustion. Another case where the ambient energy harvesting bears great advantage is the powering of wireless communication networks (namely, the "Internet of Things (IoT)"). In such smart networks, a large quantity of sensing nodes are distributed. The replacement of their batteries is expensive and time-consuming. Therefore, local renewable energy sources are urgently needed.

The reduction of power consumption of the electronic devices has been another reason why energy harvesting became appealing. For instance, the energy consumption of a typical radio frequency identification (RFID) tag reading communication node is in the order of μ J [1]. A commercialized pacemaker requires for operation an energy power density in the order of μ W/cm². These amounts of energy are actually available in the surrounding environment. By choosing an adapted transducing method, it is possible to convert ambient energy into electrical power to make these devices energy-independent.

Ambient energy exists abundantly in many forms, such as solar energy, thermal energy, radio-frequency (RF) electromagnetic radiation and mechanical energy. Depending on the type of energy, ambient energy harvesters can be categorized as photovoltaic (PV) harvesters [2], thermoelectric harvesters [3], RF harvesters [4], turbine [5] and vibration energy harvesters [6]. They are chosen according to the local available power sources and can be applied in various specific scenarios.

Kinetic energy (e.g. mechanical vibrations) is a form of ubiquitous ambient energy, presenting an ideal energy source for powering localized sensor nodes or other nomad and wearable devices. The typical principles used for this type of energy harvesting include piezoelectric [7], electromagnetic [8], electrostatic [9], [10], [11] and

magnetostrictive [12] transduction. However, most of the developed kinetic energy harvesters target a stable vibration and generally work at predefined or narrow-band frequencies (usually, in a high frequency range, e.g. 1 kHz – 100 MHz for microelectromechanical systems (MEMS)). On the contrary, the environmental vibrations or human motion are usually random signals characterized by low frequencies and a large bandwidth. Different efforts have been made, in particular, to improve the harvester performance at low frequency range. Mechanical frequency up conversion mechanism [13] and the application of rotational structure [14] are introduced to make the devices more adapted to low frequency applications. Another challenge for a kinetic energy harvester is the device miniaturization. In theory [15], the output power of a given kinetic energy harvester under a given acceleration is limited by its mass and the available proof mass displacement. Hence, the reduction of the device size is not in favor of energy conversion. Besides, from the technical point of view, miniaturized devices may require a more complicated fabrication process.

As for kinetic energy harvesting through piezoelectric effect, the transduction module usually consists of a deformable mechanical structure covered by a piezoelectric thin film. The vibration of the elastic structure will induce the deformation of the piezoelectric film, thus creating an electric field. PZT is the most commonly used piezoelectric material because of its high piezoelectric coefficient and easy shape patterning through lithography and etching process. However, it is a toxic material that is not suitable for in-vivo applications. Meanwhile, although various designs of the mechanic structures have been used to reduce the device resonant frequency [16], the miniaturization of the piezoelectric harvester remains difficult.

Since the first experimental demonstration of single ZnO nanowire piezogeneration in 2006 [17], the use of low dimension piezoelectric 1D structures has become a promising alternative for kinetic energy harvesting. Thanks to their small size and high mechanical flexibility [18], more compact and light-weight harvesters are expected to be realized. In addition, it has been reported that the nanostructures of a given material share a higher piezoelectric coefficient compared to their bulk counterpart [19]. In this context, the concept of "nanogenerator" has been widely accepted. Various piezogenerators have been fabricated by integrating different types of nanowires in the past decade. Nevertheless, a systematic assessment of the fabricated devices is not easy since the results of the literature are not given in a common normative way, but strongly vary in terms of experimental conditions and

given performance indicators.

The current PhD work focuses on the fabrication and characterization of GaN nanowire-based piezogenerators. Compared to other widely explored piezoelectric nanowires, such as ZnO nanowires, GaN nanowires have shown enhanced piezoelectric properties, which have been theoretically predicted [20] and experimentally demonstrated in [21]. The used GaN nanostructures are synthesized by either plasma-assisted molecular beam epitaxy (PAMBE) or metal-organic chemical vapor deposition (MOCVD) method. Both of the techniques can offer a good material crystalline quality which is important for piezogeneration application.

Depending on the morphology of these two types of GaN nanowires, rigid and flexible piezogenerators have been fabricated. Systematic measurements have then been performed to evaluate the electrical performance of the fabricated generators under different external deformation conditions. Efforts have been made to test the devices under a large band of frequencies ranging from 1 Hz to 3 kHz. By analyzing the obtained experimental results, a comprehensive understanding of the device functioning mechanism has been achieved. Different device designs have been made and further compared, and the corresponding equivalent electrical circuits have been proposed as well.

The structure of the manuscript

The thesis consists of 6 chapters. In the first chapter, I will give a brief introduction of various piezoelectric nanowires and their corresponding growth methods. Then GaN nanowires and their piezoelectric properties will be discussed. At the end, a review of the piezogenerator state-of-the-art will be presented.

The second chapter is dedicated to a detailed introduction of the three mechanical setups that I have used to characterize the fabricated piezogenerators. An existing three-wheel bending setup has been used to characterize rigid-matrix piezogenerators and a new vertical compression setup has been designed and assembled during my PhD work to characterize soft-matrix generators and fully flexible generators. Each of the set-ups is better adapted to a specific design of the fabricated devices.

In the third chapter, I will present the study of rigid-matrix PAMBE GaN

nanowire-based piezogenerators. I will first present the MBE nanowire growth technique and then talk about the nanowire characterization. Then electric measurements of the rigid-matrix devices will be presented and discussed.

The forth chapter reports the study related to soft-matrix PAMBE GaN nanowire-integrated piezogenerator. The adapted soft-matrix design has greatly enhanced the device piezoresponse. This has enabled device testing under smaller external forces, which in turn reduced the device degradation, extended their lifetime and allowed for an extensive experimental analysis under different deformation conditions. By testing the generator under different modes of deformation, a good understanding of the device operational mechanism has been achieved. A piezogenerator integrating GaN nanowires containing AlN/GaN heterostructures has also been reported, followed by a general discussion concerning Schottky and capacitive piezogenerator design. Based on experimental results, the equivalent circuits of different types of piezogenerators are proposed and discussed thereafter. Some additional device demonstrations will be described at the end to support the proposed electrical model, opening new possibilities for the design of future devices.

The fifth chapter dwells on the fabrication and characterization of the flexible piezogenerators based on MOCVD GaN microwires. After a demonstration of a flexible device transferred on a copper foil, a new flexible generator prototype with a crossed contact design based on Kapton film will be presented in more details. The electrical performance of the new prototype has been evaluated from different perspectives, considering its future application as either an energy harvester or a force sensor. Finally, some new devices are proposed as an improvement of the prototype in terms of differentiating these two functions.

Finally, I will make a general conclusion in chapter six. Some future prospects will be traced as well.

Chapter 1

Properties of piezoelectric nanowires and piezogenerating devices based on 1D nanostructures

In this chapter, I will give a general introduction to piezogenerating devices based on 1D nanostructures. Firstly, I will present the different piezoelectric materials as well as their nanowire (NW) formation techniques. Then focus will be made on GaN nanowires, introducing their properties in terms of piezoelectric generation. Finally, some state of the art of piezogenerating devices, mainly the energy harvesters and force sensors, integrating different types of piezoelectric nanowires will be listed and discussed.

1. Piezoelectric nanowires for energy harvesting

1.1 Piezoelectricity and piezoelectric materials

Piezoelectricity describes the capacity of some materials to create an electric polarization under a mechanical constraint (direct piezoelectricity) and reversely, to be deformed when an electric field is applied to the material (reverse piezoelectricity). The first experimental demonstrations of these direct and reverse piezoelectric phenomena have been done by Pierre and Jacques Curie in 1880 and 1881. Since then, dynamic research has been carried out in this field. With the development of solid state physics and the discovery of new materials, various applications have been realized, such as microphones [22], actuators [23], force sensors [24], etc.

The nature of piezoelectric materials may be quite different. Some of them can be found in nature, such as quartz, while others were synthesized by humans. In general, the piezoelectric materials can be classified into three categories: ferroelectric ceramics, polymers and mono-crystalline semiconductors [25].

- ➤ The ceramic is one type of inorganic non-metallic materials. It may exist in crystalline, semi-crystalline or amorphous state. Among them, only the crystalline ceramic demonstrates piezoelectric properties and it belongs to the family of ferroelectric materials. The crystalline ceramic usually exists as a mixture of binary or tertiary poly-crystals, with each grain presenting a given polarization. Therefore, it is necessary to align their polarization under electric field to achieve usable macroscopic polarization. Thanks to their easy fabrication and high piezoelectric coefficients, this type of piezoelectric materials is widely used. For example, the PZT (Lead zirconate titanate, Pb[ZrxTi1-x]O₃ (0≤x≤1)) and BaTiO₃ are the most wide-spread poly-crystalline ceramics in industry.
- Polymers are defined as macro-molecules composed of a great number of \geq repetitive sub-units (one or several type of monomers) attached with covalent chemical bonds. Some of them are found to have piezoelectric properties after certain treatments. One typical type is the polymers that have an air-trapping structure, which is usually referred to as cellular polymers. After the ionization of a trapped gas under high electric field, the residual ions in the polymer surface will render the whole polymer piezoelectric. With these implanted surface charges, this type of polymers can also be used as electret. Another type of polymers that may have piezoelectric properties is a semi-crystalline polymer. They are characterized by partial folding and alignment of molecular chains upon cooling. When the folded region demonstrates a dipole and these dipoles are aligned under high electric field at high temperature (the polling process), the polymer as a whole becomes piezoelectric. The most used piezoelectric polymers of this type are the PVDF (Polyvinylidene fluoride or polyvinylidene difluoride), the parylene-C and the polyamides. Besides, if one polymer is non-piezoelectric and some piezoelectric elements have been integrated in it, the whole composite will present piezoelectricity. This polymer-based composite is hence usually used as active material for flexible piezogenerator fabrication.
- The third category of piezoelectric materials are mono-crystalline semiconductors and the majority of them belongs to the II-VI and III-V material group, for example ZnO and GaN. These mono-crystalline materials may exist in either zinc blende (cubic) or wurzite (hexagonal) form. Due to its lack of inversion symmetry, wurzite crystal has such properties as piezoelectricity and pyroelectricity. I will talk about this structure-induced piezoelectricity in more detail when describing GaN wurzite nanowires (the active material studied in this thesis) in the next

section of this chapter.

1.2 Piezoelectric nanowires

1.2.1 Size effects

In view of making a compact, light-weight and high efficiency energy source for powering nomad electronic devices, piezoelectric materials in a low-dimensional form can offer new possibilities. Therefore, various forms of piezoelectric materials (such as thin films [26], [27], nanorods [28], nanosheets [29], nanotubes [30], nanofibers [31] and nanowires [32], [33], [34], have been intensely explored and different generators have been made during the past decade. Indeed, when the material size decreases to nanoscale dimensions, several material properties may change.

For example, PZT in its bulk form is a rigid material. However, when the crystalline PZT is fabricated into thin film or nanofiber forms, it becomes less brittle [35]. This change of mechanical properties can expand its application, especially for flexible devices integration. As for the piezoelectric polymers which are already very soft, their nano-scale forms can induce a higher surface to volume ratio with the same material quantity, thus enhancing the material piezoelectricity by increasing accepting capacitance of charges.

Material	Measured piezoelectric coefficient of low-dimension nanostructures	Measured piezoelectric coefficient of a bulk material
ZnO	d ₃₃ =14.3 - 26.7 [36]	d ₃₃ = 9.93 [36]
GaN	d ₃₃ =12.4 -13.2 [19]	d ₃₃ =2.8-3.7 [38]

 Table 1-1 Comparison of piezoelectric coefficients between bulk and nanostructured materials (unit: pm/V)

In the case of the semiconductors, the size induced effects also favor their application as piezoelectric active materials. First of all, wurtzite structure is the preferred state of these materials at nanoscale. Piezoelectric nanowires, made of ZnO or III-nitrides, typically present very good crystalline quality (free from propagating defects) compared to their thin-film or bulk counterparts [39]. Thanks to their small footprint and high aspect ratio, these low-dimensional 1D structures can receive important deformations without breaking up [18], [40] and at the same time exhibit a strong deformation in response to a small external force [41]. Besides, they demonstrate a higher robustness and resistance to fatigue than 2D materials, which may further guarantee their device operation durability. In terms of piezoelectric properties, most of the publications (either theoretical or experimental) conclude that wurtzite nanowires have exalted piezoelectric coefficients compared to their bulk counterparts [19], [20], [36], [37]. Taking ZnO and GaN nanowires as an example, table 1-1 establishes a comparison of their piezoelectric coefficients in the NW and in the bulk form. As we can see, the piezoelectric coefficients of 1D nanostructures are measured to be several times higher than that of the bulk structures.

1.2.2 Nanowire synthesis techniques

In order to form 1D nanostructures, different methods can be adopted. For ceramic materials, their nanowire form can be obtained by either material deposition in pre-defined nanostructural templates [42] or by using electrospinning technique [43]. Most of the piezoelectric polymer fibers are also made through electrospinning method which is cheap and fast [44]. As for the synthesis of single crystal semiconductor nanowires, the choice of techniques is much larger. In general, their formation techniques can be divided into two categories: top-down fabrication and bottom-up synthesis.

The top-down fabrication of single crystal nanowires is a subtractive technique. By performing lithography (e.g. optical lithography (more for microwires), electron-beam lithography, nanosphere lithography) and chemical etching, the bulk material can be patterned and then turned into nanowire structures. The nanowire geometry is determined by the lithography technique resolution and the etching anisotropy and selectivity (i.e. the etching difference between the mask and etched material or between the material crystalline orientations), hence small diameter and high aspect ratio cylindrical nanowires are difficult to obtain with this method. Besides, the crystalline quality of the nanowires depends a lot on the quality of the originally used bulk or thin film material, which may be difficult to prepare or may contain defects. The etching procedure can also introduce additional defects. However, the top-down fabrication is still enticing thanks to its compatibility with standard microelectronic industry process and easy scale-up.

In contrast, bottom-up synthesis of nanostructures is an additive approach which can be conducted in either liquid phase or in gas phase. Hydrothermal liquid phase epitaxy is one of the most widely used method to fabricate nanoscale single crystals, i.e. ZnO nanowires [45], [46]. The process is simple and cheap, offering a good quality-price ratio. However, compared to other techniques, nanostructures grown by this method suffer from some contamination (e.g. high residual doping may in hydrothermally-grown ZnO NWs). In terms of vapor phase epitaxy, depending on the source gases, there exists a distinction between the hydride vapor phase epitaxy (HVPE) and the organometallic vapor phase epitaxy (OMVPE, also called MOCVD). The synthesis is usually based on a vapor-liquid-solid (VLS) mechanism, often with the help of a catalyst, and the process involves a complicated chemical deposition (CVD) system to regulate temperature, pressure and flow rate of precursors. In particular, MOCVD is well-suited for producing II-V and III-V semiconductor compounds and alloys. It can offer a good material crystalline quality, while keeping a relatively high growth rate, thus ideal for industrial applications. Molecular beam epitaxy (MBE) is another bottom-up technique to create exquisite low dimensional structures. Based on its ingenious concept of depositing atoms layer by layer on a heated substrate under high vacuum, it can achieve very high material purity and remarkable interface sharpness in heterostructures. However, its application is at present limited to the research field due to its slow growth rate and expensive maintenance [47].

For this thesis study, GaN nanowires/microwires grown by MBE and MOCVD techniques are used as a raw material to fabricated piezogenerators. I will give a more detailed description of these two growth methods and the as-grown nanowires characterization in later chapters.

2. GaN nanowires demonstrating a high piezoelectric generation potential

2.1 Piezoelectric property of wurtzite GaN nanowires

Gallium nitride (GaN) is a binary III-V direct bandgap semiconductor. It may exist in three crystalline phases: zinc blende, wurtzite and rock-salt [48]. A phase transition to the rock-salt structure only takes place at high pressure, while at ambient conditions, the zinc blende is a meta-stable phase and the wurtzite is thermodynamically stable.

The wurtzite GaN demonstrates high piezoelectricity due to its polar bonds and a lack of inversion symmetry.

Figure 1-1 illustrates the wurtzite structure of GaN (its conventional cell and a unit cell). In each unit cell, there are two nitrogen and two gallium equivalent atoms. The lattice parameters *a* and *c* indicated in the figure are respectively 3.189Å and 5.185Å. In practice, the lattice of GaN is different from the ideal wurtzite structure. The lattice constant ratio c/a of GaN is 1.626, different from its ideal value of 1.633. The wurtzite structure of GaN can be considered as two hexagonal compact lattices (one made of gallium atoms and the other made of nitrogen atoms) intricated together, and separated by a distance of u = (3/8)c along the [0001] direction.



Figure 1-1. (a) Crystalline structure of wurtzite GaN. (b) Unit cell of wurtzite GaN. The lattice parameters are indicated as a and c. Vectors a_1 , a_2 and c are the bases in the hexagonal coordinates [25].



Figure 1-2. (a) ABAB style stacking of gallium and nitrogen atomic layers, composing the wurtzite GaN structure. (b) Schematics of gallium-polar GaN and nitrogen-polar GaN structures, with spontaneous polarization (P_{sp}) indicated in each case [25].

The wurtzite structure can also be represented as a stack of gallium and nitrogen atomic planes following the order type of ABAB, as shown in figure 1-2.a. Due to the lack of inversion symmetry, the [0001] direction and the [000-1] direction of the structure are not equivalent. By convention, the direction pointing from gallium atom to nitrogen atom is defined as the [0001] direction, also as the positive c-axis direction. Under this premise, the gallium-polar GaN and nitrogen-polar GaN are further defined. When the GaN growth direction is [0001], it is said to be gallium-polar or cationic polar. Oppositely, when the wurtzite grows in the [000-1] direction, it is referred to as nitrogen-polar or anionic polar.

Due to the different electronegativity of nitrogen and gallium, a dipole exists in each Ga-N covalent bond. Along the c-axis direction, the non-symmetric structure results in an accumulation of these innate dipoles and hence the appearance of a macroscopic polarization. This polarization oriented along the c-axis direction is defined as the spontaneous polarization (P_{sp}) of the wurtzite GaN, since it is not induced by material deformation. This spontaneous polarization is anti-parallel to the [0001] growth direction of gallium-polar GaN and is parallel to the [000-1] direction of nitrogen-polar GaN, as indicated in figure 1-2.b. The value of the spontaneous polarization of wurtzite GaN is simulated as -0.029C.m⁻² [48].

The piezoelectric polarization (P_{pz}) appears when the material is deformed. Within the linear approximation, it can be calculated as a function of strain ε or as a function of received stress σ :

$$P_i = \sum_{j=1}^{3} \sum_{k=1}^{3} e_{ijk} \varepsilon_{jk}$$
 and $P_i = \sum_{j=1}^{3} \sum_{k=1}^{3} d_{ijk} \sigma_{jk}$.

Accordingly, the piezoelectric coefficients can be expressed in two forms:

$$e_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \text{ and } d_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}.$$

To link the two presentations, as well as to calculate the received strain from external deformation, the elasticity of the material needs to be considered. For a continuous

material under elastic deformation, the relation between the strain and stress is given by the Hooke's law:

$$\sigma_{ij} = \sum_{k=1}^{3} \sum_{l=1}^{3} C_{ijkl} \varepsilon_{kl}$$

And the elasticity matrix of wurtzite GaN is given below after the simplification by crystalline symmetry and the Voigt notation:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} = \frac{1}{2} (C_{11} - C_{12}) \end{pmatrix}.$$

(The coefficients C_{11} and C_{33} present the material elasticity under a normal stress in the plane and along the c-axis direction. The C_{12} and C_{13} describe the elasticity of crystal planes under sheer stress. As for the C_{44} and C_{66} , they describe the material elasticity under torsion. All the coefficient values are in the order of GPa for GaN.)

Putting together the previous relationships, the piezoelectric polarization P_{pz} of the material under elastic deformation is proportional to its strain (ε), its piezoelectric coefficients (d) and its elastic constants (C).

$$P_{pz} \propto [d] * [C] * [\varepsilon]$$

This piezoelectric polarization induces an electrical potential difference inside the material that can be extracted to external circuit, which lays the foundation for the mechanical-electrical energy conversion. Therefore, in order to have higher energy conversion, the piezoelectric polarization of the material should be enhanced.

In the specific case of wurtzite GaN nanowires, as mentioned before, the piezoelectric coefficients of nanowires are higher than those in a bulk form because of size effects [19],[20]. Besides, the nanowires are endowed with a higher mechanical flexibility

and a higher elastic deformation level for a given force. With a small force of the order of nano Newton, the nanowires can be effectively deformed and create a piezoelectric field inside them. This high sensitivity to the applied force is an advantage in view of making piezogenerators and piezosensors based on nanowires. In order to have a better integrated piezogenerator design, the individual nanowire reaction in response to external deformation should be analyzed at first.

It is evident that, with the 1D geometry of nanowires, they exhibit an anisotropic behavior in face of deformation. When the deforming force is applied from the side, the nanowires can be easily bended. However, when the force is applied along the c-axis nanowire growth direction, the nanowires appear more rigid. I will give a more detailed discussion of the GaN nanowire bending deformation and its electric response in the next part of this section, when talking about AFM individual nanowire measurements. Here, I focus on the nanowire electric response under c-axis direction deformation. Under this deformation condition, the nanowires appear more rigid. When considering a massive integration of vertical nanowires on their growth substrate, the application of deformation in the vertical direction is a more frequent case. (I note that for a strong external force the nanowires can exhibit a mixed type of deformation composed of an axial compression and a lateral bending.)



Figure 1-3. Illustration of piezoelectric polarization (P_{pz}) of wurtzite GaN nanowire (gallium-polar and nitrogen-polar) under compression and tension.

Figure 1-3 schematizes the piezoelectric polarization of wurtzite GaN nanowires under c-axis compressing and stretching stress. As we can see, for Ga-polar and N-polar GaN nanowires, the resulting polarizations are different under the same type of deformation. This difference is linked to the opposite crystalline structural orientation of the two types of nanowires. When the 1D structure is compressed along the c-axis, the distance between gallium and nitrogen atoms decreases. A dipole opposite to the spontaneous dipole is then created. The accumulation of this deformation induced dipole then gives rise to the nanowire piezoelectric polarization, which is opposite to the spontaneous polarization of the nanowire. On the contrary, when the nanowires are stretched along the c-axis, the gallium and nitrogen atom distance increases and a piezoelectric polarization parallel to the spontaneous polarization will be created. Since the spontaneous polarization of gallium-polar and nitrogen-polar GaN nanowires are opposite, the piezoelectric polarization direction of the two are also opposite under the same deformation.

It is noteworthy that, as well as the simultaneous lateral bending of a large number nanowires, the stretching of nanowires along the c-axis is technically difficult. Specific setup is needed to apply this type of deformation to the nanowires and to see their electrical response. Therefore, the compression of nanowires along the c-axis is the most realistic way to deform them, particularly when they are integrated into a 2D macroscopic device. During this thesis study, the compression deformation is used as the solicitation mode of the fabricated piezoelectric generators. I will address this in the later chapters.

In the next section, I will introduce the AFM measurements of individual GaN nanowire piezogeneration under lateral bending deformation. Though the pure lateral deformation is difficult to be applied to macroscopic nanowire arrays, for individual nanowire characterization it is straightforward to achieve with the help of a well-controlled AFM tip. As we will see, these experiments have successfully demonstrated the high piezoelectric generation potential of individual GaN wires.

2.2 AFM measurements of individual GaN nanowire piezogeneration

The work of atomic force microscopy (AFM) measurements of individual GaN nanowire piezogeneration has been done during the previous PhD thesis of N. Jamond in collaboration with P. Chretien from GEEPS laboratory [25]. The GaN nanowires grown by molecular beam epitaxy technique have been analyzed, while taking into account their crystalline polarity and different types of doping.



Figure 1-4. (a) Simplified schema of individual nanowire AFM measurement connection. (b) Distribution of piezoelectric polarization inside a N-polar GaN nanowire under lateral bending.

The principle of the measurement is to use the AFM tip to laterally bend the individual nanowire, while at the same time measuring the created piezoelectric potential with a resiscope module. The measurement circuit is schematically illustrated in figure 1-4.a. The nanowires are half embedded into an insulating resist to mechanically solidify them and to avoid them from touching each other. For simplification, only one insulated nanowire will be considered here.

The resiscope module can be considered as an equivalent load resistance to the nanowire power source. The nanowire is connected to the external circuit at its bottom through an ohmic contact and its top is then touched by the AFM tip. The metallic or highly-doped semiconducting tip and the nanowire form a Schottky contact. (The used AFM tips are: p-doped diamond with a working function of 5.21eV and the PtSi tip with a working function of 5.03 eV. The electron affinity of GaN is 4.1 eV). When the AFM point is moving in scanning contact mode with a constant normal force, it will bend the nanowire laterally. Due to this bending force, the side of the nanowire close to the tip is stretched while another side is compressed. Therefore, different piezoelectric polarizations appear at the two sides of the nanowire.

As shown in figure 1-3, the piezoelectric polarization of a nanowire depends on its crystalline orientation. For the present AFM measurement, only the GaN nanowires with N-polar orientation are studied (growth direction [000-1]). The distribution of the piezoelectric polarization inside the nanowire when it is laterally bended is illustrated in figure 1-4.b. We can see that the electrical potential of the nanowire at compressed side is positive at the summit, while at the stretched part it is negative.

Both non-intentionally, n-doped and p-doped N-polar GaN nanowires were measured through the configuration given in figure 1-4. Due to the rectifying nature of the Schottky contact between the AFM tip and the nanowire summit, the measured voltage drop at the circuit load shows different signs for the two cases, respectively. For the n-doped GaN nanowires, negative voltage output has been recorded during AFM scanning. On the contrary, the bended p-doped GaN nanowires deliver positive voltage outputs. For a direct comparison, figure 1-5 puts together the 3D presentations of the voltage outputs of both types of nanowires. The scanned nanowire array surfaces are both 20 μ m*10 μ m. The normal force applied by the scanning AFM tip onto the n-type nanowire arrays is 98 nN, and the average voltage output of individual nanowires is about -196 mV. For the p-type nanowires, the average voltage output value reaches 220 mV with a scanning AFM tip applying a normal force of 149 nN.



Figure 1-5. AFM measurements of voltage output of a GaN nanowire array of 20 μm *10 μm surface. (a) 3D presentation of voltage outputs of a n-doped nanowire array under 98 nN normal force applied by scanning AFM tip. The tip consists of p-doped diamond. (b) 3D presentation of voltage outputs of a p-dope nanowire array under 149 nN normal force applied by a scanning AFM tip. The tip consists of PtSi [25].

In order to clarify the potential detection mechanism for this measurement configuration and to understand the observed sign difference, the carrier transport in the circuit is analyzed for each doping condition separately. Figure 1-6 and figure 1-7 help to make the explanation by schematizing the scenario when the AFM tip is in touch with the nanowire summit and exerting the lateral bending.

When an n-doped nanowire is bended by the AFM tip (figure 1-6), negative piezoelectric potential appears at the nanowire summit on its stretched side. When the deformation level is high enough and the negative potential is sufficiently low, the

Schottky diode between the AFM point and the nanowire top will be forwardly biased and becomes open. The majority carriers, the electrons, will pass through the diode and flow from the nanowire to the AFM point and to the external load. Therefore, the detected voltage drop by the resiscope module is negative by convention. The negative charges continue to move when the AFM point is on the stretched side of the nanowire, until the point moves to a position near the nanowire middle where the deformation is not enough to maintain the forward bias of the Schottky diode. As the point is further moving to the compressed side of the nanowire, the diode becomes reversely biased with the nanowire summit positive potential. At this stage, the leaking current due to non- ideality of the diode contributes to the positive voltage detected at the circuit load. However, compared to the negative voltage detected before, this positive output has a much smaller absolute value. In this way, prominent negative voltage outputs are obtained from the n-doped nanowire arrays, as shown in figure 1-5.a.



Figure 1-6. Illustration of nitrogen-polar n-doped GaN NW bended by the AFM tip: the distribution of piezoelectric potential during the deformation process (left) and the detected voltage output at external load (right).

Similarly, the deformation process and the generation of N-polar p-doped GaN nanowires are illustrated in figure 1-7. Determined by the N-polar crystalline structure, the same piezoelectric potential distribution as in a n-type wire appears in the present case. The electrical potential at the nanowire summit is negative at nanowire stretched side and positive at compressed side. When the AFM point is in contact with the nanowire at its stretched side, with the negative potential at semiconductor summit, the Schottky diode formed between the p-doped nanowire and the AFM point is under reverse bias. The negative piezoelectric potential repulses the negative charges in the

circuit from passing through the metallic point. Hence a small negative voltage output can be detected at circuit load at this period. When the AFM tip approaches the nanowire center, the diode is less reversely-biased with a decreased level of deformation. The previously repulsed charges can then restore to their balanced state. A small positive voltage peak can be detected corresponding to this process. After that, the AFM point scans over the compressed side of the nanowire and the Schottky diode is finally forwardly biased. The positive charges pass from the nanowire to the AFM tip, thus creating a positive voltage drop at the external load. This obtained positive peak has a much higher value than the peaks due to minority carriers. So it can be concluded that for the p-dope nanowires, the AFM measurements records positive voltage output.



Figure 1-7. Illustration of nitrogen-polar p-doped GaN NW bended by the AFM tip: the distribution of piezoelectric potential during the deformation process (left) and the detected voltage output at external load (right).

As we can see, due to the different doping conditions and the rectifying behavior of the Schottky contact between the tip and the NW, the dominant voltage output of the bended nanowires changes its sign although the crystal polarity remains the same. Therefore, for a nanowire array with a known crystalline orientation, the doping type of the nanowires can be determined by performing the AFM measurements under the same configuration and judging from the sign of the voltage output.

Generally speaking, the AFM measurement is an efficient way to explore the piezogeneration potential of individual nanowires. Beside the real-time tracing of the deformation-induced piezoelectric potential, thanks to the contact working mode of the AFM, the topography of the measured sample can be recorded as well. It is hence

possible to establish a correlation of nanowire position and its generation for analysis.

The first AFM analysis of the piezogeneration has been done with ZnO nanowires in 2006 [17], showing their potential in mechanical-electrical energy conversion. Since then, nanowires for energy harvesting became a hot research subject. It is noteworthy that GaN nanowires grown by MBE also demonstrate high energy conversion efficiency. With a similar deforming force (around 140 nN) applied at the individual nanowire level, GaN nanowires can deliver an average voltage output of more than 100 mV (as has been shown in figure 1-5), much higher than that of the ZnO nanowires. The reported maximum output value for p-type ZnO under 140 nN AFM tip normal force is 90 mV [49]. For n-doped ZnO, the maximum value is even lower, around 45 mV [50].

The promising aspect of using GaN nanowires for energy conversion has been confirmed by the presented AFM measurements. However, as mentioned before, when dealing with a dense nanowire array on a substrate, a pure lateral bending of nanowires would be difficult. Therefore, it is also important to explore the individual nanowire piezogeneration under c-axis direction deformation in view of latter nanowire mass integration. This part of generation exploration is on-going in our team in the framework of a collaborative project with GEEPS laboratory.

3. State of the art of piezoelectric devices based on nanowires

In this section, I will present several typical piezogenerators integrating different types of nanowires introduced previously. Some prototypes of force sensors based on piezoelectric nanowires will also be listed. The aim is to give a general view of the development of piezoelectric devices based on nanowires, while laying an emphasis on the device design and its electrical characterization.

3.1 Nanowire-based piezogenerators for energy harvesting



Figure 1-8. (a)Schematic drawing of the nanogenerator structure. (b)Aligned ZnO nanowires grown on a GaN substrate. (c)Zigzag trenched electrode fabricated by etching after being coated with 200 nm of Pt. (d)Cross sectional image of the nanogenerator at the nanowire-electrode interface (Inset: a nanowire being bent by the zigzag electrode). (e)DC current output of the generator when the ultrasonic wave was turned on and off. (f)DC current output of the device for an extended deformation time (78mins as indicated) [51].

Inspired by the AFM measurements of individual ZnO NWs, a zigzag top electrode piezogenerator was proposed in an early work of Wang's group [51]. An array of vertically-aligned ZnO nanowires (grown on a ZnO thin film on GaN or sapphire substrate by VLS technique) has been employed as the active piezogenerating material. A zigzag Si(001) electrode with parallel trenches coated by 200 nm-thick Pt film is then placed above the vertical nanowire array as top contact. The whole nanowire-electrode ensemble is then sealed at the edges to form a closed structure for piezogeneration measurement (2 mm² size). The structure is illustrated in Figure 1-8. The packaged generator is stimulated under ultrasonic wave at 41 Hz from the top electrode side. Owing to the vibration of the zigzag electrode under ultrasonic wave, the nanowires under it are laterally deflected in a similar way as if they were bended by an AFM tip. With the Schottky contact formed between the electrode Pt coating and the ZnO nanowire, DC voltage and current output from the generator are recorded. The generator can work continuously for an extended period of time, and its electrical output shows no direct coupling with the frequency of the ultrasonic wave. Although this device design offers a DC electrical output, the output values are quite small and noisy. This may be due to the random various of the nanowire deformation state under

the electrode movement. Besides, under higher level of deformation, the risk of nanowires touching each other increases, which may be detrimental for piezogeneration harvesting.

In order to prevent nanowire interconnection under deformation and further enhance the device performance, latter piezogenerator designs often embed nanowires in a dielectric material to separate them mechanically and insulate them electrically. Since the deflection of vertical nanowires in the array is difficult to control, most of the later generator designs focus on either imposing axial compressing strain on vertical nanowire arrays or creating axial tensile strain in horizontal nanowires arrays.



Figure 1-9.(a)Fabrication process and structural illustration of the generator. (b)Output voltage and output current of the generator under a periodic pressure of 0.53MPa (load resistance 100MΩ).
(c)Voltage output of the generator under impact exerted by a free-falling object with different height, ranging from 5 to 13mm. (d)Relationship between the peaks of the output voltage/output current and the height of the free-falling. The square and circle points are experimental data, and the curves are the fitting curves by a square root function [52].

L. Gu et al. have reported a flexible generator based on vertically aligned PZT nanofibers in [52]. Aligned PZT nanowires produced by electrospinning technique in textile form are stacked and rotated to form vertically-aligned PZT nanowire thin-film (figure 1-9.a). With the electrodes deposited at nanowire two extremes (two sides of the active film), the nanowire arrays are poled under high electric field to obtain an aligned electric domain. To characterize the device mechanical-electrical conversion, periodic impact was applied by object free dropping onto the device surface (2.25 cm²). In this way, the nanowires are deformed in their aligned direction and piezoelectric potential appears at the nanowire extremities. With a periodic pressure of 0.53 MPa, a peak voltage of 198 V and a peak current of 17.8 µA can be measured at 100 M Ω external load, as shown in (figure 1-9.b). Further measurement with different dropping object height has shown an increased device output proportional to the square root of the falling height, under assumption that the device action time under impact is constant(figure 1-9.c and d). At last, the study of device output frequency dependence has been carried out by ranging the impact frequency from 0.25 Hz to 2.5 Hz by a linear motor. However, due to the lack of information about impact time, the increased voltage output could not be directly attributed to the increased impact frequency.

K I. Park et al. have proposed a similar thin-film generator based on BaTiO₃ nanowires in [53], where the device is designed to be more sensitive to film bending deformations. BaTiO₃ nanowires produced by hydrothermal technique (4 µm average length and 156 nm average diameter) are mixed into PDMS polymer at an optimal weight ratio of 20% to form the active piezogenerating layer. This layer is sandwiched between two PDMS dielectric layers and supported further by ITO-coated PET top and bottom films. As illustrated in figure 1-10.a, the thin-film device is in fact a PET/PDMS/PDMS+BaTiO₃ nanowires/PDMS/PET(50 µm/50 µm/150 µm/175 µm) stacking with a 3 cm*3 cm surface. Then the device ensemble is poled at 1.5 kV electric field at 140°C during 12h to ensure the electrical performance. When the generator is deformed by a periodic bending-unbending motion as illustrated in figure 1-10.c, alternative voltage and current output can be detected at external load. Figure 1-10.d shows the device open-circuit voltage and short-circuit current when it is bended with a lateral border displacement of 5 mm. The maximum voltage output reaches 7 V and the maximum current is about 360 nA. By using the optimal load of 20 M Ω , the instantaneous power output of the device can be estimated as 1.2 μ W. It has been demonstrated further that the amplitude of the device output increases with the bending curvature at a constant strain, and a quick bending which induces a higher

strain rate may lead to a higher output than a slow bending. However, since the strain is added on the poled nanowires in a quite indirect manner (lateral film bending may induce a mixture of axial deformation and bending of the nanowires), it is difficult to establish a correlation between the device output and the nanowire actual deformation/strain state.



Figure 1-10. (a)Schematic illustration of the fabricated flexible generator. (b)Simulation model and the calculated piezoelectric potential distribution in the active layer. (c)The pictures of one flexible generator at rest, bending and unbending state. (d)The open-circuit voltage and the short-circuit current measured from the BaTiO₃ nanowire-based piezogenerator under repeated bending/unbending motions [53].

We can see from the above example of $BaTiO_3$ nanowire-based generator that, although the nanowires are not perfectly aligned, the poling process can help to achieve a uniform nanowire piezoelectric polarization under deformation. In fact, for ceramic and polymeric nanowires, the physical alignment of the array is not that demanding for piezogeneration application. On the contrary, in the case of crystalline semiconductor nanowires, a uniform orientation of the nanowire array and a good alignment of their piezoelectric polarization under deformation is critical for efficient energy conversion. Therefore, great care should be given to the nanowire alignment during device fabrication.

Xu et al. firstly reported a laterally-integrated ZnO-nanowire-based thin-film generator sensitive to bending deformation in [54]. The laterally-aligned nanowires were obtained by growing the material directly on defined positions towards the desired direction. In this way, the crystalline orientation and the piezoelectric polarization of the nanowires are well aligned for energy harvesting. The reported generator with 700 rows of aligned nanowires demonstrates an average output voltage of 1.2 V and a current pulse of 26 nA at a device strain rate of 2.13% s⁻¹ and a strain of 0.19%. Shortly afterwards, Zhu et al. updated this record and reported another flexible piezogenerator based on laterally aligned ZnO nanowires while using a different fabrication process [55]. The used ZnO nanowires are previously grown by physical vapor deposition method on a Si substrate (characterized by an average diameter of 200 nm and a length of 50 um). Then the nanowires are detached from the growth substrate and deposited on a Kapton film by using a sweeping printing method. This nanowire transfer method can maintain a good alignment of nanowires orientation, as can be seen from the SEM image in figure 1-11.b. After the transfer, the aligned nanowires are covered by 600 rows of stripe-shape Au electrode with 10 um spacing and the whole structure is packaged in a PDMS polymer for protection. The final device has an effective surface of 1 cm² and a linear motor is used to periodically deform the device from Kapton back to add stretching-releasing agitation. Owing to the much smaller diameter of the nanowire compared to the supporting substrate (125 µm thick), the bending movement of the Kapton substrate induces a uni-axial strain in the nanowires, hence piezoelectrical field is created and electrical signals can be detected. At a strain of 0.1% and a strain rate of 5% s⁻¹, an open-circuit voltage up to 2.03 V and a peak short circuit current of 107 nA have been generated by the reported device. A peak output power density of ~0.22 uW/cm² has been estimated. Later measurements have shown that the device gives a higher output with increased strain under the same strain rate. While under the same level of strain, a higher strain rate helps to increase the device output as well. However, the generator shows a quick generation saturation along an increased strain and strain rate, far before arriving the 6% fracture strain predicted theoretically [56].



Figure 1-11. (a)Schematic drawing of the laterally aligned ZnO nanowire piezogenerator without(left) and with(right) mechanical bending. (b)SEM image of the transferred nanowire arrays bonded by gold electrodes(Inset: an optical image of the flexible device). (c)The open-circuit voltage and the short-circuit current delivered by the generator when it is excited at 0.33Hz by a strain rate of 5% s⁻¹ and a strain of 0.1% [55].

Although the laterally-aligned nanowire-based piezogenerator is not easy to fabricate, this design has the advantage of being sensitive to soft bending and gentle vibrational deformation. Other techniques, such as dielectrophoresis (DEP) or Langmuir-Blodgett method, can also be adapted to laterally align detached nanowires, either for piezogeneration aim or for other application [57].

As a different approach, piezogenerators based on vertically-integrated nanowires have the advantage of keeping nanowire original orientation during fabrication. Usually, the nanowires are embedded directly on their as-grown substrate (used as a bottom electrode), and the fabricated device reacts well to a strain applied along the nanowire axial direction. Xu et al. have developed a piezogenerator integrating vertical ZnO nanowires which works under compression deformation in [54]. The used nanowires are grown on a gold-coated silicon wafer by hydrothermal technique. After embedding the as-grown nanowire array into PMMA resist, a piece of silicon coated with 300-nm-thick Pt film is placed in direct contact with the cleaned surpassing nanowire summits to form a top Schottky contact (figure 1-12.a). To measure the device (4 mm² size), a linear motor stimulator is used to apply mechanical strain at a speed of 0.1 ms⁻¹ on top of the silicon contact, deforming uniformly the nanowire array under it. With the repeated compressing and releasing deformation, alternative voltage and current output can be obtained (figure 1-12.b). It has been further demonstrated that with a higher applied compressing stress, the

output voltage of the device increases almost linearly. We can see from the figure 1-12.c that under a maximum compressing strain of 6.25 MPa at 2 Hz frequency excitation, the output voltage of the device reaches almost 60 mV. However, although the impact speed is fixed at 0.1 m s⁻¹, it is hard to know the strain rate of the embedded nanowires due to surrounding packaging material.



Figure 1-12. (a)Schematic illustration of the vertically-aligned ZnO nanowire piezogenerator.
(b)Typical trace of the generator's voltage and current output (load resistance not mentioned).
(c)Magnitude of the output voltage as a function of the magnitude of the compressive stress at a frequency of 2Hz [54].

The piezogenerator reported by Zhu et al. in [58] demonstrated a higher piezoelectric output. Similarly, the used ZnO nanowires were grown by hydrothermal technique and they were vertically integrated on their as-grown substrate. However, different from the generator in figure 1-12, the Schottky contact at the nanowires top is replaced by a thin insulating PMMA layer for this new device (figure 1-13.a). The device is then mechanically triggered by a linear motor under dynamic impact and a commercial bridge rectifier is used to convert its alternative output into a dc output. For a generator with an effective dimension of 1 cm by 10 μ m occupied by
ZnO nanowires, the open-circuit voltage and the short-circuit current reached 37 V and 12 uA under 1 MPa stress (figure 1-13.b). To show the electrical output scaling-up, an updated energy-harvesting pad with nine individual generators connected in parallel was fabricated. Under one cycle of human palm punching, the open-circuit voltage and the short-circuit-current values of the generating pad exceed 58 V and 137 uA respectively, indicating a maximum power output density of 0.78 W/cm^3 .



Figure 1-13. (a)Schematic illustration of the proposed generator based on vertical ZnO nanowires.
(b)Open-circuit voltage and (c)short-circuit current of the energy-harvesting pad rectified by a bridge rectifier under impact of a human palm (Insets: enlarged view of the red-color-highlighted one-cycle output) [58].

Compared to the widely explored ZnO nanowires, wurtzite III-nitride nanowires have demonstrated outstanding potential for piezoelectric generation during AFM single nanowire characterization [21], [37]. However, integrated piezogenerating devices based on this family of nanowires were rarely explored experimentally. The only InN nanowire based piezogenerator was reported in [59]. In this work, PAMBE grown InN nanowires with an intrinsic n-doping and an intentionally p-doping were used to fabricate piezogenerators, while keeping a Schottky top-contact design (MoO₃/Au layer) (figure 1-14.a). Both devices reacted well to the shaker applying a periodic strain from the top electrode side (device size 0.81 cm²). With a shaker acceleration amplitude of 2 m/s² at 3 Hz excitation frequency, the two devices give a 55 mV and 85 mV peak open-circuit voltage and a 0.211 µA and 0.08 µA peak short circuit current, respectively (figure 1-14.b). In particular, a potential maximum output power density of 0.012 μ W/cm² has been estimated for the p-doped device. Apart from the use of a new material, the reported work shows originality in its analysis of material quality influence on the piezogeneration output. For example, the screening of piezoelectric potential by nanowires free charge carriers was addressed in this article. The influence of the nanowire surface state on the piezogeneration was also discussed.



Figure 1-14.(a) Schematic diagram of the InN NW-based piezogenerator. (b) Measured open-circuit voltage and short-circuit current of p-type and intrinsic piezogenerators[59].



Figure 1-15. Schematic drawing of the piezogenerator integrating GaN nanowires (a) and its voltage outputs as a function of its deformation under bending cycle of 3 Hz (top) and 6 Hz (bottom)(b) [63].

As for GaN nanowire based piezogenerators, devices based on both lateral and vertical alignment have been reported [60], [61], [62]. Here I describe the previous work of our group reported in [63]. Vertically aligned p-doped PAMBE-grown GaN nanowires were used to fabricate the device. They were embedded into a rigid spin-on glass on a silicon substrate with a Schottky contact formed at their summits. In order to homogeneously strain the active nanowires in their axial direction, the generator was bended by fixing its two sides and inducing a vertical movement at its central part. Due to the difference in thickness between the substrate (350 μ m) and the active layer (around 1 μ m), the lateral bending of the device induces a stretching of the encapsulation matrix and a thinning of the nanowire embedded layer thickness by volume conservation. In this way, a homogeneous compressing strain was applied along the nanowire growth direction. With a periodic bending of the device, the device generated a voltage signal synchronized with the deformation (figure 1-15.b).

A saturated maximum voltage output of 200 mV was recorded under 1 M Ω external load, resulting in an estimated maximum power output density of about 12.7 mW/cm³.

3.2 Examples of force/compression sensors based on piezoelectric nanowires

At present, force sensors based on piezoelectric nanowires are much less investigated in the literature than piezogenerators. Some prototype devices have been demonstrated to be sensitive to small external deformation, such as finger bending [42], [64], blinking of eyes [65] or other type of small forces [61], [62]. However, a piezogenerating device cannot be at the same time a good energy harvester and a good force/deformation sensor. Specific device design and further force-generation calibration are needed for each type of devices in order to yield a high conversion efficiency or a sensitive and spatially resolved piezoelectric sensor.

Thanks to their small footprint, high resolution transient deformation sensors can be expected from piezoelectric nanowire-based materials. Among various attempts, the European project PiezoMat (http://www.piezomat.eu) has reported up-to-now the most mature piezoelectric nanowire-based force sensor [66], [67]. In fact, the project aims to realize a high-resolution finger-print sensor by using a matrix of interconnected piezoelectric ZnO nanowires. The principle is to use the local piezoelectric signals delivered by deformed nanowires to reconstruct the fingerprint related deformation. In order to achieve high resolution and microelectronic chip compatibility, selective area growth of ZnO nanowires at high density is performed on a 8-inch wafer-scale by hydrothermal technique. Including electron beam lithography, chemical etching, stripping and layers deposition, 50 clean-room steps are needed to realize the complete device. The finally reported sensor can attain a resolution of 3000 dpi, far beyond today's 500 dpi international standard.

It should be noted that this reported sensor is a successful collaboration between research and industry. Though it gives quite good results, improvements are still needed in terms of quality-price and device performance. Other approaches to fabricate piezo-sensors should be continued with a motivation of achieving high detection resolution while simplifying the process flow. In chapter 5, I will present a potential force sensor based on MOCVD GaN nanowires and make some further discussions.

3.3 Difficulties in benchmarking of different nanowire piezogenerators

Although various piezogenerators have been reported in literature, it remains always difficult to compare these device's electrical performance using a well-accepted standard. As we may notice from the above selected devices, each reported generator has its proper character. Differences exist in the integrated material, in the device dimensions and even in electrical evaluation method. It would be ideal to compare device's mechanical-electrical energy conversion efficiency to find the best performing one for energy harvesting. However, due to the small volume of active nanowires and the unknown mechanical energy input during characterizations, the conversion efficiency is usually inaccessible and no information about this parameter can be found in the vast majority of papers.

In most of the published works, the open-circuit voltage and the short-circuit current of the generator is given. These values allow to estimate the maximal reachable output power for an idealized device, but they cannot be directly used to compare the device performance. In addition, the exact deformation (namely, its amplitude and variation rate) received by each individual device should also be taken into account. Besides, the instantaneous maximum power (density) has usually been reported as an indicator of the device piezoconversion performance. Indeed, this value can show the device potential, but this value is obtained under given conditions and is not integrated over time. The piezogeneration is a dynamic process, to evaluate the device harvesting performance in a more reasonable way, the average power output should be calculated. However, the average power output of nanowires-based piezogenerators are rarely reported (maybe due to less appealing values).

Another point unclear for the piezogenerator evaluation lies in the output frequency-dependence study. In several reported works [68], [69], the voltage output of the piezogenerator increases with a higher impact frequency. However, it would be too rash to draw this conclusion under the applied measurement conditions, since the obtained voltage outputs are not continuous in time and the impact itself is time-dependent and influences the generated voltage. Most probably, the impact at different frequency conditions induces different strain variation rate of the active material that gives a higher output. In order to have a better insight into the device transient performance, more work still need to be done.

Conclusion of the chapter

This chapter is dedicated to give a general view of piezoelectric nanowires and nanowire-based piezogenerating devices. Despite the large choice of piezoelectric materials, GaN nanowires are chosen to be the active material for piezogenerator fabrication in this thesis, owning to their promising piezogeneration potential and to the accumulated knowledge of this material in our laboratory. As pointed out in the 3rd part of this chapter, the characterization of nanowire-based piezogenerators in a normative way is today lacking in the literature. Therefore, a comprehensive analysis of the GaN nanowire-based piezogenerators is set as an aim for this PhD work. Attention will be paid to the understanding of the device operational mechanism and a reasonable device performance evaluation.

Before presenting the piezogenerating devices, I'd like to first introduce in detail the characterization setups that have been used, which is the focus of chapter 2.

Chapter 2

Setups for piezogeneration characterization

In this chapter, I will introduce the three characterization setups that I used to measure the electrical response of different piezogenerators. The first one is a commercial micro-indenter. The other two, the three-wheel bending setup and the vertical compression setup, have been assembled by myself in the laboratory. They are more adapted to the specific design and structure of the devices fabricated in this thesis.

In general, to characterize a piezogenerator, there are several steps. The first step is to assess the I-V characteristics of the piezogenerator. This allows to probe the structure of the device (e.g. to distinguish between the capacitive design and the direct contact design). Then, one of the three setups is used to deform the device active region and at the same time, to record the electrical output. For the electrical signal recording, the output voltage is measured by an oscilloscope. Then, the output power density is estimated by taking account of the external load. For the three setups presented here, the electrical signal reading settings are the same. The main difference lies in the creation and control of the deformation onto the device.



1. Micro-indentation

Figure 2-1. (a) Indenter working schematic. (b) Photo of the used micro-indenter and its working environment.

Indentation is a technique used in mechanical engineering to determine the hardness

of materials. It helps to quantify the resistance of the material to a plastic deformation. There are two main classes: macro-indentation and micro-indentation. Macro-indentation is used for pressing bulk materials, with a large test load. While the micro-indentation is a hardness test with a low applied force, typically less than 2 N. It is often used for smaller scale material characterization and is well suited for thin films.

The piezo-generators studied here are all based on vertical nanowires with a length of the order of micrometer, while the whole integration of nanowire arrays in matrix forms a large flat surface of the order of a square centimeter. Therefore, the active region of the device is a thin film with well oriented nanowires embedded inside. Since the needed deformation should be in the vertical nanowire growth direction while avoiding plastic breaking of the active layer, micro-indentation is a good choice for applying an elastic deformation perpendicular to the device surface (Figure 2-1).

The micro-indenter at C2N is a commercial machine (mark CSM). It can exercise a vertical force from several nN to 3 N, with frequencies ranging from 1 Hz to 50 Hz. The pressing tips have different shapes and sizes, so various pressures can be applied to the device. Thanks to integrated sensors in the mechanical pressing head, the displacement of the device surface and the force at the interface can be recorded simultaneously. So this is an ideal way to follow the deformation conditions of the device and to later correlate them with the device electrical performance.

However, after different measurement attempts, this method proves not well suited for the nanowire-based piezo-generator characterization. The main reason is likely to be the low working frequency of the indenter. Indentation aims at leaving a certain trace on the material surface so as to analyze the material elastic properties. The deformation process can be considered as a quasi-static process, only the original and the deformed states of the material count. The value of applied force is an important parameter for later analysis, but repeating the same deformation at high frequency at the same deformation spot is not necessary for classical indentation. However, this kind of repetitive deformation is the standard working condition for piezogenerators. Higher frequency deformation is not feasible using this indentation system. It should be noted that the piezogeneration is a dynamic process: not only the maximum value of applied force influences the electrical response, but the piezo-generation depends also on other parameters such as the force changing rate, the deformation frequency, the contact states, etc. With this indentation system, the influence of these multiple parameters cannot be studied and the piezo-generators can only be tested at a very low frequency. After multiple attempts, no distinguishable electrical signal could be observed using this setup.

Furthermore, the deformation level of nanowire embedded layer is rather difficult to evaluate. In this thesis, GaN nanowires grown by MBE and MOCVD are used. As will be introduced in chapters 3 and 5, the average lengths of those nanowires are less than 2 μ m and 100 μ m, respectively. These values represent approximately the thickness of the integrated active layer. Considering the rigidity of the GaN nanowires and of the matrix material, the displacement of the device surface under elastic compression can be quite small. Thus, the real-time measurement of device deformation extent is a big challenge, especially when the locally deformed surface is hidden by the deforming head. In the literature, as far as I know, no such deformation measurement has been successfully carried out for nanowire-based devices. The micro-indenter used here is supposed to give precise top surface displacement values. Unfortunately, when working with a nanoscale displacement, it gives unreliable and wrong values.

Considering the malfunction of the micro-indenter, new setups are needed to characterize nanowire-based piezo-generators. They should be designed to have a good control of the deformation onto device, and at the same time, to be able to capture in real time the deformation level by using direct or indirect feedback. According to the different devices rigidity, mainly due to the use of a rigid matrix or a soft matrix encapsulation, the following two setups have been constructed to meet the above-mentioned needs.

2. Three-wheel bending setup

The three-wheel bending setup is aimed at characterizing rigid-matrix piezogenerators, namely piezogenerators based on nanowires encapsulated into HSQ (hydrogen silsesquioxane) resist. Figure 2-2.a gives a schematic of the setup. The sample is fixed between three wheels, actually three cylindrical isolating blocks. Two of them exert downward forces through cylinder-surface line contact at the borders. The third one is connected to a movable shaker head and applies the force in the middle of the device from its bottom. The shaker (The Modal Shop INC. K2001E01) head's movements is controlled by a wave generator (Tektronix AFG 3252). By adjusting the generated

waves, different deformation conditions can be applied to the device. An interferometric displacement sensor based on a green laser is placed above the top surface to monitor the device surface movement at the center. After calibration, the sensor delivers a voltage signal corresponding to the surface height change that can be observed simultaneously with the device electrical output through an oscilloscope. So in this setup configuration, three parameters can be recorded in real-time: the shaker control signal which gives an idea of the initial applied force; the sensor output measuring the displacement of the device's center surface, which can be considered as an indicator of the whole layer homogeneous deformation; and the voltage output of the device, which provides a direct measurement of the piezogeneration.



Figure 2-2. (a) Schematic of three-wheel bending setup. (b) Explanation of a vertical compression in a bended nanowire array. (c) Optical photo of the three-wheel bending part of the setup with a piezo-generator on it.

With fixings at two sides and forced vibration in the middle, the macroscopic device experiences a bending-releasing process in each cycle of deformation. Thanks to the good adherence of the encapsulating matrix to the substrate and the huge contrast between the active layer thickness (several micrometers) and its supporting silicon substrate thickness (around 300 μ m), the active layer undergoes a lateral stretching when the whole device is bended (Figure 2-2.b). Since the matrix material adheres also very well to the nanowires, the matrix imposes a vertical force onto the nanowire surface perpendicular to the stretching direction, for conserving the same active layer volume during the lateral stretching. This is how downward axial compression of

nanowires can be realized in this setup. I have measured a series of rigid-matrix piezo-generators with this setup, the results will be presented in detail in the next chapter.

Although this setup deforms the piezo-generators as expected and yields electrical signals, there are still aspects that need to be improved. The setup has the advantage of following the device surface movement, which helps to correlate the electrical output with the device deformation state. However it is still not a quantitative measurement of the surface displacement. Secondly, it is impossible to know the effective compressing force applied onto the nanowire ensemble, because the force is indirectly applied through the surrounding matrix material. This raises difficulties in analyzing the influence of the compression force on the device performance. Though higher macroscopic deformations of device can be achieved by pushing further from below in the center, it is not clear how the degree of stretching of the layer and compressing of the nanowires will be increased. And by doing so, the risk of breaking the sample increases as well, since the whole device on silicon is rigid. Last but not least, the initial state of the device between the three wheels is very critical. The ideal initial state is that the sample is placed in equilibrium without experiencing any constraint from the wheels. However, this is difficult to achieve by manual positioning. Once being placed between the wheels, there is always some force experienced by the device in order to make the whole ensemble stable. It is often the case that the device is not placed horizontally, but with a certain inclination between the wheels, hence the expected deformation degrades from the beginning. Besides, with repetitive pushing from the bottom, the device may get dropped and broken. This happens easily when the deformation frequency exceeds 20 Hz. For this reason, most of the measurements that I carried out with this setup were at frequencies below 10 Hz.

3. Vertical compression setup

In order to get a better insight on the deformation applied onto the piezo-generator, I have built the vertical compression setup shown in Figure 2-3.a. In this configuration, the piezogenerator is directly compressed by a shaker head along the nanowire growth direction. The compressing force is measured by a force sensor (Futek LSB200, 10lb) mounted in the shaker head. A wave generator is used to control the shaker head movement, which helps to exert different forces at various frequencies (from 1 Hz to 5 kHz) onto device. The deformed surface area corresponds to the insulating shaker

head surface (1 mm diameter circle), thus ensuring the precise estimation of the pressure applied onto the device active region. A movable supporting stage is used to hold the device and to change the device distance from the shaker head in a controlled way. The deformation force and duration is probed by the force sensor.



Figure 2-3. (a) Schematic of a vertical compression setup. (b) Examples of the force sensor output at 3 Hz, with different device deformation duration. (c) Photo of the constructed vertical compression setup.

Figure 2-3.b gives an example (at 3 Hz) of how to extract the deformation time from the force sensor output. The force sensor is calibrated to send a positive voltage when receiving a compression force. When the shaker is controlled by a sinus wave, the shaker head performs a vertical sinus movement. When the piezogenerator is far from the shaker head, no force sensor output is observed, since no contact takes place between the shaker head and the device. When moving up the supporting stage of device, the shaker head begins to tap the device surface, thus a short peak of the sensor output appears (Figure 2-3.b position 1). The duration of the peak corresponds to the deformed time of the device. As the stage keeps moving upward, the contact time between the device and the shaker head increases (Figure 2-3.b position 2), until the force sensor output shows a continuous quasi-sinus form. When the minimum value of this quasi-sinus output equals zero, it can be considered as a critical moment when the shaker head exerts a continuous deformation onto the device surface (Figure 2-3.b position 3). If the supporting stage still keeps moving upward, the continuous

quasi-sinus output of the force sensor just shifts by a positive constant value, signifying that there is already a stable compression added onto device when the dynamic deformation process controlled by sinus waves comes into play.

This setup can satisfy almost all the requirements for a piezogenerator characterization in this thesis study. The deformation of the device is directly controlled by the shaker and is no more dependent on the matrix's rigidity as in the case of the three-wheel setup. The applied force is immediately measurable and the deformation can be controlled at a large range of frequencies in a stable way. Furthermore, this setup distinguishes two different modes of compressing deformation, namely, tapping mode and continuous mode, which can help deepening our understanding of the device operation mechanism.

- The tapping-mode deformation describes the situation when the shaker head has a very short contact time with the device surface, as shown in figure 2-3.b position 1. This is the deformation type often used in the literature to obtain electrical signals from nanowire-based piezogenerators [54], [58], [59]. In these referred reports, only the maximum force/pressure applied is cited, no clear value of the deformation time has been mentioned. However, as will be discussed in the next chapter, the deformation time is a non-negligible parameter for obtaining a piezoelectric response.
- The second mode, continuous mode, highlights the situation when the shaker head vibrates while maintaining a continuous contact with the device surface. Since there is no separation, it is assumed that the mechanic energy from the shaker head vibration can be maximally transferred to the piezogenerator to produce the electric energy. It could be an ideal condition to optimize the electrical output from the piezogenerators. However, no such exploration has been carried out for similar nanowire-based generators in the literature so far. Therefore, with this setup, an original new approach can be taken to further explore the device performance.

Thanks to this well-adapted setup, all the devices fabricated in this thesis have been characterized, including rigid-matrix piezogenerators (chapter 3), soft-matrix piezogenerators (chapter 4) and fully flexible devices (chapter 5). Parameter studies are attempted in both types of deformation conditions. However, in practice, the commanded deformation frequency may limit the execution of the two compression

modes.



Figure 2-4. (a) Force sensor's noise output at 1 kHz due to inertia. (b) Force sensor output at 1 kHz when short compression signal overlaps with the inertia noise, deformation duration cannot be deduced from the obtained curve. (c) Force sensor output at 1 kHz when the device is continuously deformed, but with a certain constant pre-compression.

At low frequency deformation (less than 200 Hz), the tapping mode is easier to carry out. The shaker head can move with a higher range of amplitudes and add pulsed force onto the device. As long as the device is not broken by the tapping shock and the device surface is not damaged (surveillance by microscopic camera), the tapping deformation is considered as effective. However, in order to obtain an effective continuous compression deformation, the amplitude of the shaker head movement should be limited to a micrometer scale since only the nanowire-embedded layer should be deformed. While in practice, even with the smallest control parameter of the wave generator used here, no continuous deformation can be achieved with our setup at low frequency. For this reason, in the following chapters, the electric measurements at low frequency are all based on a tapping mode of compression. The device generation-deformation relation is presented by tracing the piezoelectric output as a function of the maximum force applied for a chosen deformation frequency and a constant deformed duration.

On the contrary, the tapping mode is not easy to apply at higher frequency. When the deformation occurs at a frequency larger than 200 Hz, the period is less than 5 ms. This is already a short time, hence adjusting a shorter deformation duration in one period is quite challenging or even impossible, especially when the duration is controlled by manually ascending and descending the device supporting stage. Therefore, the continuous compression mode is to be preferred to characterize the device's output at higher frequency. Besides, there is another reason for this choice: the force sensor cannot give a precise value of applied force during high frequency deformation process. When the shaker head's vibration frequency exceeds hundreds

of Hertz, the force sensor will give some periodic output even when there is no contact between the shaker head and the device (figure 2-4.a). This is due to the force sensor's inertia which is unavoidable in the present setup configuration (referred to as an inertia noise). As we can see in the setup configuration, the force sensor is mounted in the shaker head and the sensor's weight is not negligible. When the shaker head vibrates with a sinus control, the force sensor will also vibrate in the same way. As the vibrating frequency increases, the influence of inertia becomes more and more evident. Finally, the force sensor gives a symmetric AC signal corresponding to its anti-inertia force received during the shaker head's vibration. This noise signal can be problematic when a real deformation of the device takes place. In this case, the force sensor output will be the addition of the real device compression signal (only positive as defined) and the symmetric inertia noise signal. This addition renders the deformation duration reading impossible (figure 2-4.b), and makes it really difficult to find the critical device position for a continuous deformation without pre-compression (figure 2-4.c). Actually, in practice, there exists also the case that even with a certain pre-compression, the real vibration force contribution to the piezogeneration can be rather small compared to the inertia noise. The final sensor output signal could still have an AC form, with only a slight asymmetry above zero.

Though these mentioned artifacts are problematic, the force sensor output still helps a lot in understanding the piezogenerator's electric behaviors under different types of deformation. More specific examples and detailed analysis will be found in the following chapters.

Conclusion of the chapter

In this chapter, the three setups used for nanowire-based piezogenerator characterization are introduced with a discussion of their advantages and drawbacks. Since the micro-indentation method proves incapable to characterize the devices, no further mention to this technique will be made in later chapters. The three-wheel bending setup has only been used to characterize rigid-matrix devices in chapter 3. Apart from this, all the other devices' electrical property characterizations are obtained by using the vertical compression setup. It has been confirmed by experiments that the vertical compression method is a quite effective way to characterize piezogenerators. Therefore, it can be further applied to characterize other nanowire-based piezogenerating devices of a similar structure.

Chapter 3

MBE grown GaN nanowires for piezogenerator application: rigid-matrix devices

In chapters 3 and 4, I will present the studies of piezogenerators based on vertically-integrated plasma assisted molecular beam epitaxy (PAMBE)-grown GaN nanowires. Since the rigidity of the nanowire encapsulation material influences greatly the final device mechanical properties and electrical performance, here I divide the presentation into two parts to introduce separately the rigid-matrix piezogenerators (in chapter 3) and the soft-matrix piezogenerators (in chapter 4).

In this chapter, focus will be given to the piezogenerators with nanowires embedded into spin-on-glass rigid resist. This part of the study is the follow-up of our previous work reported in [63]. Both the three-wheel bending setup and the vertical compression setup are used here to characterize the device. But before going to the detailed characterization, I will first give an introduction of the MBE technique used to grow GaN nanowires and talk about the nanowire characterization in view of their piezogeneration application.

1. Principles of Molecular Beam Epitaxy

The Molecular Beam Epitaxy (MBE) is a crystal growth technology developed since 1960s [70]. It is a bottom-up approach to synthesize thin films and 1D nanostructures by aggregating constituent atoms. The term "epitaxy" originates from Greek "epi" and "taxis", which means deposition "from top" and "in an ordered way". There exists also a definition of homo-epitaxy and hetero-epitaxy, signifying whether the epitaxial layer is of the same type as the substrate or not. Thanks to a good material quality of the grown structures and to a slow growth rate allowing for a precise dimension control, the MBE technique has become an essential tool for nanotechnology and in particular for the semiconductor device development.

The process of molecular beam epitaxy takes place under ultra-high vacuum conditions. The reactive chamber is pumped by several pumps (namely, the turbomolecular pump and the ionic pump). It is also equipped with liquid nitrogen circulation in the cryo-panel to further trap impurities and minimize the inner pressure. The pressure of the reactive chamber is maintained in the order of 10⁻⁶ to 10⁻¹² Torr during and after the growth. The highly pure solid source materials (such as Ga, Al, In, Mg and Si) are filled in Knudsen cells and then heated up to a controlled temperature to evaporate atoms (figure 3-1). As for the nitrogen source, it can be provided by either ammonia dissociation at high temperature (NH₃-MBE, or ammonia-MBE) or by creating a plasma with the help of a radio-frequency cell (PA-MBE, or plasma-assisted MBE).



Figure 3-1. Schema of the different metal cells as well as the N₂ plasma source inside the PA-MBE growth chamber [71].

The generated atomic fluxes then reach the growth substrate at a certain incident angle in a ballistic way, since the mean free path of the atoms at ultra low pressure is much larger than the chamber size. The growth substrate is rotated and heated from the back to promote homogeneous nucleation. The nucleation of the crystal on the substrate is a complex process. The impinging atoms may experience different kinetic phenomena, such as a physisorption, a desorption, a chimisorption and a diffusion, and then finally be incorporated into the growing crystal on the substrate. Apart from the substrate surface physical and chemical properties, the substrate temperature and the source element flux rate are the two factors which influence most strongly the nucleation process. Therefore, a precise calibration of those parameters is critical.

One of the advantages of the MBE system is the in-situ characterization of the growth surface by RHEED, the Reflection High Energy Electron Diffraction [25], [71]. This module, which is integrated in the MBE chamber, serves as a real-time indication of the growing surface morphology. By sending an electron beam onto the growth substrate at a grazing angle (<4 degree), the electrons diffracted at the growth surface are detected by a fluorescent screen and further visualized by a CCD camera. The diffracted pattern differs according to the on-going modification of the surface during the growth. For example, the diffracted pattern of an elongated 1D nanowire is schematized in figure 3-2.a. In this example, the electrons are diffracted in the nanowire volume giving rise to a spotty pattern. For a flat surface, contrary to the nanowire case, a streaky pattern is observed corresponding to a surface diffraction (from this pattern it is possible to extract information about the surface reconstruction). In addition, RHEED is also used to calibrate the growth rate of a 2D surface by means of RHEED oscillations (figure 3-2.b). In this mode, the reflected spot of the electron beam is observed. The intensity of this reflected spot varies along the degree of completeness of the last layer of the growth surface. It is traced as a function of time. During one cycle of the mono-layer growth, the spot intensity reaches its minimum when the layer is half-complete and attains its maximum when the whole layer is fully deposited. Each RHEED oscillation corresponds to one mono-layer deposition. This method allows to calibrate the growth rate in mono-layers per second.



Figure 3-2. (a) Schematic and RHEED pattern (bottom) corresponding to the 1D elongated material morphology during MBE growth. (b) Principle of the RHEED oscillation technique used to calibrate the growth rate [71].

In general, the MBE technique can guarantee a high material purity and crystal quality. With its in-situ monitoring RHEED technique, different growth mechanisms can be further investigated. It bears also the advantage of obtaining sharp and flat atomic interfaces during heterostructure growth, which is quite critical for quantum well based devices. However, in terms of mass production, this technique suffers from a low growth rate and a limitation of substrate size. The cost of the main-d'œuvre and the machine maintenance is also quite high. Therefore, it is presently more used in the research domain for new device demonstration.

2. GaN nanowires grown by PAMBE

Most of the free-catalyzed self-assembled GaN nanowires investigated in this thesis study have been grown by PA-MBE (using Riber Compact12 equipped with a N_2 plasma cell) following a standard growth recipe developed in the team [72] and adapted to piezoelectric devices in the PhD thesis of N. Jamond [25].

A 350 μ m - thick silicon (111) is chosen as the GaN nanowires growth substrate. Compared to sapphire, SiC and GaN substrates, the Si(111) substrate has the advantage of low price and high availability. Besides, it has a good thermal and electrical conductivity in contrast to Al₂O₃. Though it has a relatively important lattice mismatch (17% with GaN) and a superior thermal expansion coefficient in comparison with GaN (-2×10⁻⁶ 1/K difference), the influence of these parametric mismatches is less critical in nanowires than in thin films and bulk materials. Indeed, the strain induced by the lattice or the thermal coefficient mismatches can be relaxed in nanowires with a small footprint thanks to an elastic deformation at the wire free facets.

In the PA-MBE chamber at C2N, the temperature of the substrate is measured by a pyrometer and further calibrated by observing the disappearance of Si(111) 7×7 surface reconstruction occurring at 830 °C [73]. Then the III-element atomic fluxes (Ga, Al and In) are calibrated with a flux gauge while the nitrogen flux is calibrated through the GaN growth rate measured by RHEED oscillations in the stoichiometric conditions [25]. The metallic flux can be adjusted by changing the temperature of Knudsen cells, while the nitrogen plasma is adapted by varying RF input power and flux. In general, the GaN nanowires are grown under nitrogen-rich condition.

Prior to the GaN nanowires formation, an AIN buffer layer of several nanometers is deposited. This buffer layer may influence the polarity of GaN nanowires. More detailed exploration of the GaN nucleation mechanism can be found in [25], [71], [72], [74]. In our case, this buffer layer is doped with Si to render it electrically conductive for device integration. The growth of GaN nanowires is then performed in a temperature window from 770 °C to 810 °C. For the same atomic fluxes, the nucleation of GaN nanowires on AlN depends on the growth temperature. In this way, different morphology of nanowire arrays can be obtained.

Figure 3-3 shows a group of SEM images, illustrating some typical morphologies of the as-grown GaN nanowire arrays. From figure 3-3.a to 3-3.c, the density of GaN nanowires decreases, but with a 2D layer at the foot of nanowires becoming more and more prominent. This modification of the morphology is obtained by decreasing the growth temperature. As can be seen, the as-grown 1D structures are vertically oriented and have a hexagonal shape delimited by {10-10} direction [76]. For the study of this thesis, the used nanowire length is generally less than 3 μ m (determined by the growth time), while the diameter is usually around 50 nm. The array density can be varied in the range from 10⁷ NWs/cm² to 10⁹ NWs/cm². As an example, the average values obtained from a statistical analysis of the SEM images of the three samples demonstrated in figure 3-3 can be found in table 3-1.

It should be noted that each growth has its proper uniqueness, since the nanowire auto-assembling is a random process. Although the growth mechanism of these nanostructures has been much studied and standard recipes have been developed, it is not easy to reproduce two nanowire samples with exactly the same morphology and demanded properties. Even for one sample, a temperature gradient on the substrate introduces a difference between the nanowires grown in the substrate center and those grown at the substrate border. Therefore, when the nanowire arrays are integrated into piezogenerators, the growth variability adds up with the fabrication variability and the differences between devices become more evident. Hence, the macroscopic-scale nanowire devices (e.g. piezogenerators studied in this work) may demonstrate performance variations from sample to sample, and even at different positions of the same wafer.



Figure 3-3. SEM images (cross section view, top view and 45 degree tilted view) of the as-grown GaN nanowires. Groups (a), (b) and (c) demonstrate the typical morphology types of the nanowires encountered in this thesis study. The white scale bar is 1 μm in all the images.

	Sample a	Sample b	Sample c
Diameter (nm)	49.6 ± 16.7	52.9 ± 9.5	56.2 ± 11.4
Length (µm)	1.42 ± 0.08	1.69 ± 0.13	1.23 ± 0.09
Density (NWs/cm ²)	5.3×10^9	1.1 × 10 ⁹	8.7×10^8

Table 3-1 Statistical comparison of the nanowires shown in figure 3-3

In order to characterize the as-grown nanowires, the sample is firstly checked by X-ray diffraction (XRD) $2\theta/\omega$ scan, verifying its crystalline planes. The nanowire structure is confirmed to be wurtzite GaN growing with the elongated direction along its c-axis. Then the rocking curve is traced to evaluate the nanowire array vertical uniformity. As indicated in figure 3-4.b, the FWHM value of 0.59° confirms a good verticality of the nanowire arrays. The in-plane orientation of the 1D array can be explored by XRD pole figure projection [63] (figure 3-4.c). As characterized by HR-TEM, the as-grown nanowires are characterized with a hexagonal cross section delimited by {1010} planes [25], [76].



Figure 3-4. (a) XRD 2θ/ω scan curve and rocking curve of the as-grown GaN nanowire (By courtesy of Ludovic Largeau). (b) XRD pole figures for GaN nanowires recorded by using the Bragg reflection of GaN (10–11) planes [63].

The distribution of the nanowire polarity is of great importance when integrating the array to make a macroscopic piezogenerator. CBED analyses in TEM demonstrated that PA-MBE grown GaN nanowires have a predominant nitrogen polarity [75]. Apart from using CBED in TEM to check the atomic arrangement, KOH etching can be an easy-carry method to check the nanowire polarity since Ga-polar and N-polar surfaces react differently to this chemical attack. In addition, photoluminescence (PL) can be used to verify the existence of Ga-polar GaN inversion domains in the N-polar nanowire structures.

As reported in the literature, a luminescent peak at 3.45 eV in the near band edge emission of GaN is a signature of inversion domain boundaries in GaN [77], [78]. Figure 3-5 shows a low-temperature PL spectrum of a typical nanowire array used for piezogenerator fabrication (the one demonstrated in figure 3-3.a). A slight peak at 3.45 eV appears in the spectrum, implying the existence of inversion domains among N-polar nanowires. However, the relative intensity of this inversion domain related peak is quite low, indicating that this defect is not present in all nanowires. This can be further visualized by performing GaN nanowire KOH etching.



Figure 3-5. A typical PL curve at 4 K of as-grown GaN nanowires (shown in figure 3-3.a). The peak around 3.45 eV is a signature of Ga-polar inversion domains in N-polar GaN (circled in purple)(By courtesy of Lorenzo Mancini).

It has been found that the Ga-polar surface of GaN is chemically inert to the KOH solution while the N-polar surface can be continuously etched. The dangling bond of nitrogen is suggested to play a critical role in this selective etching. Once the OH⁻ ions remove the Ga layer in Ga-polar GaN, the hydroxide ions can no longer attack the remaining N-terminated surface due to the large repulsion from the three occupied dangling bonds of nitrogen. In contrast, there is only one single dangling bond of nitrogen atom upward in N-polar GaN. The OH⁻ ions can attack the back bond of the Ga atoms and be adsorbed around Ga atoms. Then the hydroxide ions react with GaN and form gallium oxide and NH₃. When the gallium oxide is dissolved in KOH, the GaN surface is left as nitride-polar again. By repeating these reactions, N-polar GaN can be continuously etched by KOH. More detailed exploration of this etching selectivity mechanism can be found in [79]. Here, we dip the as-grown GaN nanowire arrays into KOH solution of 0.5M at 40°C during 5 minutes. Figure 3-6 displays the SEM images of the sample before and after etching. As can be clearly seen, almost all the GaN nanowires are etched and bear pyramidal facets at their summits after the chemical attack. These facets are the typical signature of an anisotropic etching of N-polar GaN surface. Therefore, we can conclude that the as-grown GaN nanowires present mainly nitrogen-polarity, defined by the c-axis (000-1) direction. The Ga-polar inversion domains occupy a minor volume (an example can be seen as a narrow tip in panel b) and we can therefore neglect them while considering later the

piezogenerator operation.



Figure 3-6. SEM images of the GaN nanowires before (a) and after (b) KOH etching.

Apart from the classical substrates such as Si, GaN nanowires have also been grown by MBE technique on other substrates: graphene [80], SiO₂ [81] and even Ti foil [82]. These new types of growth may lead to new designs of optoelectronic devices with improved performances. In particular, the use of a metallic substrate such as a Ti foil opens new possibilities to construct flexible devices directly on the growth substrate. In terms of the uniformity of the GaN nanowire polarity, it is reported that the growth realized on graphene and SiO₂ substrates shows even less inversion domains. I have not considered these substrates in my work, however, this can be one approach to further improve the piezogenerators electrical performance.

Previously, the piezogeneration potential of the as-grown GaN nanowires was demonstrated on a single nanowire level by extensive AFM measurements [21], [25]. One important issue that has been analyzed in these single wire characterizations and should be addressed for macroscopic devices is the impact of doping of the GaN nanowires on the piezogeneration.

As shown by the AFM measurements, the doping of GaN nanowires may influence

the Schottky contact formed between the nanowire summit and the AFM tip, and may further influence the current extraction from the nanowires. It is predicted that the doping of GaN may have some effects on the electrical performance of the macroscopic nanowire-integrated piezogenerators (as in the case of InN nanowire based piezogenerator reported in [59]). Therefore, in order to better understand the device operation and to be able to perform a comparison between the devices, the piezogenerators studied in this thesis are based on non-intentionally doped GaN nanowires.

To analyze the doping, we have performed electron beam induced current (EBIC) measurements, which allow to estimate the doping type of the as-grown GaN nanowires [83]. The EBIC experiments were performed by O. Saket, a PhD student in our team. The results are illustrated in figure 3-7, which shows a secondary electron image (left) and the associated EBIC maps under different biases applied to the nanowire tip (-3 V and 0 V). No signal was observed neither under a zero bias nor under a positive bias, showing that the band bending at the nanowire/tungsten tip interface is not sufficient to separate the electron-hole pairs generated under the electron beam. However, when a negative bias is applied, a bright contrast in the top part of the wire is observed. The direction of the induced current is consistent with the band bending in a Schottky contact on an n-type doped semiconductor. The external bias enhances the built-in field and makes it possible to detect the signal. This measurement indicates that the residual doping in GaN nanowires is n-type.



Figure 3-7. SEM image showing the explored single GaN nanowire touched by the probe (left) and its associated EBIC maps under -3 V and 0 V bias (By courtesy of Omar Saket).

I should note that previously a determination of doping using AFM piezogeneration measurements was performed on some samples indicating a residual p-type doping. However, the samples analyzed in this thesis were grown after the reactor cleaning.

Based on the EBIC experiments, I suppose that a natural n-type background typical for nitride was recovered in the analyzed samples. Further AFM measurements and their comparison with EBIC analyses will be performed in the future to confirm the doping type.

Apart from the piezogenerators integrating non-intentionally doped GaN nanowires, it would be interesting to fabricate and explore the same devices based on nanowires with different controlled doping levels. This would provide a more comprehensive understanding of the nanowire piezoelectric performance. This investigation will be performed in the future in our team.

After this introduction to the MBE GaN nanowire properties, in the next section, I will focus more specifically on my work and I will present the fabrication and the characterization of rigid-matrix piezogenerators based on the above-described GaN nanowires. As mentioned previously, the fluctuation of the nanowire morphology within the same sample could introduce location-dependent variation of the device performance, which is even more pronounced for different growth runs with different growth characteristics. While taking into account the possible fabrication-induced inhomogeneity, it is difficult to rigorously compare different devices. Therefore, the best results obtained among all the measured devices coming from the same wafer will be presented.

What I aim to demonstrate and to discuss is the typical responses of the piezogenerator subjected to various external deformations. Only with a systematic interpretation of the experimental results, a good understanding of the working mechanism of the device could be achieved.

3. Fabrication and characterization of the rigid-matrix piezogenerators

The rigid-matrix piezogenerator consists of a macroscopic GaN nanowire array integrated into HSQ resist (hydrogen silsesquioxane). The nanowires are kept on their growth silicon substrate, which is used as a bottom contact. The HSQ resist (Dow Corning FOX15 flowable Oxide) is widely used as a planarization material. In this study, it is used as a spin-on dielectric to fill the space between the nanowires in order to insulate them from each other and to prevent a shortcut between the top and the bottom contacts. After a high temperature annealing, the inorganic compounds $(-[HSi_{3/2}]_n)$ in the resist decompose and an amorphous SiO_x is formed. The dielectric matrix is important for the device operation since it is used to transfer the deformation to the nanowires. When the macroscopic device is laterally bent with the three-wheel setup introduced in chapter 2, this amorphous silicon dioxide encapsulation experiences a tensile strain parallel to the substrate and thus gets compressed in the direction perpendicular to the substrate. Since the layer adheres to the nanowires, this vertical compression is transferred to the nanowire arrays. This compression along the nanowire c-axis leads to a piezoelectric generation.

3.1 Fabrication of the rigid-matrix piezogenerator



Figure 3-8. Schematic of the fabrication process of a rigid-matrix piezogenerator. SEM images (a) and (b) show the nanowire summits before and after HSQ encapsulation. (c) Optical image of the macroscopic device after fabrication; (d) Schematic of a reference device without nanowires.

Figure 3-8 illustrates the fabrication process of the rigid-matrix piezogenerator. The as-grown GaN nanowires are spin-coated by HSQ resist and then annealed at 400°C during one hour to transform the HSQ polymer onto SiOx. Reactive ion etching is then applied to expose the nanowire summits from the dielectric encapsulation. Top Schottky contacts Cr/Pt (5 nm/145 nm) are deposited by a sputtering method through a shadow mask with 2 mm diameter circular patterns. Finally, the bottom ohmic contact Ti/Au (5 nm/145 nm) is deposited by sputtering on the Si substrate while protecting the previously patterned regions. A reference sample without nanowires is also fabricated following the same process, except that the pure HSQ layer is thinner

when spin-coated using the same parameters on a nanowire-free surface. Figure 3-8.c gives a representative optical image of the piezogenerator after fabrication.



Figure 3-9. (a) I-V curves measured between different indicated top contact pads (inset image) and the bottom contact, confirming the Schottky diode design. (b) Schematic of the fabricated generator.

The I-V measurements are firstly conducted between each top circular contact and the bottom contact. As we can see in figure 3-9.a, the rectifying behavior of the I-V curves confirm the diodic nature of the Schottky top contact. Some variations of the I-V curves can be observed among the different contacts on the same sample. As discussed before, this variation cannot be avoided in devices based on self-assembled nanowires. For devices based on different growths, the current voltage behavior varies more strongly. Despite these minor variations, for the present design, all the current-voltage curves bear the same Schottky rectifying behavior.

For the piezogeneration measurements of these rigid-matrix devices, both the three-wheel bending setup and the vertical compression setup are used to apply compression. The deformed top contact pad is connected to the oscilloscope with 1 M Ω impedance while the transient output voltage is recorded along the deformation process.

3.2 Characterization of the rigid-matrix piezogenerator using the three wheel bending setup

After placing the piezogenerator in a stable position between the wheels, the shaker

head is positioned at the middle of the device back side. Then a vibration is applied to the head, which is transformed into the sample bending. Here I choose two modes of vibration for the shaker head: either it vibrates in a gentle sinusoidal way or in a more abrupt way imposed by pulse controlling signal, which has a rectangular temporal profile. Figure 3-10 and figure 3-11 demonstrate the recorded output signals in the two respective cases.



Figure 3-10. Recorded transient performance (black curve) of one rigid-matrix piezogenerator when it is deformed by the three-wheel bending setup at 2 Hz under a sinusoidal shaker control. The effective device deformation period is indicated by t_c.

The red curve shown in figure 3-10 is the shaker controlling input. Here a sine input at 2 Hz frequency is employed to drive the shaker head. The blue curve is the reading of the device central surface displacement by the laser sensor (i.e. the real displacement, which differs from the control input). The sensor is calibrated in a way that its higher output value corresponds to a higher surface position, meaning that the device is more bended upward (shaker head pushes stronger from the back in the device center). The black curve is the voltage output obtained from one circular contact. It shows repeatable though not quite identical outputs through several bending cycles.

The two pink dashed lines highlight the duration of time t_c when the device is effectively deformed during one bending cycle. When the bending begins, the nanowires embedded in HSQ are compressed and a negative output voltage is

collected from the contact. When the bending ends, nanowires are released and a positive output voltages is obtained. However, as can be seen, these negative and positive outputs are not well-defined single peaks that are expected from one deformation cycle, but are superimposed with a non-reproducible noise-like output. In my opinion, the noisy signal comes from the unstable fixing of the device in-between the wheels. As discussed in chapter 2, the three wheel bending setup suffers from the problem of the device instability. Even during one period of bending, there can still exist some frictions or uncontrolled relative displacements that may affect the nanowire deformation state. Therefore, this non-reproducible output is not a measurement noise, but is a piezogeneration signal, which reflects the sample uncontrolled vibrations in the three wheel set-up. This parasitic signal complicates the analyses. Only the transient after the release of the deformation at the end of each t_c can be extracted with some reproductibility.



Figure 3-11. Recorded transient performance (black curve) of one rigid-matrix piezogenerator when deformed by the three-wheel bending setup at 4 Hz under 70% duty cycle pulse mode shaker control. The effective device deformed period is indicated by t_c.

With an abrupt rectangular pulse signal (70% duty cycle) deformation, the same problem exists. The black output voltage curve shown in figure 3-11 bears a similar noisy form under device compression. We can see from the blue displacement curve that, even during the effective bending duration t_c , the device surface height changes. Though it should be stable according to the pulse input order. This indicates that the control signal form is not strictly respected and that the deformation state of the

nanowire-integrated layer changes as well, but in an uncontrolled way. Therefore, the output negative peaks are noisy. However, differently from the previous sinus vibration case, the effective bending ends in a more abrupt way. The positive output obtained at the moment of releasing is thus clearer. We can observe a repeatable positive output around 7 mV.

Different rigid-matrix piezogenerators have been tested, with both sinusoidal or pulsed signal shaker control and with different deformation levels. Due to setup limitations, all the measurements are realized at frequencies under 10 Hz. The absolute maximum voltage output remains in the order of several tens of millivolts.

I note here that previously rigid matrix piezogenerators were analyzed in the PhD work by N. Jamond. The best results of this type of generators measured with three wheel set-up have been reported in [63]: the maximum voltage output was close to 200 mV. The output saturated with increasing deformation. I wanted to analyze the origin of this saturation, but unfortunately, during my PhD study, no similar saturation behavior has been observed. This could be linked to the difference in the material growth (the nanowires analyzed in [63] and in my work may have a different background doping level) or to other reasons unknown at present.

In general, the sine-signal controlled device bending is less destructive but the effective bending duration is quite random. It depends a lot on the device initial position, which is randomly governed by the manual device placing. The square pulse signal controlled bending can bring higher deformation which promotes higher voltage output, but at the same time it increases the risk of device breaking or dropping. In both cases, the exact compression received by the nanowire-integrated device cannot be quantified and the parasitic noise-like signal prevents further analyses of the device performance. To address these issues, a different set-up was further used to characterize rigid-matrix piezogenerators.

3.3 Characterization of the rigid-matrix piezogenerator using the vertical compression setup

Compared to the three wheel bending setup, the vertical compression setup deforms the nanowire-integrated active region in a more controllable way. The force applied to the device can be read using a force sensor output and the deformation frequency can reach several kHz. In order to characterize the fabricated piezogenerator, one top circular contact is deformed directly by the shaker head and the voltage output between this top contact and the bottom contact is recorded by an oscilloscope with 1 M Ω impedance.

Here, I use both the sine and the square pulse signals to control the shaker movement as in the three wheel set-up. Firstly, the rigid-matrix generator is compressed at 3 Hz with a sine-signal controlled shaker head movement. Figure 3-12 demonstrates the recorded applied force (the blue curve) and the corresponding device output (the black curve). Both short-time (figure 3-12.a) and longer-time (figure 3-12.b) compression durations have been exerted. However, the device voltage output is difficult to be distinguished from the noise. Some spikes can be observed in figure 3-12.b in the blue curve corresponding to the force sensor readings. This is an artifact of the set-up corresponding to bouncing of the shaker head yielding fast vibrations when it hits the device surface. Only at those vibrational moments, some small noisy voltage output can be detected from the measured piezogenerator.



Fig 3-12. Transient voltage outputs (black curves) of one rigid-matrix piezogenerator when deformed by the vertical compression setup at 3 Hz under sine-signal shaker control. For the two measurements, the effective device deformed periods t_c are 0.05 s and 0.12 s, respectively.

Then, square pulse signals are applied to control the shaker head movement. It should be noted that when the shaker head executes the square pulse signal without touching the device, the force sensor gives a non-zero output. Figure 3-13 helps to give a closer look at this phenomenon. A 3 Hz 30% duty cycle pulse signal (pink curve) is applied to control the shaker head. While keeping the shaker head well above the surface (no contact between the shaker head and the piezogenerator), no device voltage output is detected (black curve remains zero). However, the force sensor gives quite distinct peaks (blue curve), which are supposed to signify the existence of "device compression and stretching". In fact, these peaks are artifacts of the used setup that can be reasonably understood accounting for the force of inertia. The first AC peak at the beginning of the pulse corresponds to the downward accelerated movement of the shaker head to approach the device surface. The force sensor gives a positive signal when receiving this push (compression from the shaker head side) and gives a smaller negative peak due to its inertia once the push stops. Vice-verse, when the shaker is retrieving from the lower position, it pulls the force sensor upward. The force sensor hereafter gives a negative peak indicating the stretching force received and then a positive peak when the pulling stops. The amplitude of this non-contact force sensor output varies depending on the acceleration of the pushing and pulling of the shaker head. Since it is the sharp pulse that controls the movement, the acceleration of the shaker head depends on the movement amplitude. This means that because of these inertia artifacts we cannot use the force sensor reading to determine the real force applied to the piezogenerator surface.



Figure 3-13. Measurements recorded when the piezogenerator is not deformed. Without touching the piezogenerator, the force sensor gives spiky outputs (blue curve) due to its movement inertia when the shaker head is controlled by an abrupt square pulse signal.

Figure 3-14 illustrates the situation when an effective compression has been exerted onto the piezogenerator by using the same 30% duty cycle square pulse-signal shaker control at 3 Hz (shown in figure 3-13, pink curve). Only the force sensor output (blue curves) and the piezogenerated voltage output of the device (black curves) are traced in the images. The duration of the commanded compression can be recognized

through the inertia-induced force sensor output in figure 3-14.a (small positive and negative peaks in the force sensor signal). In each cycle, the generation output shows one prominent sharp peak which corresponds to the effective compression received by the device. This effective compression process is highlighted with a pink dashed line in figure 3-14.a, and zoomed and noted as t_c in figure 3-14.b.

As illustrated, the effective contact time marked as t_c does not correspond to the nominal 30% duty cycle and is quite short, only 2 ms. This is also an artifact of the set-up: the shaker head could not keep the constant lower position for a long time, when commanded with a square pulse. The maximum applied compressing force reaches 5.8 N. At the effective device compressing moment, a negative voltage output of 1 mV is detected from the generator. While a positive voltage peak of 0.5 mV is recorded at the releasing moment. Both these two peaks are single clear peaks, distinct from the noise and stably repeatable.



Figure 3-14. Rigid-matrix piezogenerator voltage output under 30% duty cycle pulse-signal controlled shaker compression. The generation happens only at the effective deformation period t_c , as indicated in the zoomed image on the right (b).

A larger voltage can potentially be produced under a stronger compression. However, increasing the compression is risky in practice, since the shaker head taps very hard onto the device. It is very easy to break the generator when adding more pressure on the device under the square pulse control. Besides, increasing the compression frequency in square pulse mode can also lead to device damage.

Compared to the sinusoidal signal control, the square pulse signal control of the shaker movement yields a faster compression of the device and delivers a better voltage output. However, neither the compression duration nor the maximum applied force can be controllably tuned. As discussed above in figure 3-14, it is quite difficult

to achieve a compression duration equivalent to the time period defined by the duty cycle. On the contrary, when a sine control signal is applied to the shaker head, its movement is much better controlled and in particular, the compression duration can be well defined. The force applied onto the device can be adjusted by changing either the device relative position to the shaker head or by increasing the input control signal. Since there is no abrupt displacement of the shaker head under sinusoidal control, the output of the force sensor is less perturbed by the previously discussed pushing-pulling inertia artifact. Furthermore, with a sine control of the shaker head, it is safer to apply a compression onto the generator at high frequency. In addition, a less abrupt deformation resembles more to the environmentally accessible vibrations. Considering all the aspects listed above, the sinusoidal signal control of the shaker is selected for all further experiments on piezogenerators under a vertical deformation. Although some uncertainties of the force sensor output can still appear due to the movement inertia at high frequency measurements (mentioned in chapter 2 and will be further discussed in this chapter), this is the best controllable deformation condition that can be achieved with our home-made vertical compression setup.

The electrical performance of the rigid-matrix piezogenerator has been further explored with the sine-signal controlled deformation at higher frequencies. From the results shown in figure 3-14, we can deduce that the short-time compression, defined in chapter 2 as a tapping deformation, favors the generation of the device. Therefore, short-contact tapping compression has been applied. As shown in figures 3-15 and figure 3-16 presenting the results at 20 Hz and 100 Hz respectively, the fabricated rigid piezogenerator responds well to the external applied force. Distinct voltage outputs are collected. For each effective device compression, the piezogenerator delivers a negative voltage peak at compressing and a positive peak at releasing. We can see that those voltage outputs are quite repeatable, as long as the compression condition remains the same. (Unfortunately, the magnitude of the signal in Figure 3-15 and 3-16 cannot be directly compared since different forces were used. Due to our set-up limitations, it is very difficult to maintain a constant force when varying the frequency.)



Figure 3-15. Voltage output of the rigid-matrix piezogenerator when one of their top circular contact is deformed at 20 Hz frequency under a sine control of the shaker head with a tapping compression. The black curve shows the output signal, the blue curve below shows the reading of the force sensor. A zoom of one deformation cycle is presented on the right. The effective deformation duration can be read as 1.4ms.



Figure 3-16. Voltage output of the rigid-matrix piezogenerator when one of their top circular contact is deformed at 100 Hz frequency under a sine control of the shaker head with a tapping compression. The black curve shows the output signal, the blue curve below shows the reading of the force sensor. A zoom of one deformation cycle is presented on the right. The effective deformation duration can be read as 2 ms.

Tests of the generator at higher frequency deformation have been performed, however no clear piezogeneration could be observed. The example of results is presented in figure 3-17 for a 1 kHz frequency. Figure 3-17.a shows the force sensor output in blue when there is no physical contact between the shaker head and the device. The visible non-zero output is attributed to the noise due to inertia. Figure 3-17.b shows the case when the shaker head is lowered to exert a compression. The compression duration cannot be precisely determined at this high frequency, it presumably corresponds to a tapping mode. However, we can see from the voltage output black curve that no piezogeneration signal could be detected. I suppose that this is due to a smaller amplitude of the shaker head movement and a small deformation level of the nanowires that can be achieved at high frequency with our set-up. The generation may be too weak to be detected at the present noise level.



Figure 3-17. (a) Demonstration of the force sensor output noise at 1 kHz shaker vibration (shaker head is lifted to avoid contact with the device). (b) Similar noise to the one presented in panel (a) and no voltage output of the rigid-matrix piezogenerator can be detected when one of its top circular contact is deformed at 1 kHz shaker vibration.

For all the rigid-matrix devices that I have fabricated, independently on the deformation method (either the three wheel bending setup or the vertical compression setup), the obtained voltage outputs were quite low. Taking the risk of breaking samples, the maximum observed absolute voltage output reached only several tens of millivolts (the best record is 23 mV). The expected mechanical-electrical energy conversion has been demonstrated, however, with a conversion efficiency too low for practical applications

It can be assumed that this low energy conversion efficiency of the rigid-matrix piezogenerators is mainly due to the high rigidity of the encapsulation material. As introduced in chapter 2, this rigid matrix is critical to realize the vertical compression on the nanowires by the three-wheel bending setup. However, in the case of direct vertical compression, this rigid encapsulation absorbs the mechanical energy by itself and prevents an efficient deformation of the nanowires. Thereby, the vertical deformation of the nanowires is small and the effective mechanical energy transferred to the piezoelectric nanowire arrays is low. In consequence, the piezoelectric response of the generator is limited and the mechanical-electrical energy conversion is low.

To solve this difficulty, I have decided to change the device design and to replace the rigid encapsulating matrix by a flexible one. In the next chapter, the soft-matrix
piezogenerator will be presented as an improved version of the energy harvester, and a complete experimental analysis of the device behavior under different deformation condition will be made.

Conclusion of the chapter

At the beginning of this chapter, the MBE technique and the related GaN nanowire growth have been introduced. Discussion of the nanowire structural, optical and electrical properties has been made thereafter. Then, the rigid-matrix piezogenerator has been presented, from its fabrication to electrical characterization. Two different deformation setups have been used to excite electrical responses from the generator. Although the tested device has shown some response to the applied mechanical deformation, its piezoelectric output is rather low. In order to enhance the device mechanical-electrical energy conversion, the rigid encapsulation material needs to be replaced with a flexible one. The characterization and the analysis of the improved soft-matrix device will be made in the following chapter 4.

Chapter 4

MBE grown GaN nanowires for piezogenerator application: soft-matrix devices

To improve the transfer of the mechanical energy to nanowires, soft-matrix piezogenerators have been fabricated and comprehensively characterized. This chapter is dedicated to the study of these devices.

In the first section, the piezogenerators integrating pure GaN nanowires will be reported in great detail. The devices' electrical performance have been explored under an external mechanical excitation in a wide range of frequencies from 1 Hz to 3 kHz. The results will be presented in the order of increasing frequency while taking account of the different applied deformation modes (namely, the tapping mode and the continuous mode defined in chapter 2). Based on the extensive experimental results, a summary of the generator transient behavior under various deformation conditions will be made. The best piezogeneration results will be highlighted and further compared with the state-of-art values reported in literature. The best average power output density of our devices is in the order of mW/cm³, indicating its great potential to be used as a compact energy source.

In section two, the piezogenerators integrating GaN nanowires with AlN/GaN heterostructures will be introduced and compared with the pure GaN nanowire-integrated generators. Then, the equivalent circuit models of the compared generators will be presented together and discussed in section three. Some new generators with capacitive designs have been further proposed and experimentally characterized in order to validate the proposed device working mechanisms. This part of work will be shown in the fourth section. Finally, as a perspective, two attempts to render the piezogenerators fully flexible will be demonstrated and discussed in section five.

1. Soft-matrix piezogenerator integrating vertical GaN nanowires

1.1 Fabrication of the soft-matrix piezogenerator

The soft-matrix piezogenerators were inspired by the idea of using an insulating encapsulation material that does not influence (or only weakly influences) the nanowire mechanical performance. When the nanowire arrays are in their free-standing state instead of being strained, they can be more sensitive to external forces. Therefore, to improve the mechanical-electrical conversion, I have fabricated soft-matrix piezogenerators using PDMS encapsulation.



Figure 4-1. Schematic of the fabrication process of the soft-matrix piezogenerator. On the right bottom, the structure of the reference device without nanowires is presented.

Figure 4-1 illustrates the fabrication flow of the soft-matrix piezogenerator. Firstly, a standard PDMS (Sylgard 184 silicon elastomer) is prepared by mixing its base and the curing agent with 10:1 mass ratio. After an out-gassing process under vacuum bell, the PDMS is diluted by toluene with 1:5 mass ratio. This step aims at reducing the polymer viscosity in order to facilitate its penetration in-between the highly dense nanowires in the array. Then, the diluted PDMS solution is spin-coated onto the as-grown nanowires on silicon substrate with a high spin-coating velocity (4000 rpm – 6000 rpm) depending on the nanowire density and their length. A fast annealing of 2 minutes at 115°C is then performed. Reactive ion etching is applied to get rid of the excess PDMS and to expose the nanowire summits from the embedding polymer. Finally, the top circular Cr/Pt (5 nm/145 nm) contacts and the bottom Ti/Au (5 nm/145 nm) contact are deposited by a sputtering method, as in the case of a rigid matrix device. A sample without nanowires is also fabricated following the same

process. It serves as a reference to confirm that the device electrical signals come from the active nanowires in the later electrical measurements.

One optical image of the fabricated piezogenerator is given in the inset of figure 4-2.a. A typical I-V curve between one top contact (marked with a white dashed line in the inset image) and the bottom Ti/Au contact is presented in figure 4-2.a. It shows a rectifying behavior, thus confirming the Schottky diode formed at the nanowire summits (figure 4-2.b).



Figure 4-2. (a) I-V curve between the encircled top contact pad shown in the inset and the bottom contact of the soft-matrix piezogenerator. Inset – optical image of the device. (b) Device design.

With a soft PDMS encapsulation, the three wheel bending setup is no longer suitable for the device characterization, since the soft matrix cannot add strain onto the nanowires during the device bending. In order to measure the piezogeneration, the vertical compression setup is employed.

When compressing the piezogenerator by the shaker head, I used here a sine signal to control the shaker movements. As explained in the previous chapter, compared to a square pulse signal, the sinusoidal signal better controls the compression conditions of the piezogenerator. However, there still exist some uncontrollable vibrations due to the shaker head rebounding. When the shaker head strikes the device surface with a high velocity, it exerts a big compressing force on the active surface layer. At the same time, it receives the same force. Since the movement of the shaker head is actually the vibration of a magnet core under the electrical field created by a conducting coil, the magnet, or to say the shaker head, can move under other external

forces as well. When this reaction force is big enough, the shaker head may move upward and detach from the device surface. This detachment from the device surface is the rebounding of the shaker head. Depending on the different compression conditions, the rebounding phenomenon may vary. Although the shaker head rebounding can be clearly captured by the force sensor output, it is still difficult to control its duration and amplitude. During the measurement, I tried to analyze and compare the device performance when this uncontrollable rebounding effect is less pronounced. Despite my efforts, in the following sub-sections I will still demonstrate several rebounding occasions that have been observed during the flexible matrix piezogenerator characterizations.

The electrical measurements of the piezogenerators have been carried out under deformation frequencies ranging from 1 Hz to 2 kHz, with variable compressing forces. I will first present the device performance at low frequency compression, and then move to high frequency piezogeneration observation. The earlier mentioned short-time tapping mode and the continuous mode of deformation will be both discussed. During the following presentation, I will give voltage output examples under deformations of different frequencies in order to give a more general view of the device energy conversion performance. If not stated otherwise, the output voltages are obtained using a 1 M Ω load resistance, which is the input impedance of the used oscilloscope.

1.2 Electrical characterization at low frequency deformation (tests between 1 Hz and 750 Hz)

1.2.1 Piezogeneration under a tapping deformation

In figure 4-3.a, the black curve traces the piezoelectric voltage output from one circular top contact when it is deformed by the shaker head at 3 Hz. The blue curve records the applied force. As we can see, the voltage output of the device is correlated with the application of the force in each cycle of deformation. The area highlighted with a pink dashed line is shown in fig 4-3.b, giving a closer look on one effectively compressed period. Between the two pink dashed lines, the duration of the compression can be read as 39 ms. During this time, many phenomena take place. For the sensor output, we can observe sharp spikes at the beginning of the compressing moment. Those spikes correspond to the rebounding of the shaker head. After this

vibration, the force sensor output follows the chopped quasi-sine form, which implies a stable and continuous deformation of the device (refer to chapter 2). Finally, the force sensor output returns to zero when the effective compression is over. As for the voltage output of the device, prominent AC signals are obtained at the beginning of the compression, when the bouncing of the shaker head takes place (encircled in yellow). Then the output drops to zero during the stable compression phase. At the moment of releasing, a positive voltage peak appears (encircled in green).



Figure 4-3. (a) Voltage output of the soft-matrix piezogenerator when one of its top circular contacts is deformed at 3 Hz tapping compression. The black curve shows the output signal, the blue curve below shows the reading of the force sensor. A zoom of one deformation cycle is presented in (b).

By correlating the voltage output with the shaker head movement, it can be assumed that the piezoelectric output of the device depends not on the maximum applied force, but on the force changing rate. To rephrase, it depends on the piezoelectric material's transient deformation. At the beginning of the compression, the shaker head induces big deformation variations due to rebounding, thus high piezoelectric outputs are obtained at that moment. On the contrary, during the stable compression period, the force changing is slow, the nanowire deformation follows a series of quasi-equilibrium states when the free carriers have time to move and screen the generated piezoelectric potential. Therefore, the voltage output drops to zero. At the separation moment, the compression is released fast enough and a readable output is observed. It is noticeable that at the compression moment, the voltage output is firstly negative, while at the releasing, the output is positive. Since the releasing is done in a less abrupt way than the compression (no shaker head rebounding and probably influenced by the PDMS viscous inertia), the output voltage during this process is smaller.

In order to test the above-described hypothesis that the piezoelectric response of the

generator is proportional to the deformation changing rate, a longer duration compression was tested, as shown in figure 4-4. The generator is deformed at 3 Hz by the shaker head under the same sine signal control as in figure 4-3. However, the device position is vertically shifted upwards, thus the effective compression lasts longer. As we can see from the force sensor output in figure 4-4.a, the generator is compressed during almost half of the deformation period. With the same sine signal control, the deformation changing rate is bigger at this device position. Indeed, the deformation rate is proportional to the derivative of the applied force. For a sine control signal, this derivative increases with compression duration for deformation times shorter than one half of the period, reaches its maximum for a compression lasting exactly a half of the period and then it decreases. In practice, this faster variation is reinforced by the shaker head's reboundings. More prominent alternative electrical signals are detected at the beginning of the device compression. As shown in the black curve in figure 4-4.b, a maximum negative peak of -114 mV and a maximum positive peak of 90 mV are obtained as voltage output of the generator. On the other hand, although the maximum force during the effective compression period reaches 5.9 N in the middle of the effective compression duration, there is no voltage output of the device at that moment. This experiment confirms again that it is the applied force changing rate that defines the device electrical output. From this point of view, in order to have a detectable piezoelectric output from the generator, the derivative of the force (or the deformation variation) should be larger than a minimal threshold value. This value depends on the time which is required for the free carriers to screen the piezogenerated charges.



Figure 4-4. (a) Voltage output and the force sensor trace of the soft-matrix piezogenerator at 3 Hz under a taping mode with a long-duration effective compression. (b) A zoom of the traced curves at the beginning of compression.

The problematic point of the above-described tapping measurements is the

uncontrolled shaker head rebounding at the beginning of the compression. The spiky form of the voltage output at the beginning of the compressing process hinders the quantitative analysis of the device performance. Efforts have been made to perform a tapping on the device at 1 Hz and 10 Hz with a gentle force that doesn't induce the shaker head rebounding. By keeping the same effective deformation time (t_c) for each measurement at a fixed frequency, the piezogeneration of the device is demonstrated to increase linearly with the increasing of the maximum applied force, as shown in figure 4-5. This can imply a linear increase of the piezogeneration with the force changing rate, since the deformation duration is constant.



Figure 4-5. When keeping a constant compression duration (t_c), the device voltage output increases linearly with compressing force. 2 examples are given at 1 Hz and 10 Hz tapping deformation.

In fact, the applied force changing rate is closely linked to the deformation change of the device (more precisely, the deformation change of the active piezoelectric nanowires embedded in the device). In literature, the deformation change of the piezoelectric device is usually referred as the "strain rate". Some experimental studies have been made, reporting that a higher strain rate can induce a higher electrical output of the piezogenerator [53]. Our observation here is coherent with this conclusion. Indeed, the maximum deformation level (the final strain state) defines the maximum piezoelectric potential that can be created in the material, whereas it is the deformation changing rate (the strain rate) that decides the maximum output value attainable at the external load. However, another work has reported a linear increase of the piezogeneration along the maximum pressure received by the device [54]. To

make this conclusion more rigorous, the device deformation time should be mentioned, giving an idea of the strain rate during the measurement. By definition, the strain rate of a material under elastic deformation depends not only on its maximum pressure received, but also on the time period necessary to reach the maximum deformation. Only when the deforming time is fixed, the linear pressure-dependent generation under elastic tapping can be validated.

With the vertical compression setup used here, the strain rate of the device cannot be read directly. Nevertheless, by fixing the compression duration and varying the maximum applied pressure, the strain rate of the piezogenerator can be adjusted accordingly. Figure 4-7 gives another example when the tapping measurements have been carried out at 20 Hz. The deformation of the device is controlled at a very-short time, only 2 ms. While increasing the maximum applied force (or to say, the maximum pressure), the device output increases proportionally.



Figure 4-6. When deformed at 20 Hz with a tapping compression, the piezogenerator output increases with the external force. The effective compression duration of the device is kept at 2 ms for all the measurements.

To give a closer look, I zoomed one generation event from figure 4-6 in figure 4-7. As we can see, with a compressing duration of 2 ms (period between the pink dashed

lines) and a maximum tapping force of 4.7 N, the peak-to-peak voltage output of the device reaches 84 mV (from -57 mV at compression to 27 mV at releasing). To calculate the force changing rate or the strain rate, the compressing time should be taken into account. Reading from the blue force sensor curve, the compressing time is about 1 ms. The compressing time combined with the 4.7 N maximum force determine the strain rate of the piezogenerator during this measurement. It is obvious that, this 1 ms has nothing to do with the pre-defined deformation frequency 20 Hz (50 ms period). Therefore, for the tapping mode deformation, the commanded tapping frequency doesn't influence the device performance. The frequency-dependent piezogeneration study at tapping mode deformation is meaningless. Only when the deformation frequency is linked to the effective device deformation time, a rigorous frequency-dependence study can be made. This is the reason why the full-time continuous mode deformation is employed during our device characterization. I will present this part of work in the later section 1.3.



Figure 4-7. Voltage output of the soft-matrix piezogenerator when one of its top circular contacts is deformed at 20 Hz with a tapping compression. The black curve shows the output signal, the blue curve below shows the reading of the force sensor.

Now we continue to explore the device performance under a tapping mode deformation, but with a longer effective deformation duration. Figure 4-8 shows some measurements performed at 25 Hz deformation with a different effective deformation time (t_c) (from panel a to d, the t_c increases). We can see from the force sensor output in the 4 separate images, the rebounding times of the shaker head increases when the deformation duration becomes longer. Even though, for each shaker head rebounding, the device generation follows well the deformation change and shows pretty high values. In addition, this demonstration helps to explain the difficulty of realizing a

deformation without separation (continuous mode deformation) onto the generator at low frequency (mentioned in chapter 2). When vibrating at low frequency, even with the smallest signal control, the shaker head moving amplitude is quite large. Prolonging the contact duration may induce multiple shaker head reboundings (as shown in figure 4-8), and it is impossible to maintain the shaker head all the time on the generator surface without destroying the device. Therefore, the low frequency deformation tests made here are all executed in tapping mode.



Figure 4-8. Demonstration of the increased shaker head rebounding with increasing compression duration. Measurements conducted at 25 Hz.

When the fast tapping deformation is performed at even higher frequencies, another rebounding artifact of the shaker head can be observed. When the piezogenerator is within the shaker head moving range but close to its limit, the shaker head may not tap the device every time as commanded by the original input signal. Figure 4-9 illustrates this case happening at a 250 Hz shaker vibration. In the two images, the input control signals are shown in pink as a frequency reference. The blue curves trace the output of the force sensor which gives a presentation of the effective device deformation. The black curves are the voltage outputs of the piezogenerator during the compressing and releasing process. Between figure 4-9.a and 4-9.b, the only parameter that was changed is the piezogenerator vertical position. In figure 4-9.a, only half of the tapping deformations reaches the device surface as can be seen from

the force sensor output (the control signal has twice as high frequency as the force sensor output). After re-positioning the generator closer to the shaker head, all the deformations become effective (figure 4-9.b). It is good to see that, in both half frequency tapping and full frequency tapping, the piezogenerator stably responds to the external deformation. It gives an output following the received effective deformations. The piezogenerator response is always fast enough to follow the high frequency tapping of the shaker head.



Figure 4-9. Demonstration of the half-frequency rebounding phenomenon of the shaker head. The two measurements in (a) and (b) are realized in same conditions except for the device vertical position, which is slightly lower for (a) than for (b).

In practice, this half-frequency rebounding phenomenon of the shaker head has been observed during a large range of frequencies tested, from 200 Hz to 750 Hz. By adjusting the device vertical position, the aimed full frequency deformation can be achieved. In the following, I only consider the stable full frequency deformation for analysis and I disregard the situation when the shaker head vibration frequency deviates from the command signal.

Figure 4-10 illustrates the best device performance observed under a tapping deformation. With a 300 Hz shaker head vibration, the stable voltage output of the

device is recorded. In each cycle of the deformation, the effective compressing process lasts for 1.2 ms. The maximum force applied on the generator is 7.2 N and the obtained voltage output has a peak to peak value of 1.216 V (from -504 mV at compression to 712 mV at releasing).



Figure 4-10. Best recorded performance of the soft-matrix piezogenerator under a tapping deformation at 300 Hz. The AC voltage output of the device traced in red curve reaches a peak to peak value of

1.216 V.

I note here that it is difficult to compare the performance of our devices with the literature. Indeed, the generator output depends not only on the maximum applied deformation (maximum applied force), but also on the deformation changing rate (strain rate), whereas this parameter is rarely given. To give an example, I compare our devices with the work of Xu et al. reported in [54], where the vertically-aligned ZnO nanowire-based piezogenerator gives a voltage output of 60 mV at a compression force of 6 N (2 Hz tapping) (refer to chapter 1, figure 1-12.c). At first glance, our GaN nanowire-based device shows a better piezoelectric response: voltage output is more than 500 mV absolute value under a maximum applied force of 7.2 N. However, to be more rigorous, the comparison should be made while considering the device received strain rate (the input mechanical energy for both device is unknown). As mentioned before, the commanded tapping deformation frequency doesn't influence the effective strain rate of the piezogenerator. Though the reported ZnO-based device is measured at 2 Hz tapping and the GaN-based device is measured at 300 Hz tapping, the deformation condition for the two are of the same type. The

GaN-based device reported here receives the 7.2 N maximum force after 0.6 ms of mechanical compressing. While the compressing time of the ZnO-based device is not mentioned in the article. Noting that in the publication, the mechanical strain of the device is reported to be applied "with an impact speed of 0.1m s⁻¹", here I use the presented force curve in figure 4-10 to estimate the impact speed received by our device. For the measured device here, the thickness of the active piezogenerating region is defined by the used GaN nanowires length, which is around 1 μ m. Taking the extreme case that the piezogenerator is deformed by 1 μ m during the 0.6 ms shaker head compressing motion, the impact speed can be estimated as 1 μ m/0.6 ms = 0.0016 m s⁻¹. This value is hundreds of times smaller than the reported 0.1 m s⁻¹ in the article, indicating a much smaller strain rate of our device. We can therefore conclude that in a less favorable compressing regime our generator largely outperforms the ZnO nanowire-based device.

It should be further noted that, the instantaneously abrupt deformation used in Xu et al. is quite difficult to find in the surrounding environment apart from strokes that can be destructive. Realistic mechanical deformations present a finite rise time. A sine signal controlled deformation is more realistic to model ambient vibrations. With a longer compressing time, the force changing rate is slower. The GaN nanowire-based piezogenerator response decreases accordingly, but still remains high. This good performance of the device should be attributed to the high crystalline quality of GaN nanowires provided by the molecular beam epitaxy technique, and to the enhanced mechanical coupling guaranteed by the soft encapsulation matrix.

1.2.2 Piezogenerator transient behavior analysis - part I

Above I described the generators tests in a tapping mode under deformation frequencies from 1 Hz to 750 Hz, which is a much larger span of frequencies than published in the literature. I refer to this frequency range as low and medium frequency measurements since the period of the command signal is much longer than the effective compression duration of the piezogenerator. The output signal of the device is captured at the moment of the compression and at the separation. In between, when the device is deformed with a force changing according to a quasi-sinusoidal law, no signal is recorded. As mentioned before, this is a quasi-static regime, in which the device undergoes a sequence of quasi-equilibrium states with free carriers

screening the generated piezoelectric field. For this reason, no signal can be recorded when the shaker head is all time in contact with the device. In the tapping mode in a low and medium frequency range, the compression duration can be known from the force sensor output (no inertia artifacts) and the effective compression duration can be well controlled by adjusting the device vertical position. Because of the separation between the shaker head and the generator surface, the output voltage of the device is a non-continuous alternative signal. It is evident that a negative voltage peak appears when the device is compressed and a positive peak emerges at releasing.

In figure 4-11.a, I zoom the force sensor and the voltage output traces of one deformation event given in figure 4-10 to better understand the device physics. We can observe that after reaching the maximum negative value, the output voltage drops in an exponential way, as highlighted in the dashed square. Once the piezoelectric potential of the nanowire is created under the external compression, the free carriers in the circuit move according to the induced potential difference. At the same time, the free carriers in the nanowire itself move as well. Their movement may lead to a screening effect of the generated piezoelectric potential and reduce the voltage output recorded at the external load (here at the oscilloscope with a 1 M Ω inner impedance).



Figure 4-11. (a) Zoomed image of one deformation event in measurements given in figure 4-10. (b) The exponential fitting of the first signal decay highlighted with a green rectangle in panel (a).

It should be noted that, from the force sensor output in figure 4-11.a (blue curve), the force changing rate dF/dt remains non-zero during the whole negative voltage peak decay period. Indeed, the shaker head follows the sine control signal, so it has a non-zero derivative and the compression of the device is maximal at the middle of the effective compression duration. This non-zero changing rate may modify the nanowire piezoelectric state and add some additional influence on the voltage decay

process. If we want to avoid this dynamic influence, square pulse signal shaker control should be applied. In this way, the force derivative is non-zero only at the beginning of the compression, therefore the voltage decay would be easier to interpret. As I mentioned previously, the square pulse shaker control is difficult to realize with our setup. So in the following analysis, I will neglect the influence of the force changing on the signal decay when the shaker head and the device surface are in contact.

An exponential fitting of the negative peak decay is done by:

$$\mathbf{U}_{\text{out}} = \mathbf{U}_{\text{max}} \ast \mathbf{e}^{(-t/\tau)} ,$$

where the decay time τ is extracted equal to 0.13 ms (zoomed fitted curve in figure 4-11.b) as a characteristic parameter of the measured generator in the circuit. Due to the statistical variations of the nanowire array, this decay time varies for contact pads at different device positions. The fluctuations of the decay time remain within 0.15 \pm 0.05 ms.

Now let's take a look at the positive voltage decay after releasing the compression. The example at 300 Hz plotted in figure 4-11.a is not suitable for this analysis. By examining the force sensor output curve encircled in the orange dashed line, it can be assumed that the separation of the shaker head from the device surface is not instantaneous in this example. Some minor shaker head rebounding and vibration can still reach the device surface after the commanded releasing. Hence, I will discuss this second signal decay using the results obtained at 20 Hz tapping deformation, where the releasing is better defined.



Figure 4-12. (a) Zoomed image of one deformation event from measurements given in figure 4-6. (b) The exponential fitting of the second signal decay highlighted with a pink rectangle in panel (a).

One effective deformation period from the trace shown in figure 4-7 is represented in figure 4-12.a. It is clear that after the releasing, a maximum positive output appears and decays in an exponential way (highlighted with a pink dashed rectangle). By performing the same exponential fitting as before, the decay time of this second peak is extracted as 0.41 ms. This value is slightly higher than the previous decay time $\tau = 0.13$ ms.

In fact, if the influence of the changing force during the device deformation can be neglected, and if the mechanical compressing and releasing processes are symmetric, the reported two signal decay times should be the same. This is because the two decay processes are both the characteristic responses of the generator and they are determined by the outer circuit and the inner nanowire resistance.



Figure 4-13. Equivalent circuit of the vertically-integrated nanowire based piezogenerator.

To better explain this point, an equivalent circuit of the piezogenerator is drawn in figure 4-13. For this abstraction, each deformed piezoelectric nanowire is represented as an alternative voltage source. Own to the nanowire non-intentional doping, a shunting resistance is added as R_{NW} in parallel to the individual voltage source. The Schottky contact at the nanowire summits is presented as a diode in series with each individual nanowire. The Schottky diode is not ideal, so a shunt resistance is added in parallel with diodes (which can be very big for high quality Schottky contacts). For small voltage signals observed in our experiments, the Schottky diode cannot be forwardly biased and the diode is equivalent to its series resistance. Then all the individual powering units (deformed nanowires) are connected in parallel to the same deformed contact pad but not receiving deformation (device deformed area is limited

by shaker shape, and it is smaller than the top contact pad), they remain inactive. They are represented as an equivalent resistance R_{rest} in parallel with the active nanowires, with a Schottky diode on top.

When the deformation is applied onto the device, piezoelectric potentials will be created inside each of the deformed nanowires (figure 4-13, indicated as NW_1 to NW_n with resistance R_{NW_1} to R_{NW_n}). The potential difference between the nanowire summit and the bottom induces the free carrier movement in the circuit. At the same time, the free carriers (due to non-intentional nanowire doping) will redistribute in the wire to screen the generated piezoelectric potential, hence attenuating the effective electrical potential that can be detected externally. Once the compression varies in amplitude, the electrons will pass through the top diode resistance and then pass through the external load, a negative voltage can be detected at the load. When the compression variation is less prominent (i.e. when the force derivative is smaller) and the free carrier movement is fast enough to screen the generated potential, the recorded output voltage decays. The non-deformed nanowires contribute little to the decay process since they are separated from the generating nanowires by a Schottky diode in series which has a big shunt resistance.

Reversely, when the compression is released after the established circuit equilibrium, the piezogenerated fixed charges disappear and the mobile carrier will redistribute according to the releasing rate. Ideally, the decay time of the second positive voltage peak will be the same as the decay time of the first negative peak. However, in practice, the soft PDMS encapsulation may slow down the recovery rate of the deformed nanowires, hence the releasing peak is smaller and its decay time is longer.

For the circuit illustrated in figure 4-13, it is impossible to precise the resistance of each single nanowire and to know the diode resistance on top of each individual power source from experiment. However, by simplifying the circuit as shown in figure 4-14.a, a relation between the proposed model and the measured devices can be established. In the schema of figure 4-14.a, all the deformed nanowires are equivalent to an alternative power source with a general shunting resistance R_{NWs} and a top Schottky diode. Since the Schottky diode cannot be opened with a small generation signal, it is symbolized by a series resistance R_{sch} in the circuit. In fact, the I-V curve of the piezogenerator traced before the deformation contains information about these two equivalent resistances. At 0 V bias, the big resistance of the circuit may correspond to the diode resistance R_{sch} . It is measured as 148 k Ω (figure 4-14.b, inset).

While by fitting the I-V curve after the diode opening, a much smaller resistance can be estimated (about 80 Ω). This value may give an idea of the resistance coming from numerous nanowires connected in parallel. Compared to the external 1 M Ω load, the estimated shunt resistance of the nanowire power source is quite small (80 Ω). The diode-related resistance is relatively high, but still much smaller than the load resistance.



Figure 4-14. (a) Equivalent circuit of the analyzed piezogenerator. (b) I-V curve used to extract characteristic R_{NWS} and R_{Sch} parameters of the generator (Inset, the R-V curve of one generator pad).

If we want to further predict the device electrical behaviors in response to external dynamic mechanical deformations, the characteristic transient parameter τ of the device/circuit should be taken into account. I will present this part of transient study in more detail in the next section 1.3, after analyzing the device performance under high frequency deformation.

1.2.3 Device output power calculation (under tapping deformation)

Before moving on to the high frequency measurements, I'd like to use the best voltage output shown in figure 4-10 to calculate the power output of the fabricated piezogenerators under low-frequency tapping deformation.

By using the expression:

$$P_{ave} = \frac{\int_0^T U^2}{T^* R},$$

with the period T = 1/300 s (300 Hz) and the load resistance R = 1 M Ω , the average power output of the device is calculated as 25.8 nW. Under each tapping event, an energy of 86.1 pJ can be delivered by the device.

The peak power output can be calculated by:

$$P_{\max} = \frac{U_{\max}^2}{R},$$

with the maximum voltage $U_{max} = 0.712$ V. The P_{max} is calculated as 506.9 nW, which is much higher than the average power output value.

If we consider the effective deformed surface of 0.0078 cm² (determined by the shaker head 1 mm diameter circular shape) and the active layer thickness of 1.5 μ m, the average power output density and the maximum power output density of the device can be calculated as 3.31 μ W/cm² (22.1 mW/cm³) and 64.98 μ W/cm² (433.2 mW/cm³), respectively. All these values are summarized in table 4-1.

	Average value	Peak value
Power output	25.8 nW	506.9 nW
Power output density	3.31 µW/cm ²	64.98 μW/cm ²
(per unit surface)		
Power output density	22.1 mW/cm ³	433.2 mW/cm ³
(per unit volume)		$= 0.43 \text{ W/cm}^3$

Table 4-1 Device power output under tapping mode low-frequency deformation

*Measurement conditions : 300 Hz tapping frequency. 1.2 ms effective deformation duration. 7.2 N maximum applied force. Impact speed < 0.0016 ms^{-1} . 0.0078 cm^2 deformed device surface. 1.5 μ m active layer thickness.

It is noteworthy that the best vertically-integrated ZnO nanowire based piezogenerator reported in [58] delivers a maximum power output density of 0.78 W/cm³. The peak output power density of our device is 0.43 W/cm³, which is quite similar to the record value. In fact, for the reported device in [58], the deformation condition is not clearly described. The 0.78 W/cm³ power density is said to be obtained with a energy-harvesting pad (with a surface area larger than 9 cm²) under palm punching. The average power output of the device is not mentioned, which is however more important than the peak value. Neither the external load nor the deformation rate are given. For our GaN-based generator, the average power output density reaches to 22.1

mW/cm³, demonstrating its great potential to be used as a compact energy source.

Meanwhile, it should be noted that the power output of the generator depends on the load circuit. All the values presented in table 4-1 are obtained when the measurements are carried out with a 1 M Ω external load, which is not the optimal load for the energy transfer from the fabricated device. It is possible to have a higher energy output of our generator if a good impedance matching is realized.

1.3 Electrical characterization at high frequency deformation (>1 kHz)

1.3.1 Piezogeneration observation at high frequency deformation - difficulties and puzzles



Figure 4-15. The voltage output of the piezogenerator (black curves) and the force sensor output (blue curves) at 1 kHz. The deformation conditions are changed by reducing the relative distance between the shaker head and the generator from panel (a) to panel (f).

As mentioned in chapter 2, when the shaker head vibrates at high frequencies, the inertia of the force sensor movement introduces a large uncertainty in the interpretation of its output. For the present measurements, once the vibration frequency surpasses 1 kHz, the force sensor output is no more reliable to determine the applied force value. The effective deformation duration cannot be identified neither. For the generator voltage output, although it is still an alternative signal, it is smoother and does not have the sharp alternative peaks discussed before. In addition, a small change of the device vertical position can induce a big change of the device electrical output.

The measurements displayed in figure 4-15 give a general illustration of the above described problems. The black curves trace the device voltage output and the blue curves are the readout of the force sensor. For this group of measurements, the shaker head vibrates under a fixed sinusoidal controlling signal (1.75 V control amplitude) at 1 kHz. The distance between the shaker head and the piezogenerator has been changed by increasing the device vertical position (i.e. reducing the device to shaker head distance). As a result, the effective compression duration of the generator is increased from figure 4-15.a to figure 4-15.f.

- Graph (a) presents a reference situation when the shaker head does not touch the piezogenerator. The voltage output of the generator is zero. Whereas, the force sensor gives inertia induced output, which is of a sine form (following the control signal) and has both positive and negative values;
- In graph (b), the shaker head begins to compress the device, since a readable small voltage output can be detected from the generator. The force sensor output starts losing it sinusoidal form, due to the appearance of a real compression signal;
- Measurement (c) displays the maximum output of the piezogenerator during the upward approaching of the device towards the shaker head;
- Once higher than the device position in situation (c), the voltage output of the generator reduces, as shown in image (d). The negative part of the force sensor output is reduced greatly as well;
- The voltage output of the generator keeps decreasing when it gets even closer to the shaker head, as captured in graph (e). The force sensor output begins to be all positive and smooth;
- > The results in (f) are recorded at the highest possible position of the generator. At

this moment, the generation is quite small, but with a more continuous and smooth form. The positive constant shift of the force sensor output from zero indicates a stable continuous compression of the device superimposed to the periodical vibration. It is undoubted that the shaker head is in contact with the generator all the time.

Indeed, for all the measurements of the generator at high frequency, it is difficult to know the effective compression duration. The force sensor output is strongly disturbed by the inertia noise to give a precise contact time. With the device surface monitoring camera, the separation of the shaker head cannot neither be observed with a sufficient precision. However, the voltage output of the generator which follows a regular evolution can be considered as an indicator of the device deformed state.

Since the voltage output of the piezogenerator is proportional to its deformation changing rate (as concluded from the previous tapping mode deformation analysis), it can be assumed that the situation in figure 4-15.c, where the maximum voltage output is obtained, satisfies the condition of the maximum deformation change rate (maximum strain rate). Presuming that the shaker head vibrates with a sinusoidal form at the generator surface, its maximum displacement change happens at half period (maximum derivative of the sine function), corresponding to the maximum deformation change of the generator. Therefore, figure 4-15.c presents the critical situation when the generator deformation lasts for half of the period of the voltage output of the generator is smaller due to the slower device strain rate, as has been shown in figure 4-15.b and 4-15.d, respectively.

The original motivation of measuring the device under a continuous contact vibration was to analyze the frequency-dependence of the generation. In addition, in this mode, the linearity of the piezogeneration with deformation was expected to be explored. If the sinusoidal displacement of the shaker head remains small (much less than the nanowire/PDMS active layer thickness), a continuous surface deformation may be added. In the ideal case of a deformation going from a zero value for the minimal force to a maximal value, the force sensor output should display a continuous smooth quasi-sinusoidal form with its minimum value reaching zero. This minimum zero force corresponds to the state when the shaker head touches the generator surface without adding any deformation, while the maximum positive force value indicates the maximum compressed state of the device. We can find this ideal state by adjusting shaker head vibration amplitude. Then, by progressively increasing the shaker head vibration amplitude while keeping a zero minimum applied force, the nanowire deformation would increase and it may be possible to explore the eventual saturation of the piezogeneration under high deformation [55], [63].

However, in practice, this kind of ideal experiment is difficult to conduct. The amplitude of the shaker head cannot be easily tuned under 1 μ m which is a typical piezoelectric active region thickness of the fabricated generators. The precise measurement of the displacement is also a challenge. In addition, the displacement of the shaker head depends on the frequency and is greatly reduced when vibrating at a kHz level, therefore the comparison of the output at different frequencies is compromised by the difficulty to maintain a constant vibration amplitude. Moreover, even if the force sensor output remains all positive with its minimum value at zero (as shown in figure 4-15.e), we cannot rely on these readings, since the inertia-induced noise is superimposed to the real compression signal. Due to all the above-mentioned difficulties, the piezogeneration saturation exploration has not been done with the present devices.



Figure 4-16. The voltage output of the generator and the readout of the force sensor when the generator is deformed at 1.5 kHz vibration.

When the measurements are carried out at an even higher frequency, the output interpretation becomes more complicated. As the shaker head vibrates at less than 1.5 kHz frequency, the force sensor output can still give an indication of the contact since it may experiences an evident shape change after touching the generator surface (i.e. the blue curves are different in figures 4-15.a and 4-15.b). However, at frequencies higher than 1.5 kHz, despite of the generator's vertical position, the output of the

force sensor remains quasi-sinusoidal with just a slight change of its amplitude. The only way to distinguish the non-deformed and the deformed states of the generator is to monitor the force sensor output symmetry and to check if there is a generation output detected from the device. As shown in figure 4-16, from the force sensor output blue curve, it cannot be known whether the generator is deformed or not (the sine form distortion is ambiguous). By reading the device's non-zero voltage output traced in black, we can know that the generator is compressed. However, the exact deformation duration and the applied force are unknown.

In order to characterize the generator operation at high frequencies in a systematic way, I defined the following measurement protocol:

1. Find one vertical position of the generator for which it is deformed by the shaker head and gives a voltage output. In the example shown in figure 4-16, the generator is stably deformed by the shaker head at 1.5 kHz with a sine-signal shaker control of 0.2 V amplitude;

2. While fixing the generator's vertical position, adjust only the sine-signal shaker control amplitude to vary the deformation. The applied force increases with the input control amplitude, so does the deformation level of the generator. Under different shaker control amplitudes, the voltage outputs of the generator are recorded. Then, the maximum absolute values of these outputs are traced as a function of the controlling amplitude, as displayed in figure 4-17. A linear fitting can be then employed. From this measurement, the piezogeneration of the device is confirmed and the obtained linear scaling meets the expectation.



Figure 4-17. Linear relation between the generator's absolute output voltage and the sine-signal control amplitude of the shaker head.

3. Finally, the measurements for different generator positions are performed as previously described in the example of figure 4-15 for 1 kHz deformation. Here, 1.7 V amplitude sinusoidal signal of 1.5 kHz is used to control the shaker head vibration. While changing the vertical position of the generator from low to high, the transient voltage output of the generator has been recorded. However, differently from the previously described 1 kHz vibration case, two maxima in the generator approaches the shaker head, the device output increases from zero to the first maximum output captured in figure 4-18.a. Then by further ascending the generator, the voltage output first drops and then increases again, until it reaches the second maximum captured in figure 4-18.b. If the generator is further lifted closer to the shaker head after obtaining the second maximum, the device output decreases again.



Figure 4-18. The two best voltage outputs of the generator captured during the device ascending procedure when deformed at 1.5 kHz. The black curve in (a) and (b) demonstrate respectively the first and the second maximum transient voltage output. The blue curve in each graph is the corresponding force sensor readout. The amplitude reduction of the applied force from (a) to (b) is due to the mechanical performance change of the shaker head under different non-separation and separation working conditions.

It is not intuitive to understand these two maxima in the output. If the presented measurement procedure is carried out by descending the generator, the two maxima of the output are observed again, but in a reversed order. Therefore, it cannot be an experimental error, we indeed observe two optimal deformation conditions for the device piezogeneration. For measurements at different frequencies up to 3 kHz, these two characteristic maxima in the output were always observed. However, at 1 kHz and lower frequency deformation, only one maximum was present.

1.3.2 Piezogenerator transient behavior analysis - part II

In order to understand the puzzling two-maxima observation, we need to consider all the measurements (from 1 Hz to 3 kHz) to make a panoramic analysis. As has been mentioned in section 1.2.2, the characteristic signal decay time of the device in the circuit influences greatly the device electric behavior. Here I will make a compact definition of all the time-related parameters that are later used to describe the piezogenerator electrical performance.



Figure 4-19. Definition of the time-related parameters, using the voltage output trace of the generator under one tapping deformation.

Let's take the example depicted in figure 4-19. This trace demonstrates the alternative output of the generator during one deformation event in a tapping mode. Here I define T, the deformation period commanded by the shaker control signal, it equals 1/f (f being the frequency). The effective compression duration of the generator is noted as t_c . It can be varied by changing the device vertical position relative to the shaker head, from 0 to T. The indicated τ_1 and τ_2 are the decay times of the two peaks that can be fitted from experimental traces. By theory, the two decay times should be the same since both of them are determined by the interplay between the nanowire array inner resistance and the external load circuit. However, for the measured piezogenerator, due to a slight difference of the device mechanical compressing and releasing conditions, the empirical values of the two are a little bit different (as have been reported previously, one is about 0.14 ms and the other is about 0.4 ms). To simplify the later analysis and discussions, here we take a unique characteristic decay time τ for the piezogenerator under test. An average empirical value of around 0.1 ms ~ 0.2 ms can be attributed to this parameter in view of device topological inhomogeneity and deformation condition variations.

	Condition	Operation description	Frequency
			range
1	$T = t_c > \tau$	Low frequency deformation without	
		separation. Voltage decay is faster than	$f \ll 1/\tau$
		the generation. Or strain rate is too low to	
		have generation. <no output=""></no>	
2	$T = t_c > \tau$	Medium frequency deformation without	
		separation (around 1 kHz as tested with	$f < lpha 1/\tau$
		our sample).	
		An output voltage can be obtained, but	
		the values are small.(eg. Figure 4-15.f. 4-18.b)	
3	$T > t_c > \tau$	Low frequency tapping deformation.	
4	$T > t_c = \tau$	An output voltage decay can be fully	
		observed. (eg. Figure 4-11)	$f < 1/\tau$
5	$T > \tau > t_c$	Low frequency tapping deformation.	
		The output voltage decay is incomplete	
		due to early releasing. (eg. Figure 4-12)	
6	$\tau > T > t_c$	High frequency tapping deformation.	$f \ge 1/\tau$
7	$\tau = T > t_c$	(eg. 4-18.a, later 4-20)	
8	$\tau > T = t_c$	High frequency, full-time continuous	
		compression	
9	$\tau = T = t_c$	The device voltage output is a continuous	$f \ge 1/\tau$
		alternative signal. (eg. 4-18.b, later 4-21)	
10	Full time	High constant pre-compression may lead	
	deformation with	to device output saturation, and even	
	constant	cause nanowire damage.	
	pre-compression	For condition 2, 8 and 9, the output may	
		be reduced. For condition 1, no voltage	
		output.	

 Table 4-2. Summary of piezogenerator responses under various vertical compression conditions.

Here I summarize in table 4-2 all the possible deformation conditions that can be created with a vertical compression setup. The three parameters, T, t_c and τ , are used to describe the various deformation conditions. A short description of the device operation is also provided in the middle column. The corresponding measurement for

each situation can be found from the previously presented results or from the examples in the following parts.

With the table 4-2 in mind, let's now return to the question: why are there two maxima in the voltage output at 1.5 kHz and higher frequencies, but not at 1 kHz and lower frequencies? In fact, the reason lies in the comparison between the generator's characteristic decay time and the deformation period. From the previously discussed 1 kHz measurements at different generator/shaker head distance (figure 4-15), it can be confirmed that the maximum generator output happens at the half period tapping when the device deformation rate is the biggest (i.e. dF/dt is the biggest). To rephrase in a mathematical way, this optimal generation condition is: $t_c = 0.5T$. This specific case may belong to the tapping mode deformation described in categories 3, 4 or 5 with $T > t_c (T > \tau)$ in table 4-2. By calculation, when the generator is deformed by tapping mode compression at 1.5 kHz, the optimal condition of $t_c = 0.5T$ can also be satisfied. Therefore, we can attribute the first maximum generation output at 1.5 kHz (figure 4-18.a) to this optimized tapping deformation condition (refer to category 6). As for the second maximum output at 1.5 kHz, the most straightforward explanation is that this second maximum corresponds to a switching from the tapping mode to a full-time continuous deformation mode. With a non-separation of the shaker head from the generator surface, at 1.5 kHz vibration, the deformation condition may go into the described categories 8. Moreover, by repeating the measurements under vibrations from 1.5 kHz to 3 kHz, the existence of this second maximum confirms the proposed explanation. It should be noted that there exist an ambiguous situation, the category 2 as described in the table. Due to the lack of precision of the decay time, for a deformation frequency lower but not too low from the $1/\tau$, it is still possible to observe certain device voltage output under a full-contact continuous deformation. But still, the fast signal decay deteriorates the output signal, the voltage output at this condition will not be comparable to the one obtained at half period tapping. This means, no second maximum output at full time compression condition. This may explain why the measurement illustrated in figure 4-15 at 1 kHz does not have a second output maximum.

All the above presented conclusions and explanations are based on representative experimental results selected among numerous recorded measurements. The presented output curves doesn't give a complete demonstration of possible output shapes. In fact, by making a systematic comparison between τ and $T - t_c$, while considering the different cases presented in table 4-2, a more precise prediction of the device output

can be achieved.

Another parameter that I have not discussed is the time for the generator to reach its output peak values. This time can be considered zero if the tapping deformation is a perfect sharp square pulse. In the current study, when the compression is commanded by a sinusoidal signal, this time is finite, but we can still consider it short enough. In practice, the finite value of this time may reduce the output, since the device inner decay may hinder the effective deformation-created potential from reaching its maximum. However, this time is always shorter than τ as observed and can be neglected in the device performance analysis.

1.3.3 Device output power calculation (under high frequency deformation)

To conclude this section, I'd like to present the two best results of the piezogeneration at high frequency vibrational deformation. One is obtained under tapping mode deformation, another is under full-time continuous compression.



Figure 4-20. Best recorded output of the soft-matrix piezogenerator under high frequency tapping deformation at 1.3 kHz. The AC voltage output of the device traced in red curve can reach a peak to peak value of 200 mV.

The first tapping-mode maximum generation is displayed in figure 4-20. The vibration frequency of the shaker head is 1.3 kHz. Considering the force sensor readout and the regular form of the voltage output, we can approximately indicate the compression duration t_c in the zoomed generation cycles presented in figure 4-20.b. Although it is the maximum output, it seems that the noted t_c is not perfectly equal to 0.5*T*. This can be due to a wrong determination of t_c . However, it is also possible that

in practice due to the mechanical interaction between the device surface and the shaker head, the expected sinusoidal deformation shape can be modified. Therefore, the maximal deformation change can take place for a t_c different from the exact 0.5T value.

As can be seen from the present curve, the generator gives a peak to peak voltage output of 200 mV (from -110 mV to 90 mV). With this information, we can calculate the maximum and the average power output of the device, which equals 12.1 nW (by taking U_{max} =110 mV) and 3.7 nW, respectively. Considering the effective deformed surface and volume, the maximum power output density and the average power output density of the device can be further calculated as 1.55 μ W/cm² (10.3 mW/cm³) and 0.47 μ W/cm² (3.1 mW/cm³).



Figure 4-21. Best recorded voltage output of the soft-matrix piezogenerator under high frequency full-time compression deformation at 2 kHz. The alternative voltage output traced in red reaches a peak to peak value of 260 mV.

The second best output is depicted in figure 4-21. This measurement is carried out under device full-time non-separation compression. Although at 2 kHz frequency the force sensor readout gives almost no indication of the deformation state, we can still confirm from the zoomed continuous generation curve shown in figure 4-21.b that the effective deformation lasts for the whole compression cycle, $t_c = T$.

The peak to peak voltage output is 260 mV (from -130 mV to 130 mV). The maximum and the average power output of the device can be calculated as 16.9 nW and 7.5 nW, respectively. The maximum power output density and the average power output density can be further estimated as 2.17 μ W/cm² (14.5 mW/cm³) and 0.96 μ W/cm² (6.4 mW/cm³).

All the above calculated device output values are summarized in table 4-3 for a direct comparison. We note that the differences between the calculated peak values and the average values are smaller for continuous mode measurement. This trend may be linked to the longer effective operational time of the generator. In practice, the tapping mode deformation is less favorable than the continuous compression in view of device average power output.

		Average	Peak value		
		value			
1.3 kHz	Power output	3.7 nW	12.1 nW		
Tapping mode	Power output density	$0.47 \ \mu W/cm^2$	$1.55 \ \mu W/cm^2$		
	(per unit surface)				
	Power output density	3.1 mW/cm ³	10.3 mW/cm ³		
	(per unit volume)				
2 kHz	Power output	7.5 nW	16.9 nW		
Continuous	Power output density	$0.96 \ \mu W/cm^2$	$2.17 \ \mu W/cm^2$		
mode	(per unit surface)				
	Power output density	6.4 mW/cm ³	14.5 mW/cm ³		
	(per unit volume)				

Table 4-3 Device power output at high deformation

*0.0078 cm² deformed device surface. 1.5 µm active layer thickness.

As emphasized before, all the presented device generation traces are measured at 1 M Ω external load condition, which is non-optimal. We can expect even better performance of the device if a better impedance matching is provided. Even though, the calculated average power output density of the device remains in the order of μ W/cm² or mW/cm³.

I remind here that the best average output power density obtained at low frequency tapping deformation is $3.31 \ \mu\text{W/cm}^2$ (22.1 mW/cm³) (table 4-1). The average power values presented here for a continuous deformation are slightly lower. However, it is worth mentioning that at high frequency measurement condition, the deforming force monitored by the force sensor is generally lower. Therefore, I cannot conclude that the device generates more at low frequency tapping. What I want to stress is that, under both tapping and continuous deformation, the measured piezogenerator can deliver an average power output density as high as the state-of-the-art values reported in the literature. Besides, here we report for the first time the piezogeneration performance

of nanowire-based devices at high frequency, which has never been addressed in the literature.

If we compare the studied nanowire-based piezogenerator with a commercial PZT-layer based energy harvester, we can notice that the PZT-based device output is more independent from the deformation conditions. It can generate well at both low and higher frequencies, under either tapping deformation or continuous compression. This good adaptability to the external deformation condition should be linked to the PZT insulating properties. Once the piezoelectric potential is created at the two sides of the material, there are no inner free carriers to screen this potential. Therefore, a maximum generated potential can be extracted to the external circuit. With a very long decay time τ , PZT-based generator can always meet the generation condition of $f > 1/\tau$. According to the table 4-2 (more precisely, categories 6 and 8), the PZT-based harvester can generate under any type of attainable deformation.

The above comparison with a PZT-based device has inspired us to try to improve the nanowire-integrated generator performance by increasing the nanowire inner resistance. Since non-intentionally doped GaN nanowires have already been employed, we now choose to replace the binary homogeneous nanowires with non-intentionally doped GaN nanowires containing an AlN/GaN heterostructure as the new active material for device fabrication. With the insulating AlN sections, we expect to localize the free carriers inside the GaN insertions, leading to a higher resistance of the nanowires. Besides, AlN itself is also a piezoelectric material. The study of the piezogenerator based on this type of heterostructured nanowires will be presented in the next section.

2. Piezogenerators based on GaN nanowires with an AlN/GaN heterostructure

The growth of the GaN/AlN heterostructures in GaN nanowires by PAMBE is a well mastered process in C2N laboratory. At first, GaN nanowire bases are grown by using the standard recipe. Then the AlN barriers are grown by opening the Al Knudsen cell while closing the Ga cell. The AlN/GaN sequence is repeated 20 times and then a GaN segment is grown to form the top part of the wires. In figure 4-22, the images a and b show the SEM cross section view and the top view of the as-grown nanowires. The GaN/AlN heterostructure can be distinguished as a lighter contrast in the cross-sectional SEM image. Panels c and d of figure 4-22 display HRTEM images of

one typical nanowire from the ensemble, giving a closer view of the obtained heterostructure.



Figure 4-22. Cross section (a) and top (b) view SEM images of the as grown GaN nanowires with a AlN/GaN heterostructure (scale bar is 1 µm). Images (c) and (d) are HRTEM images of one typical nanowire. The light grey parts of the nanowire are composed of GaN, while the darker parts are AlN insertions (By courtesy of Ludovic Largeau).

It should be noted here that AlN is also a piezoelectric material. During the AlN growth, the polarity of AlN insertions follows the polarity of the GaN NW stem. In our case, when the GaN grown at the base is nitride-polar, AlN will present the same polarity since it is not energetically favorable to reverse the crystal orientation into metal-polar. Therefore, in the nanowire growth direction, the polarity of the two material are aligned. In this way, the two material will behave in a similar way under a compressive deformation. No deterioration of piezoelectric potential due to polarity mismatch is expected.

The obtained GaN nanowires with AlN/GaN heterostructures demonstrate a similar morphology to the standard pure GaN nanowires. They share an average length of 0.9 μ m, an average diameter around 80 nm and a density about 10⁹ NWs/cm². The thickness of each AlN insertion is about 4 nm and the GaN quantum discs between the

barriers are about 1 nm. In order to fabricate a comparable soft-matrix piezogenerator as those studied before, the same device design, fabrication process and parameters have been applied (refer to figure 4-1). Since the top of these heterostructured nanowires is composed of GaN, the same Schottky diode can be formed by using Ct/Pt deposition. Figure 4-23.a displays the schematic of the fabricated piezogenerator. (In order to avoid misunderstanding, in the schematic I neglect the thin AlN layer at the foot of nanowires which is highly doped and serves for GaN nucleation). The AlN insertions are indicated as "non-doped AlN" in the schema.



Figure 4-23. (a) Schematic of a piezogenerator integrating GaN nanowires with AlN/GaN heterostructures. (b) Typical I-V curve of the device measured between one top contact pad and the bottom contact.

The I-V curve measurement helps to verify the device design at the first stage. As shown in figure 2-40.b, the rectifying behavior of the curve confirms the Schottky design of the fabricated piezogenerator. However, different from the pure GaN nanowire-based piezogenerators (refer to figure 4-2), the current passing through each contact pad in this device is quite small, only of the order of μ A. This shows that the resistance of the heterostructured nanowires is increased with respect to binary GaN NWs in agreement with our expectations. Therefore, the movement of free carriers due to residual doping in the nanowires is limited. A prolonged generation decay time could be expected.

The fabricated generator is then characterized with the vertical compression setup. As usual, one top contact is deformed by the shaker head while connected to the external oscilloscope for voltage measurement (1 M Ω load).



Figure 4-24. The voltage output (black curves) and the force sensor output (blue curves) of the piezogenerator integrating GaN nanowires with an AlN/GaN heterostructure under a tapping deformation at 40 Hz.

Figure 4-24 demonstrates a typical generation trace of the device at 40 Hz tapping deformation, with one compression cycle highlighted by a yellow dashed line and zoomed on the right. We can see that the device gives out a positive peak under compression and a negative peak at releasing. However, in the presented trace, the first peak cannot fully decay before the releasing since the deformation time is shorter than the decay time τ . In order to capture the full decay of the generation peak at device compression and to evaluate the τ , efforts have been made to increase the deformation duration by decreasing the device and shaker head distance. However, the duration time of 1.1 ms as presented in the figure 4-24 is the maximum that has been achieved without inducing measurement artifacts. If continuing increasing the compression duration t_c , the multiple bouncing phenomenon described in figure 4-8 would appear. Therefore, the value of the first peak decay time τ could not be extracted from the experimental data. Nevertheless, the missing observation of the first generation peak full decay (at compression) can still be an indicator of the increased device decay time τ . If we go back to the summary table 4-2, the generation behavior of this device under tapping deformation matches well the one described in category 5. Due to an early releasing, which means $\tau > t_c$, the generation decay is not complete. Hence, we can deduce from the trace in figure 4-24 that $\tau > t_c = 1.1$ ms. Compared to the previously discussed pure GaN nanowire piezogenerator, which has an estimated decay time of around $0.1 \sim 0.2$ ms, the piezogenerator integrating GaN nanowires with an AlN/GaN heterostructure bears at least a several times longer signal decay (>1.1 ms).


Figure 4-25. The voltage output (black curves) and the force sensor output (blue curves) of the piezogenerators integrating pure GaN nanowires (a) and GaN nanowires with an AlN/GaN heterostructure (b) under tapping deformation at 250 Hz. Highlighted compression cycles for each device are zoomed on the right.

To give a more direct comparison between a pure GaN nanowire generator and an AlN/GaN heterostructured GaN nanowire generator, the voltage outputs of both devices at 250 Hz tapping deformation are presented together in figure 4-25. For each device generation trace, the dashed line highlighted one compression cycle is zoomed on the right. The figure 4-25.a is the output of a pure GaN nanowire generator. The effective compression time t_c of the device is 1.3 ms. As clearly demonstrated in the zoomed image, a full output voltage decay can be observed and the decay time τ can be estimated as around 0.3 ms. Whereas, for the voltage output of the heterostructured-nanowire generator traced in figure 4-25.b, no complete generation peak decay can be observed at device compression. Hence, the τ of the device can be estimated as longer than 1.16 ms.

From the presented curves in figure 4-25, we may have the impression that a pure GaN nanowire-based piezogenerator has a better performance than the one containing heterostructured NWs. In fact, it is difficult to compare the electrical performance of these two types of generators. The aim of using GaN nanowires with a AlN/GaN

heterostructure is to localize the free carriers and prevent them from a fast screening of the piezoelectric field. In some sort, we are aiming to mimic the PZT insulating property to make the generator adapted to a wider range of external deformation condition. However, once the nanowire array inner resistance is increased, the 1 M Ω impedance of the used oscilloscope is no longer superior to that of the generator. Hence, the small voltage output value of the heterostructured nanowire device (around 10 mV) may be due to a bad impedance matching. As one perspective of the present study, the electrical performance of these two types of generators should be further compared in terms of open circuit voltage and optimal load voltage, under the same deformation condition (and ideally with the NW morphology and density as close as possible). Only by doing this systematic comparison we can verify if the device with heterostructures indeed helps to increase the generator power output and thus helps to better converting mechanical vibration into electrical energy.

Apart from the voltage output absolute values, there is another prominent difference between the output of the pure GaN nanowire generator and of the heterostructured AlN/GaN nanowire generator: the signs of the alternative voltage output of these two devices are reversed during one effective deformation cycle. As can be seen from figure 4-25, the pure GaN nanowire piezogenerator gives a negative voltage peak at compression and a positive peak at releasing. On the contrary, for the piezogenerator with an AlN/GaN heterostructure, positive voltage peaks are observed at device compression and negative peaks appear at releasing. This trend is observed repeatedly on different tested devices, and the sign reversal was surely not due to an experimental error like a wrong external circuit connection. Since the fabrication processes of the two types of generators are the same, the deformation setup and the applied conditions are the same as well, the only reason that causes this difference should be the existence of the AlN insertions.

In order to explain the observed voltage sign reversing from heterostructured nanowire piezogenerator, I propose to consider these insulating AlN insertions as integrated capacitors in the middle part of the GaN nanowires. Indeed, for each heterostructured GaN nanowire, the 20-times repeated AlN/GaN heterostructures can be considered as nanoscale capacitors connected in series with the NW base and the top GaN segments. These GaN NW segments can be considered as piezogenerators. When the individual nanowires are bounded together in parallel under one top contact pad, the nanocapacitors in individual NWs are combined in one effective capacitor connected in series with the GaN nanowire array generator composed of the NW base

and top segments. As will be explained in the next section, it is this effective capacitor in series that reverses the direction of the current passing through the load resistance and renders the voltage output sign different. From this point of view, the introduction of AlN insertions actually change the device design. Although the fabricated generator has a Schottky contact formed at nanowire summits, it does not belong to a pure Schottky design, but possesses a capacitor connected in series. In the next section, I will make a more detailed discussion of this sign reversing taking into account this design difference.

3. Equivalent circuits of the fabricated piezogenerators

In this section, I will compare the pure GaN nanowire based piezogenerator and the heterostructured GaN nanowire based piezogenerator from device design point of view. As introduced in chapter 1, there are mainly two types of design for vertically-integrated nanowire-based piezogenerators: Schottky design [54] and capacitive design [58]. At the beginning of this thesis study, I chose the Schottky device design to better compare the macroscopic device performance with the AFM measurement of individual nanowire generation. However now, with the introduction of the AIN/GaN heterostructure in GaN nanowires, it seems that the new device's output sign reversing behavior can only be explained by considering an effective capacitor integrated inside the wires.

To clearly discuss and compare the devices' difference, here I make a simplified device schema in figure 4-26. The two types of device designs, Schottky contact design and capacitive design, are presented respectively in the figure 4-26.a and 4-26.b. The upper part of each image helps to explain the device operation mechanism, with the indication of current flow direction in the external circuit. The bottom part of the images shows the proposed equivalent circuit of the designed piezogenerator.

Let's firstly focus on the pure GaN nanowire integrated piezogenerator as schematized in figure 4-26.a. When the nitride-polar GaN nanowire is compressed, a piezoelectric field E_{pz} from nanowire summit to the bottom appears, as indicated in the figure. Since the nanowires are non-intentionally doped, the residual free carriers (in our case, we assume that the residual doping is n-type, so we will talk about electrons) will circulate to screen the created piezoelectric field. By definition of the electric current, its direction is defined as the direction in which positive charges are

circulating. This means that the electron flow is reversed with respect to the current I. The current in the external load (here the oscilloscope 1 M Ω load) has the same direction as the current in the NW. This current I is by convention negative. Hence the voltage recorded on the load is negative at device compression. After the quasi-static deformation period where no evident output occurs, the reverse electron flow appears during the device releasing and a positive voltage is detected in the external load. Therefore, during one effective deformation cycle, the piezogenerator gives alternative output with negative peak at compression and positive peak at deformation releasing.



Figure 4-26. Schematic and equivalent circuit of both Schottky diode piezogenerator (a) and capacitive designed piezogenerator (b). R_{NWS} represents the energy source inner resistance, C_s it the capacitance of the equivalent capacitor in series with the generator.

If we compare the observed macroscopic piezogenerator electrical performance with the AFM individual nanowire generation characterization (refer to chapter 1), we can find that for our macroscopic integrated device, the Schottky diode does not work as a rectifier. For the individual nanowire generation measurement, the Schottky contact formed between the nanowire and the AFM tip blocks effectively one half of the generation, making the voltage output always of the same sign. Whereas, the macroscopic piezogenerator yields an alternative signal with both positive and negative values. This can be understood by comparing the generated voltage with the voltage necessary to open the diode. By referring to the I-V curve displayed in figure 4-2.a, we can estimate the opening voltage of the created Schottky diode to be around 1 V. However, as reported in the previous sections, a typical voltage obtained from the generator under various deformations is in the range of tens to hundreds of mV with a maximum of about 0.7 V. It can be concluded that, since the fabricated device generates a voltage below 1 V, the Schottky diode never opens. However, the Schottky diode shows a non-negligible leakage, which can be modeled as a shunt resistance. In the electrical circuit the Schottky diode manifests itself as a resistance in series with the generator. Therefore, both negative and positive outputs are observed. In the equivalent circuit in figure 4-26.a, the circuit of a small signal Schottky diode is used. The diode is connected in series with the nanowire-integrated generator, which is depicted as a source generator in parallel with a certain inner resistance (given by the NW resistance R_{NWs}).

Although it is useless for voltage output rectifying, the existence of this Schottky diode is important for the proper functioning of the piezogenerator. For the device with a small value of generated voltage, the diode is a resistance in series, much bigger than the nanowire inner resistance. When some nanowires are deformed under the contact pad, there exist others non-deformed nanowires under the same contact pad as well (figure 4-13). If there is no Schottky diode on top of each individual nanowire to separate them, the piezogenerated potential in one deformed nanowire would induce current in non-deformed nanowires. If this is the case, no voltage output can be detected at the external load. Thanks to the big resistance of the top diode, the non-deformed nanowires will not perturb the piezopotential generated in deformed nanowires. Hence the voltage extraction from the device can be guaranteed.

I'd also like to note that the load resistance (oscilloscope 1 M Ω) of the circuit is much bigger than the diode resistance 148 k Ω (estimated empirically from I-V curve, refer to figure 4-14). The generated voltage of the nanowires is distributed between the Schottky resistance and the load resistance which are connected in series. Hence a higher voltage output can be expected by increasing the circuit load. While for the maximum power output, there should be one optimal load for the generator.

Now let's take a look on the proposed capacitive device design displayed in figure 4-26.b. One simple way to achieve the capacitive design of the device is to add a dielectric layer at the nanowire summits, separating the nanowires from the connecting top contact, as has been reported in [58]. (This simple case is represented

in the schematic of figure 4-26.b instead of a more complex design containing GaN/AIN heterostructured nanowires, but the two are equivalent). When the nitride-polar GaN nanowires are compressed, the created piezoelectric field E_{pz} is the same as in figure 4-26.a. With the dielectric cap layer, the piezoelectric potential of the nanowire attracts charges on the metallic contact on the other side of the dielectric. In this way, electrons from the external circuit are attracted to the device top contact and a positive current (by convention) *I* passes through the external load. Finally, a positive voltage peak is detected at the external load during device compression. It can be considered that the dielectric cap layer behaves as a capacitor connected in series with the nanowire energy source and the external load. During the device compression, the capacitor is charged. While for the device releasing, the capacitor is discharged. The equivalent circuit of the capacitive design generator is displayed in figure 4-26.b.

Now we look back to the generation behavior of the heterostructured nanowire-based piezogenerator presented in the previous section. It is obvious that the output voltage of the device bears the character of a capacitive designed device. Different from the traditional top-layer capacitive design, the capacitor of our device is not external to the wires, but is integrated in the NWs internal structure in a form of the AlN insulating material. As long as this capacitor is connected in series with the nanowire arrays, the device equivalent circuit may go to the category depicted in figure 4-26.b. Indeed, there exists an additional Schottky diode at the nanowire summits (I will give a more precise structure illustration in the next section), but at small signal range this diode is equivalent to a series-connected resistor. It does not reverse the sign of the output signal. It is the existence of the inner capacitor (AlN dielectric material) that makes the output voltage sign reversed in comparison with the pure GaN nanowire piezogenerator output.

In order to confirm the discussed device operation mechanism, I will present the exploration of several new piezogenerators in the next section. Inspired by the AlN nanowire-middle-positioned capacitor, I explore different possibilities to create a capacitor connected in series at different positions of the generators. The objective is to validate the capacitive design functioning model and to investigate the generation efficiency of the capacitive design devices.

4. Validation of the proposed piezogenerator working mechanism by other types of generators with a capacitive design

In this section, I will first compare two piezogenerators fabricated exactly as depicted in figure 4-26. Then one generator integrating GaN nanowires grown on insulating SiN layer will be discussed. At last, I will make a summary of the presented devices and draw some conclusions.

4.1 Comparison of piezogenerators with Schottky diode design and top insulating capacitive design



Figure 4-27. (a) Schematics of the Schottky diode and the top insulating capacitive piezogenerators. (b) and (c) SEM cross section view of the fabricated 2 devices before top contact deposition.

Here I described two piezogenerators fabricated for comparison, one is of Schottky diode design and another is of top insulating layer capacitive design (schematics in figure 4-27.a). By using two pieces of a nanowire sample from the same growth, I try to minimize the difference between the two generators except from the device design. The Schottky diode piezogenerator is made by following the standard process described in previous section 1, figure 4-1. As for the capacitive design device, the

same fabrication flow is respected except that the thickness of the PDMS encapsulation layer is increased by lowering its spin-coating speed. Since it is a dielectric material, the excess of PDMS on top of the nanowire summits can serve directly as the insulating cap.

The SEM cross section view of the two devices after nanowire encapsulation are displayed in figure 4-27.b and c. We can clearly see that for the Schottky diode generator, nanowire summits pass through the PDMS layer. Whereas for the capacitive design generator, excessive PDMS covers the nanowires tops as a continuous layer.



Figure 4-28. I-V measurement of the Schottky diode piezogenerator (a) and of the top insulating capacitive piezogenerator (b) between one top contact pad and the bottom contact.

After performing the same top and bottom metallic contact deposition, the devices are ready for characterization. The first step is to do the I-V curve measurement to be sure of the PDMS top layer insulating properties. In figure 4-28, one I-V trace of each of the devices is demonstrated for comparison. The figure 4-28.a shows the I-V measurement of the Schottky diode generator. We can see that it displays the typical diode rectifying behavior, same as the general I-V curve presented in figure 4-2. Although the current value here is slightly different from the previously presented one, it remains in the same order of mA. The variation of the current value from device to device, and even from contact pad to pad, is due to the uniqueness of each growth and certain fabrication variation. As long as the current remains in the order of mA, it can be confirmed that the nanowires are effectively connected and are conducting.

Figure 4-28.b displays a representative I-V curve of the capacitive design piezogenerator. Although there exists a continuous top PDMS insulating layer, the measured current is not zero, still it is reduced by six orders of magnitude. The current

is in the order of nA, and bears a diode rectifying behavior. To explain this, the inhomogeneity of the nanowire length should be taken into consideration. Some long nanowires may pass through the insulating PDMS top and form a Schottky diode with the deposited metal. Since the leaking current of the capacitive device is six orders of magnitude smaller that the Schottky diode one, we can assume that the majority of the nanowires are insulated from the top contact. The generator is of top insulating capacitive design.

To explore their electrical performance, the two piezogenerators are deformed with the vertical compression setup under the same controlled conditions. Figure 4-29 and figure 4-30 demonstrate respectively their voltage output when both of them are under 20 Hz tapping mode compression.

Figure 4-29 shows the output of the generator with a Schottky diode design. On the right, the device generation under one compression cycle is zoomed. As can be clearly seen, the device gives out a negative voltage peak when compressed and a positive peak at the moment of releasing. On the contrary, positive voltage peak is observed at device compression for the capacitive design piezogenerator, as shown in figure 4-30. In fact, the demonstrated voltage output sign reversing between the two generators is expected, as explained in the previous section. This experiment presents a direct comparison of the two designs, and gives a direct experimental support of the previously discussed device operation mechanism.



Figure 4-29. The voltage output (red curves) and the force sensor output (blue curves) of the fabricated piezogenerator with a Schottky diode design under tapping deformation at 20 Hz (effective compression duration $t_c = 2$ ms).



Figure 4-30. The voltage output (pink curves) and the force sensor output (blue curves) of the fabricated piezogenerator with top-insulating-layer capacitive design under tapping deformation at 20 Hz (effective compression duration $t_c=2$ ms).

In addition, the capacitive design piezogenerator seems to be less sensitive to the external forces. Indeed, when the Schottky diode piezogenerator receives a maximum tapping force of 0.5 N at 20 Hz, it gives a peak-to-peak voltage generation of 67 mV (from -38 mV to 26 mV) (figure 4-29). Whereas for the capacitive piezogenerator, even with a maximum tapping force of 1.6 N, its voltage output is only 35 mV peak-to-peak (from 20 mV to -15 mV) (figure 4-30). The top insulating PDMS layer is the main reason for this sensitivity degradation. Since it is a soft polymer, it can act as a damping layer in face of a compression shock. Therefore, for the capacitive designed generator, the mechanical energy transfer efficiency to the nanowires is lower than in the Schottky design device. By thinning the top PDMS layer, we can expect a higher device sensitivity and a better generation performance [61].

4.2 Capacitive design piezogenerator with bottom insulation

In this part, I use the GaN nanowires grown on SiN layer (formed due to Si substrate nitridation) to fabricate a piezogenerator with an ultra-thin capacitor at the NW foot.

For the AlN/GaN heterostructured generator, it behaves as a capacitive-designed device due to the insulating AlN insertions in the middle of the nanowires. Since it is possible to add a series-connected capacitor to the piezogenerator source from nanowire array top (top insulating layer) and inside the nanowires themselves (AlN heterostructure insertion), here I choose to move the equivalent capacitor to the nanowire foot with the help of an insulating ultra-thin SiN buffer layer. This layer is

formed prior to the NW growth by exposing the Si substrate to nitrogen plasma. As a result, an SiN layer of few nanometers is formed on the Si surface.

Figure 4-31.a displays the used nanowire array morphology. Different from the GaN nanowires grown on a doped AlN buffer layer, the nanowires grown on a SiN buffer layer demonstrate a high density and a more prominent length homogeneity. In addition, according to our laboratory on-going analyses, this type of growth demonstrates an even higher nanowire polarity conformity (namely, the inversion domain boundaries present in the standard GaN NWs on an AlN buffer have never been observed in NWs grown on SiN).



Figure 4-31. (a) SEM cross section view (left) and top view (right) of the used GaN nanowires grown on a SiN layer, demonstrating a morphology of high density and high nanowire length homogeneity. (b)
Schematic of the piezogenerator integrating GaN nanowires grown on a SiN buffer layer. (c) Typical I-V curve of the device, between one top contact pad and the bottom contact.

To fabricate this new capacitive type piezogenerator, I follow the same fabrication process as displayed in figure 4-1. As expected, the GaN nanowire summits and the

Cr/Pt top contact form a Schottky contact, while at the foot of the nanowires, the insulating SiN layer serves as an equivalent capacitor (figure 4-31,b).

The Schottky diode forming at nanowire summits is confirmed by the I-V curve measurement, as displayed in figure 4-31.c. We note that the current values (tens of μ A) are in between the ones observed for a Schottky contact design generator (mA) and the capacitive design with a PDMS cap (nA). This shows that there is a certain leakage through the SiN layer. As for the equivalent capacitor introduced by the SiN insulating layer, its effects can be revealed by the device piezogeneration measurement.

The same 20 Hz tapping deformation is applied on the new device, with a compression duration around 2 ms. One voltage output trace of the device is shown in figure 4-32. As confirmed from the zoomed image, the generator yields a positive voltage output peak at device compression and a negative peak at releasing. Since the only difference of this device from the standard Schottky diode generator is the introduction of the bottom insulating layer, I can conclude that with an effective bottom-located insulating section, the characterized piezogenerator is of equivalent capacitive design.



Figure 4-32. The voltage output (brown curves) and the force sensor output (blue curves) of the fabricated piezogenerator with a SiN bottom insulating capacitive design under tapping deformation at 20 Hz (effective compression duration $t_c=2$ ms).

4.3 Summary of different device designs

Here I make a summary of the various tested generators according to their different growth and design. Table 4-4 helps to give a panoramic view, with the four main categories of generators marked as a, b, c and d. Correspondingly, in figure 4-33, simple electronic component symbols are used to schematize the four device categories.

As demonstrated experimentally, once there exists an equivalent capacitor in series with the active generator source, the generator goes to capacitive design device category. They act differently (i.e. deliver the opposite voltage) compared with the Schottky diode design device.

	8	8	v
	GaN NWs	GaN NWs	GaN NWs with
Growth Design	Growth on AlN	Growth on SiN	an AlN/GaN
	doped	insulating buffer	heterostructure
	(conducting)	layer	
	buffer layer		
Schottky diode	a	*Schottky diode	*Schottky diode
design		exists for <i>c</i>	exists for d
Capacitive	b	с	d
design			

Table 4-4 Piezogenerator design summary



Figure 4-33. Schematics of different piezogenerators integrating different types of nanowires and different designs. The schema noted as a. b. c and d correspond to its counterpart defined in table 4-4.

As shown in figure 4-33, although the generator c and d may have a diode at the nanowire summits, as long as the device works at low voltage output range, the diode is always blocked and acts as a resistor in series. The diode does not influence the final output voltage sign. I remind that for all samples containing a Schottky contact, it does not play a rectifying role, but acts as a protection from shunting the generation by non-deformed inactive nanowires.

It is difficult to compare the four categories of generators regarding their energy harvesting performance, since there are too many differences in terms of their material growth, fabrication and solicitation mode. By using the same material and deformation condition, we noted from the comparison of figures 4-29 and 4-30 that the Schottky design device demonstrates a higher deformation sensitivity than the top insulating capacitive generator, since the later suffers from mechanical damping (however, I need to note that the fast signal decay of a Schottky diode piezogenerator is not favorable for energy harvesting). Concerning the three types of capacitive design generators (noted in table 4-4 as type b, c and d), from a simple comparison of the output voltage in figures 4-29, 4-30 and 4-32 the two with a resistive Schottky diode on top (the type c and d, figure 4-33) seem less advantageous. However, this simple comparison does not account for the impedance matching with the load circuit, so this conclusion may be erroneous. I also note that the two devices with a Schottky diode are not expected to suffer from mechanical damping issues and the durability of the metallic contact was observed to be better. The metallic contact on the PDMS top-insulated capacitive generator degrades more easily in face of deformation shocks. As discussed above, a compromise between the device design and the performance should be found depending on the desired application.

5. Flexible piezogenerator integrating PAMBE GaN nanowires

The research of flexible electronic devices is nowadays prospering, since a higher device flexibility may enlarge its application in various scenarios (e.g. in applications requiring a conformal integration on a curved surface or in medical implants). At the end of this chapter, I'd like to present my progress to render the designed piezogenerators flexible.

Considering the small size of PAMBE grown nanowires (typical length about 1 µm),

integrating them into a membrane and making a flexible piezogenerator is quite challenging. For short dense NWs used in my analyses, the most critical step is to detach nanowires from the rigid growth substrate while keeping their vertical orientation as well as their aligned polarity. The peeling process, which consists in integrating nanowires in a soft membrane and then mechanically detaching the whole ensemble from the substrate, was hence intensively explored during my thesis.

In the first part of this section, I will present a fabrication process which offers the possibility of peeling nanowire arrays as short as 1 μ m. The nanowires are vertically integrated in a PDMS matrix and detached from the substrate. Metallic contacts were added on both membrane sides. Since there are metals on both extremities of the nanowires, the aimed piezogenerator is of a Schottky diode design. As will be discussed below, the fabrication of this kind of a generator appears to be extremely challenging and the device is fragile. Then, in the second part, I will demonstrate one successful flexible piezogenerator based on a capacitive design together with its fabrication process. Thanks to the capacitive design, the active membrane peeling is easier and the final device is more robust.

5.1 Ultra-thin active membrane peeling process for flexible piezogenerators

The aim of the process is to obtain a macroscopic 2D soft membrane embedding active vertically-aligned GaN nanowires. By adding top and bottom metallic contacts, the active membrane can be functionalized as an independent piezogenerator. The proposed nanowire peeling and piezogenerator fabrication process is displayed in detail in figure 4-34.

At first, the bottom part of the as-grown nanowires is encapsulated into a thin photo-resist layer. Then the rest of the nanowire bodies is fully embedded into a diluted PDMS soft matrix. After a gentle RIE etching of the PDMS excess and of the residual photo-resist on the nanowire summits, the device top is covered by a top contact metal (here it is Cr/Pt). The metallic deposition is performed on the whole device surface except from the device border. Then a much thicker non-diluted PDMS layer is spin-coated on the whole device. This thick PDMS layer can attach well to the active nanowire-embedded membrane layer through the previously exposed membrane border. Hence, after dipping the whole sample in acetone for a while until the photo-resist at the nanowire feet is completely dissolved, it is possible to peel off

the active nanowire-integrated thin membrane from its substrate together with the top thickened PDMS layer (figure 4-34.f). After the peeling, the whole peeled-off membrane is flipped and fixed on a temporal support with nanowire bottom side upward. Then, the device bottom contact is deposited after the nanowire foot deoxidation by sputtering method. Finally, the membrane ensemble is flipped again to be attached to the chosen flexible substrate (here I used a flexible copper tape) from the nanowire bottom side. By cutting the membrane borders to get rid of the parts where the active membrane is connected to the thick PDMS cap, the top thick PDMS layer can be easily removed by tweezers thanks to a poor metal-PDMS adhesion. The remained vertical-nanowire-integrated active membrane, together with its supporting substrate and deposited contacts, can be considered as a 2D flexible piezogenerator ready for electrical characterization.



Figure 4-34. Fabrication process of the flexible piezogenerator with ultra-short PAMBE GaN

nanowires.

Figure 4-35.a displays a tilted cross section view SEM image of one fabricated flexible piezogenerator (with the schematic of the structure shown in figure 4-35.b). As we can see, the nanowires are quite short, about 1 μ m long. They are fully encapsulated into a diluted PDMS matrix and constitute the active piezogenerating device membrane. Top and bottom metallic layers are deposited on the two sides of the active membrane, they can be recognized through the SEM image color contrast. We may also notice that on the top metallic contact, some nanowires surpass the surface and form some small pimples. Those surpassing nanowire summits are

actually connected to the metallic layer.



Figure 4-35. (a) SEM image of one GaN nanowire-integrated membrane sandwiched between the top and the bottom metallic deposition. (b) Schematic of the fabricated flexible generation shown in (a).

Unfortunately, this prototype device suffers from electrical defects due to its extreme thinness and fragility. The less-than-2 µm device thickness is extremely small in comparison with its active macroscopic surface, which is around 5 mm*5 mm. Although it was treated with great care, the manual peeling process still induces many micro-scale membrane cracks on the active nanowire-integrated area. Hence, with the metallic contact deposition on the two sides of the active membrane, unwanted short circuiting occurs, and the fabricated generator is shortened. The short circuiting between top and bottom contact has been evidenced with I-V curve measurement. Efforts have been made to reduce the short circuiting probability by cutting the device into small individual pieces. However, due to the microscopic scale membrane cracks, these efforts were unsuccessful. Technically, to avoid short circuits through micro-cracks, an additional insulating layer can be used. Before the metallization of the nanowire bottom side (figure 4-34.h), diluted PDMS can be further spin-coated to fill the mechanical cracks (under the condition that the membrane is flatly fixed). Otherwise, it is possible to improve the flexible device reliability by using longer wires. In my point of view, if the nanowire length can be increased to around 4 μ m, the short circuiting problem can be avoided. It would be of interest to try this fabrication process with longer wires.

Besides, the same fabrication flow can be applied for other types of nanowire-based flexible device fabrication, such as nanowire-embedded LED devices. As long as the two extremities of the nanowires are reliably connected, external voltage can be

applied onto the studied device. For MOCVD grown microwires, such flexible LED devices have already been demonstrated in our team [84]. If further device size reduction is needed, or other new material growths by MBE technique is indispensable for the LED application, the proposed device fabrication process may be of interest to reliably integrate ultra-small size structures.

5.2 Demonstration of a PAMBE nanowire based flexible piezogenerator with a capacitive design

Figure 4-36.a illustrates the process flow to make a PAMBE nanowire-based capacitive piezogenerator. As depicted, the as-grown nanowires are firstly encapsulated into non-diluted PDMS. Due to the high viscosity of the standard PDMS, this process cannot be applied to very dense nanowire ensembles since the PDMS would not penetrate between the NWs and the membrane would not be formed. In the present case, a sparse NW array was used. After a complete curing of the polymer matrix, the nanowire-integrated membrane is peeled off manually with a razor blade. Then, the lifted membrane is fixed on a supporting substrate with the nanowire bottom side upward and the device bottom metallic contact is deposited. After a second flipping of the membrane, the nanowire bottom side is then fixed on the final flexible substrate (flexible copper tape). The original nanowire top side of the membrane, which is characterized with a thick excessive PDMS layer, is etched to reduce the insulating layer thickness (to decrease the mechanical damping effect). Finally, the device top contacts are realized, enabling the device electrical measurements.

In order to make this flexible piezogenerator, less dense and relatively long MBE nanowires (about 2 μ m) were used. In fact, I choose one piece of sample from the same growth that have been used for design comparison in section 4.1 (figure 4-27), with a purpose of a subsequent device performance comparison. Figure 4-36.b shows an optical image of the peeled macroscopic active membrane. In addition, figures 4-37.a and b display the SEM images of the active membrane before and after peeling process. We can confirm from these images that the nanowire arrays are compactly integrated with their desired orientation guaranteed. For the final device, the top PDMS cap layer is thinned to about 4 μ m, and the standard top contact deposition is performed.



Figure 4-36. (a) Fabrication flow of the flexible piezogenerator following a capacitive design. (b) An optical image of the peeled-off nanowire-embedded membrane. This device processing step corresponds to the schematic description in panel (a)-b.



Figure 4-37. SEM images of the nanowire-embedded membrane before (a) and after (b) peeling process. They correspond respectively to the membrane states described in figure 4-36.a-a and figure 4-36.a-b (before metal deposition).

Figure 4-38 displays one trace of the device I-V curve measurement (with an optical photo of the generator in the inset). The capacitive design of the device is confirmed by its strong resistance. Contrary to the previous Schottky diode flexible generator, no leakage through micro-cracks was observed.



Figure 4-38. Typical I-V curve of the fabricated flexible capacitive generator (inset: optical image of the device from top. The blue circles indicate the 2 mm diameter circular top contacts).



Figure 4-39. The voltage output (orange curves) and the force sensor output (blue curves) of the fabricated flexible piezogenerator of capacitive design under tapping deformation at 20 Hz (effective compression duration $t_c = 2$ ms).

The piezogeneration characterization of the device is then carried out at 20 Hz tapping deformation condition, which is the same condition as applied in section 4.1 for the other two rigid devices fabricated from the same NW wafer. As can be seen from figure 4-39, the flexible device generates a peak-to-peak voltage output of 23 mV (from 18 mV to -5 mV) under a maximum compression force of 5 N (however, the force sensor readings for fully flexible devices may be unprecise due to the deformation of the device as a whole). Compared with the generation results of its rigid device counterparts discussed previously in figure 4-27, this flexible energy harvester is less efficient. Apart from the PDMS damping induced output voltage

reduction, we can also observe an eminent output signal asymmetry from this device. The higher voltage output at compression in comparison to the lower output at releasing can also be explained by the PDMS thick insulating layer. Its slow recovery from the compression slows down the deformation changing rate of the nanowire arrays, thus limiting the device output peak at releasing.

After comparing the developed flexible generator with its rigid device counterparts, we may have the impression that increasing the piezogenerator flexibility deteriorates its energy conversion efficiency. Indeed, with a soft membrane encapsulation, it is more difficult for the integrated piezoelectric material to feel the external mechanical solicitation. However, with an increased flexibility, the piezogenerator can be applied in some specific situations (e.g. in-vivo device energy delivery) where rigid devices cannot be used. Although with some efficiency loss, it can be interesting to create new application possibilities. Further optimization of the design to ensure a better transfer of the mechanical deformation to the NWs will be performed in future studies.

In the next chapter, I will present MOCVD micro-wire based flexible piezogenerators. Compared to the above presented PAMBE nanowire-based flexible generator, these devices demonstrate a better electrical performance and a higher reliability which are related to their different morphology.

Conclusion of the chapter

In this chapter, a systematic study of the vertically-integrated piezogenerators based on PAMBE-grown nanowires has been presented. A comprehensive understanding of such device operation mechanism has been achieved based on a broad experimental exploration under different solicitation parameters (tapping versus full-contact deformation, different deformation frequencies and forces, etc).

Under the tapping mode mechanical solicitation, the average power output density of the studied piezogenerators can reach a maximum value of 22.1 mW/cm³ (corresponding to an average power of 25.8 nW), which compete with the state-of-the-art values reported in the literature. For the first time, continuous deformation has been applied to excite the device and a good piezoelectric response from the generator has been observed. The best recorded average power output density of the device attains 6.4 mW/cm³ (corresponding to an average power of 7.5

nW).

Demonstrations of the energy harvesting and the discussions in terms of different device designs have been made as well. Equivalent circuits of the devices are proposed and compared with experimental observation, revealing the operational mechanisms of the studied nanowire-based piezogenerators. If I may say so, this systematic study fill the existing gap in the literature on the piezoelectric nanowire energy harvesting. Although the current study is based on GaN nanowires grown by PAMBE technique, the conclusions drawn in this chapter about the device operation principle are applicable to other similar devices based on the same physical principle.

Chapter 5

Energy harvesting and pressure sensing with piezoelectric GaN microwires grown by MOCVD

This chapter presents the development and characterization of piezoelectric devices based on MOCVD grown GaN microwires. At the beginning, I briefly introduce the MOCVD technique and the GaN microwire growth procedure. Then I will talk about the fabrication and measurements of a flexible piezogenerator integrated on a copper foil using a circular contact design. After that, I will present a new design of flexible piezogenerators using Kapton films with crossing contacts. A detailed description of the design and fabrication will be given and a complete exploration of their electrical performance will be made. Starting from the device prototype with a crossing contacts design, further improvement of the mechanical to electrical conversion efficiency has been done by reducing the thickness of PDMS layers, which damp the deformation. A new generator with better electrical performances will be presented thereafter. Finally, a preliminary realization of a microwire-based force/position sensor and perspectives for further improvement of this sensor are discussed.

1. Metal-Organic Chemical Vapor Deposition (MOCVD) for GaN microwire growth

1.1 The principles of MOCVD

The metal-organic chemical vapor deposition (MOCVD), also known as the organo-metallic vapor-phase epitaxy (OMVPE) and other permutations of the same letters (MOVPE and OMCVD), is a deposition method developed since 1960s to produce single or poly-crystalline layers on different substrates [47]. Thanks to its high growth rate, good layer quality and the possibility for large area production, this growth method is nowadays widely used in the semiconductor industry to fabricate thin film LEDs, lasers and other optoelectronic devices.

In contrast to the molecular beam epitaxy, which works under ultra-high vacuum and is based on a physical deposition of atoms, MOCVD is a vapor-phase epitaxy method taking place at a certain pressure and is based on the chemical reactions of the injected gases. The working mechanism of chemical vapor deposition is quite complex [47]. To give a short summary, its principal working steps can be synthesized as following:

At first, the chosen gases containing organometallic materials are introduced into the reactive chamber as precursors. The high temperature of the sample deposited on a susceptor decomposes the input gases and favors the chemical reactions between the decomposed elements. Thereafter, different intermediate products are formed. Some effective products experience a process of diffusion, absorption and desorption from the substrate. Some atoms can then be incorporated into the growing crystal, while the remaining volatile by-products, which do not contribute to the deposition, are finally evacuated out of the chamber.

All the steps listed above take place simultaneously. Hence, a harmony of all the influencing parameters such as the temperature, the pressure, the rate and the quantity of gas flux is required to realize the targeted deposition. The book [47] gives very detailed discussions of the dynamic processes happening in the MOCVD chamber. I will now move on to a more specific case: the MOCVD growth of GaN quasi-1D structures on a sapphire substrate.

1.2 GaN microwire grown by MOCVD

The MOCVD growth of the auto-assembled GaN microwires on sapphire substrate was initially developed in CEA-INAC in 2007. Since then, several PhD works have been dedicated to control the wire growth and to progress toward device applications of these nanostructures [85], [86], [87]. At present, not only auto-assembled GaN microwires can be properly grown, but also the selective area growth (SAG) of 1D structures has been demonstrated [87]. Even further, more complex 1D nitride structures with radial or axial segments combining different semiconductor alloys are achievable by using the same technique. All these developments have pushed forward the material engineering and offered new possibilities to realize more compact, efficient and flexible optoelectronic devices [84].

In this PhD study, binary GaN microwire arrays grown at CEA-INAC are used for piezoelectric application. They are auto-assembled GaN microwires grown on sapphire substrate in an Aixtron 3x2" MOCVD reactor [87], [88], following the standard growth recipe developed in [86].

Generally, the precursors for GaN formation are ammonia (NH₃) gas and the organometallic compounds, namely, the trimethyl-gallium (TMGa) and the triethyl-gallium (TEGa). The organometallic compounds are stored in a liquid form and then their molecules are transported into the reactive chamber by a carrier gas (N₂). The silane (SiH₄) and the bis(cyclopentadienyl)magnesium (CP₂Mg) can be used during the growth as n-dopant and p-dopant, respectively (however, only n-doped wires were considered in my work). According to the reactor's close-coupled shower-head design [87], all the precursor gases are injected from above in the direction perpendicular to the sample substrate with their flux well controlled. The temperature of the substrate is controlled in the range of 1000-1050°C. In this temperature range, the growth rate is mainly determined by the flux of active gases.

In order to achieve a spontaneous GaN wire growth, there are three key points that should be addressed [85], [86]. Firstly, the sapphire substrate needs to be cleaned at high temperature and then nitridized to form a discontinuous SiNx layer necessary for wire nucleation. This step not only initiates the growth process but also adjusts the polarity of GaN microwires. As we already know, the uniformity of the nanowire polarity within the array influences a lot their macroscopic piezoelectric performance. From this point of view, the uniform nucleation at the beginning of the growth is important for piezoelectric devices.

Secondly, a very low V/III flux ratio should be applied. The NH₃/TMGa flux ratio is adjusted at 50, much lower than for a standard GaN film growth (ratio>1000). This limitation of flux actually prohibits the GaN lateral growth and promotes the wire growth along its c-axis direction.

Thirdly, the use of silane (SiH₄) can help to achieve high aspect ratio wires (10 to 100, for example). A high injection flux of silane enables the formation of a thin SiNx passivation layer onto the m-plane of hexagonal wires. This layer stops the material lateral growth and helps conserving the diameter of microwires. However, silane is an active n-dopant. It can introduce free carriers everywhere in the wires. For

piezoelectric applications, a high concentration of free carriers is unfavorable, as they can screen the piezoelectric field created by an external deformation.

In this thesis study, I mainly use the MOCVD grown GaN microwires with a length around 20 μ m (much longer wire going up to 500 μ m can be produced by the same growth technique). The silane flux (200 nmol/min) is maintained stable during the whole growth duration (1000 s), therefore the as-grown microwires are n-doped. Figure 5-1 shows the SEM images of the as-grown microwires, giving a general idea of their morphology. Statistically, the microwire arrays are characterized with an average diameter of 820 ± 260 nm and a density of 1 microwire per 10 μ m². The majority of them have an average length of 17 ± 1.5 μ m. However, there exists a certain amount of extra long wires that can reach a length of 33 ± 2 μ m.



Figure 5-1. SEM images of the MOCVD GaN microwires grown on a sapphire substrate (a. cross section view, b. 45-degree titled view, c. top view)



Figure 5-2. SEM 45-degree tilted images of the as-grown GaN microwires before (a) and after (b) KOH etching. Inset shows a zoomed image of the microwire top parts.

KOH etching is performed to check the microwire polarity distribution. Figure 5-2 shows the SEM images of the microwires before and after this chemical attack. The chemical etching shows that the wires have a predominant nitrogen polarity, but inversion domains exist in the wires. Indeed, after the chemical bath, most of the

microwires summits are etched. This is the characteristic marker of nitrogen-polar GaN. On the contrary, the non-etched sticking parts in the wires are of gallium polarity. We note that these parts produce an opposite piezoelectric potential with respect to the nitrogen-polar parts when they are deformed (refer to chapter 1). However, their volume is small with respect to the volume of their N-polar counterparts. Therefore, when compressing forces are applied, the macroscopic piezoelectric output should follow the behavior of the nitrogen-polar microwires.

2. Demonstration of a flexible piezogenerator on copper film with separate circular contacts

The growth substrate of GaN microwires by MOCVD is sapphire, which is an insulating material. It is thus impossible to directly use the microwires on their native growth substrate to make a functional device as in the case of MBE grown GaN nanowires. However, thanks to their bigger size, it is much easier to transfer these microwires than MBE nanowires onto other substrates by encapsulation and peeling process. PDMS has already been proved to be a good material to integrate nanowire arrays. After encapsulating the microwires into a PDMS matrix, the microwire-integrated PDMS membrane can be mechanically detached from the original sapphire substrate. This transfer process is easy, efficient and has already been successfully applied to make flexible MOCVD microwire LED device [84] and force sensor [61].

Here I use a similar procedure as presented in chapter 4, section 5 to transfer MOCVD microwires and then to fabricate a flexible piezogenerator. This procedure preserves the vertical orientation of the microwires with the N-polar facet on one side, which is more favorable compared to the in-plane geometry [62]. As for the energy harvesting design, I choose the capacitive structure to thicken the active layer and increase the device robustness.

2.1 Device fabrication

The device fabrication steps are presented in figure 5-3.a. Firstly, standard PDMS is spin-coated onto the as-grown GaN microwire arrays on their sapphire substrate. By adjusting the spin-coating parameters and adding a short step of reactive ion etching,

the PDMS layer thickness is controlled at around 30 µm. A quick annealing of 20 min at 115°C is then performed. While keeping the membrane on the sapphire, the Cr/Pt (10 nm/150 nm) top contacts are firstly deposited through a shadow mask by sputtering technique for a better conformal coverage and metal adhesion. The top contacts are of a circular shape with a diameter of 2 mm. Then, the mechanical peeling of the active membrane is realized assisted by a sharp scalpel. In fact, if the membrane layer is thicker than 20 um, it is possible to detach it with a tweezer directly. However, using a scalpel avoids the over-stretching of the film and guarantees a better breaking position at the foot of the microwire array. Once the active layer is detached, it is flipped, flattened and fixed onto a larger rigid substrate with its bottom side on top. A whole surface Ti/Au (10 nm/150 nm) bottom contact is then deposited by sputtering as well. Finally, the active membrane is cut at the border to avoid short circuit and freed from the fixation. It is flipped again to be sticked onto a copper tape from the bottom side to realize the final device. In addition to this device of interest, a reference sample containing a PDMS layer without the active wires is also fabricated following the same procedure (structure shown in figure 5-3.b).



Figure 5-3. (a) The fabrication flow of the flexible piezogenerator on copper film with circular top contacts. (b) the schematic of the reference sample.

Figure 5-4.a shows a 45-degree-tilted SEM image of the microwire-integrated membrane edge after spin-coating. As we can see, there is a large distance between the microwire summits and the membrane top, so there is no direct contact between the wires and the metal and the capacitive structure is confirmed. Figure 5-4.b

presents the optical images of the fabricated piezogenerator and of the reference sample. Both of them are of a macroscopic size and mechanically flexible.



Figure 5-4. (a) 45-degree tilted SEM view at the border of the microwire-integrated membrane. (b) optical images of the fabricated piezogenerator and its reference.

2.2 Device electrical measurements

2.2.1 Current-voltage characteristics



Figure 5-5. (a) I-V curve of one of the top circular contacts of the fabricated device. (b) Schematic of the piezogenerator in cross section view. The red dashed circle indicates a group of ultra-long wires that reach the top contact. The green dashed line shows the fully embedded microwires which give the main contribution to the output of the macroscopic device.

First, the I-V curve is measured on both devices. As expected, the reference sample gives no measurable current since it is a thick dielectric layer sandwiched between two metal contacts. The piezogenerator's I-V curve is shown in figure 5-5.a. As we can see, the microwire-integrated membrane is not perfectly insulating, it conducts

with a very high resistance at zero bias equal to 2.6 T Ω . Actually, this is understandable when considering the inhomogeneity of the microwires length. As previously mentioned, there are some ultra-long microwires present in the array that can reach the PDMS top and serve as conducting channels of the membrane (as schematically illustrated in figure 5-5.b). However, the quantity of these ultra-long microwires is not large. Most of the microwires are fully embedded in the PDMS matrix. So statistically, the device follows the capacitive design for piezogeneration (with the exception of the ultra-long wires).

2.2.2 Piezogeneration assessment and further analyses

After the I-V curve analyses, the device piezogeneration was tested using the vertical compression setup described in chapter 2. In the following measurements I used a sine control signal at a given frequency and I fixed the deformation duration (i.e. the time that the shaker head remains in contact with the surface) by adjusting the sample-to-shaker distance with the micro-control stage. In order to confirm that the electric signals obtained from the flexible generator come from the GaN microwires rather than from the measuring setup, the generator and its reference are measured in the same conditions for comparison. Both of them are fixed, deformed by the shaker head at one circular contact and the voltage trace is measured between the top and bottom contacts using an oscilloscope (load impedance 1 M Ω).



Figure 5-6. Output voltage of the reference sample (a) and the piezogenerator (b) when one of their top circular contacts is deformed at 50 Hz frequency with a tapping compression. The black curve shows the output signal, the blue curve below shows the reading of the force sensor.

Figure 5-6 displays their electrical performance for a 50 Hz frequency tapping

deformation. The generator demonstrates a peak-to-peak output voltage of 50 mV with a maximum tapping force of 0.5 N (figure 5-6.b), while the reference sample gives no readable electrical signal even when the tapping force increases to 1.5 N (figure 5-6.a). It can be thus concluded that the reference sample is just a passive capacitor, while the GaN microwire-integrated device is an active piezogenerator. In order to further check the absence of artifacts in the measurements of the piezoelectric response, the contacts of the generator are inversely connected to the measuring circuit. An output voltage of the same form but with an opposite sign was measured, confirming that it originates from the piezoelectric activity of the microwires.



Figure 5-7. Voltage outputs of the piezogenerator under a gentle compression (50 Hz), when the force sensor's output is non-readable (a) and slightly discernible (b).

The generator's performance is then further explored under different deformation conditions. The external force exercised by the shaker head was reduced until the force sensor of our set-up could no longer detect it and the output of the piezogenerator was recorded as shown in figure 5-7. We observe that the fabricated piezogenerator is more sensitive to the external tapping force than the commercial force sensor. The dashed lines show the device deformation duration. When the compressing force is big enough, both the force sensor and the piezogenerator give a distinguishable peak (as shown in figure 5-7.b), however the signal-to-noise ratio for the piezogenerator voltage trace is much better. When the compressing force is further reduced, the output of the force sensor is no longer correlated with the shaker movement (figure 5-7.a), while the piezoelectric output of the generator is still well above the noise level. I would like to note that, we cannot directly conclude that the piezogenerator is more sensitive than the commercial force sensor, since the two of them operate in two different working conditions: the piezogenerator is fixed on an immobile holder, while the force sensor is attached to the sensor head in motion and is therefore experiencing inertia effects. However, this demonstration with a very small

compression force confirms the potential of the microwire-integrated membrane to be used as a sensitive layer for external deformation detection.

Piezogeneration measurements at different frequencies have been carried out thereafter. Figure 5-8 presents the device performance under 10 Hz tapping deformation. The effective deformation duration in figure 5-8.a is 25 ms, while in figure 5-8.b, it is much longer, 66 ms. The generator produces a measurable output voltage under both deformation conditions. Evidently, the device gives a positive peak at compressing and a negative peak at releasing, which corresponds to our expectation from a capacitive designed device.



Figure 5-8. Voltage outputs of the piezogenerator at 10 Hz tapping compression with varied compression duration: very short contact (a) and longer contact duration (b) conditions.



Figure 5-9. The generator voltage ouput under one cycle of deformation at 10 Hz (Zoomed from figure 5-8.b).

A zoom of one deformation cycle from figure 5-8.b is displayed in figure 5-9 to give a closer look at the output voltage signal decay. The signal decay time, referred in

chapter 4 as device characteristic decay time τ , can be estimated from the presented curve as being about several ms (the first peak decay time is about 5 ms, and the second peak decay time is about 3 ms). We note that these values are much larger than the times $(0.1 \sim 0.2 \text{ ms})$ observed in Schottky contact design piezogenerators based on MBE nanowires discussed previously. In addition, it is not possible to fit the first peak decay (at compressing) with an exponential function. It may be due to the measurement set-up artefacts (such as the oscillations superimposed to the sine function seen in the force sensor output in figure 5-9). Another possible explanation of a non-exponential decay during contact may be due to the fact that the signal decay process is influenced by the on-going deformation change during the contact period. In general, when the shaker head is in contact with the device surface, the device deformation change is non-zero since the shaker continues to move following a sine function. For the case of MBE-grown NW piezogenerators discussed in chapter 4, the internal screening time of piezogenerated charges was very short with respect to the deformation change rate. Therefore, the contact phase could be considered as a sequence of quasi-equilibrium states and its impact on the decay was neglected. The time needed to screen the piezogenerated charges by the free carriers in the wire depends on the wire length, diameter and residual doping level. It may be longer in MOVPE wires, so that the variation of the deformation during the contact duration may influence the shape of the decay signal.

For a capacitive design generator, the signal decay time τ is linked to the RC constant of the external circuit. This means that the internal screening time (i.e. the time needed to screen the piezogenerated charges by the free carriers in the wire) does not impact the generation decay. In contrast, this time impacts the signal build-up. Indeed, after the creation of piezogenerated charges at the moment of compression, the external circuit reacts with a characteristic RC time constant to charge the capacitor. At the same time, the free charges in the wire also move to screen the piezogenerated charges. The competition of these two phenomena defines the signal rise time, which is 2.1 ms in the example of figure 5-9. For comparison, the capacitive generator with MBE-grown nanowires shows a signal rise time of about 0.1 ms (see figure 4-30, chapter 4). The difference of the rise times points to a difference in the internal screening times between the MBE and MOVPE-grown wires. The shape of the second signal in figure 5-9 generated at releasing differs from the first peak, which may be ascribed to the PDMS viscosity slowing down its shape recovery.

Similar to the case of MBE wire generators, when the device is deformed by a

continuous compression deformation at low frequency, no output can be recorded. However, since the decay time in the analyzed MOCVD generator is longer, when the tapping deformation is applied at a high frequency, the output signal shape gets smoothed, as illustrated in figure 5-10. For a tapping deformation at 100 Hz with a 4 ms contact duration, the voltage output is rather continuous. Since the deformation contact time t_c is shorter than the estimated device characteristic decay time τ , the second output peak at deformation releasing arrives before the first peak's full decay. With this non-complete signal decay process, the recorded output signal obtains a continuous shape when the tapping frequency gets above $1/\tau$.



Figure 5-10. Voltage output of the piezogenerator at 100 Hz tapping compression.



Figure 5-11. Voltage outputs of the piezogenerator at 500 Hz (a) and 1 kHz (b) under continuous compression.

The device performance under full time continuous deformation is illustrated in figure 5-11. In order to have detectable output at this condition, relatively high deformation frequencies (500 Hz and 1 kHz) were chosen for the two measurements. As we can

see, the generator's piezoelectric response follows well the external deformations at both frequencies and are quite smooth.

As shown in the optical image of the piezogenerator (figure 5-4.b), there are several circular contacts on the device. In fact, each circular contact with its underlying membrane constitutes an independent piezogenerator. All of them can be measured following the steps presented above, and they share similar behaviors.

For a fixed microwire-integrated membrane surface, if we want to increase the output voltage, it is possible to connect separate generators in series. (We can draw an analogy with minimodules composed of solar cells connected in series aiming to increase the output voltage at a fixed output current.) However, it is technically hard to reliably connect all the separate devices with circular contacts using external wires. From this point of view, I propose the following "crossing-contact design" to facilitate the connection in series between generators. Besides, since each localized piezogenerator is sensitive to external deformation, it becomes possible to use this prototype design for the deformation detection (detecting both the position and force). The next section describes the fabrication of a device demonstrator implementing these ideas.

3. Prototype flexible piezogenerator on Kapton film with crossing contacts

In this section, I will first present the device prototype design and its fabrication, and then move to its electrical characterization.

3.1 Prototype generator fabrication

Figure 5-12 schematizes the design and the fabrication flow of the generator with crossing contact design. The fabrication procedure is straightforward. Firstly, the PDMS encapsulation of microwire arrays is done through standard spin-coating and annealing steps, followed by a mechanic peeling from sapphire substrate. Secondly, Kapton films of 65 μ m-thickness are patterned to create conducting parallel metallic lines of 1 mm in width and with 1 mm spacing. Then by using a very thin (~1 μ m) diluted PDMS layer as an adhesion layer, GaN-microwires-integrated PDMS

membrane can be sandwiched in between the two layers of Kapton films with contact lines. The two Kapton films are overlapped in a way that, looking from the device top, the top contact lines are perpendicular to the bottom contact lines. Therefore, only the microwires-integrated membrane at top-and-bottom line contact crossings can contribute to the piezogeneration.



Figure 5-12. Fabrication steps of the prototype generator with crossing contacts.



Figure 5-13. (a) Schematic of a piezogenerator at one top-bottom contact lines crossing. (b) SEM cross section view of the active membrane, showing the microwire total insulation. (c) An optical image of the fabricated prototype generators, with its parallel top lines defined as "a to e" and its bottom rows noted as "1 to 5". The piece of sapphire is placed on top as an indicator of the active membrane size.

Seeing from aside, as shown in figure 5-13.a, each effective crossing represents a generator of vertical microwires contacted in a capacitive design. A thickened membrane is more robust to manipulate. The size of individual generators is defined by the pre-patterned contact line width, while the whole device surface is determined
by the microwire initial sample size. The figure 5-13.c shows an optical image of the fabricated device with 5*5 crossings/generators. In the photo, the transparent sapphire substrate (after peel-off) put on top of the device serves as a reference of the GaN microwire-integrated membrane size. As we can see, since the substrate is not of a square shape, not all the 5*5 crossings are positioned on the active membrane. For the validation of the fabrication procedure, the I-V curve measurement is a good method (I will discuss this later in the electrical measurements part).

This prototype has the advantage of integrating separated piezogenerators in one device in a more compact way. It is possible to measure each of them by using their corresponding contact lines. It is also possible to connect separate generators in series by using extended contacts to have higher voltage output. It also offers the possibility to detect localized deformation by reading piezoelectric signals from generators in the 2D matrix formed by the crossed contacts. For both types of applications, the electrical characterization of each generator in the 2D matrix is necessary.

In the next sections, I will present a series of measurements that have been carried out with this prototype device. Meanwhile, its performance will be discussed in view of its potential application as an energy harvester or a force sensor.

3.2 Device piezogeneration measurement

3.2.1 I-V curve measurement and capacitance analysis



Figure 5-14. (a) Table presentation of the separate crossings defining individual piezogenerators. Working devices are marked in black. (b) Typical I-V curve from one generator. (c) Typical I-V curve of one contact crossing where there is no active microwire-containing membrane.

Before adding a deformation onto the whole device to see its piezoelectric response, I-V measurements and capacitance analysis are firstly performed on separate piezogenerators defined by the contact crossings.

Figure 5-14 demonstrates typical curves of the I-V measurement. Among the 25 contact line crossings, there are mainly two types of I-V behavior. Both of them show a dielectric nature of the sandwiched membrane under contact crossing, but with different levels of insulation. I note all the crossings in a 5*5 matrix table (figure 5-14.a) following the previous contact lines-rows definition. Coordinates of all the crossings exhibiting the I-V behavior exemplified in the figure 5-14.b are marked in black. positions correspond to active These generators based on the microwire-integrated membrane. As we can see, these generators' coordinates follow well the previously mentioned sapphire substrate form. Their I-V curve demonstrates a high degree of electrical insulation with a certain hysteresis which corresponds well to polymer (PDMS) dielectric property. As for the rest of the crossings marked in white in figure 5-14.a, they exhibit similar isolating behavior with a hysteresis but with a more prominent leakage current. As I mentioned before, not all the 25 crossings are covered by microwire-integrated membrane. During the sandwiching step of the device fabrication, thin PDMS ($\sim 1 \mu m$) is deposited on both Kapton films as adhesion layers. When the two Kapton films are sticked face-to-face while without the effective microwire-integrated membrane in-between, those two thin layers of PDMS form an insulating layer. This layer contains only PDMS ($\sim 2 \mu m$), but is much thinner than the microwire-integrated membrane, which results in a higher leakage current.



Figure 5-15. The nine separated generators in the middle of the device and their capacitance measurements. An average value of 3.67 pF can be extracted.

The capacitance measurement is then conducted using an impedance analyzer (Hioki

IM3570). The nine separated generators in the middle of the device (encircled in red dashed line in figure 5-15) are measured under a frequency sweep from 5 Hz to 3 MHz under a DC offset of 1 V. As shown in the graph, these generators demonstrate a certain variation of capacitance, but their values remain in the same order of magnitude. The variation of capacitance may arise from possible fluctuations of microwire local density or fabrication-induced active membrane layer thickness differences or contact line width changes. If we compare the empirical capacitance average value of one separated generator $(3.7\pm1.5 \text{ pF}$ from the measurements) with its theoretically calculated value (0.9 pF, obtained using the GaN microwires filling ratio of 0.05 and the membrane thickness of 30 um), the two remain in the same order of magnitude. The bigger empirical value may be linked with the additional capacitance of the external connecting wires. This comparison validates again the expected capacitive design of the prototype generator.

3.2.2 Device piezogeneration explorations



Figure 5-16. Two configurations to deform the prototype device: (a) compression added from the microwire-top side. (b) deformation added from the microwire-bottom side. All the following electrical measurement results are obtained under the deformation configuration (b).

In order to have a comprehensive analysis of the device's piezoelectric performance, a series of measurements have been carried out. In the first step, a single localized generator is tested in the same way as the circular pad generator described in the previous section. Low frequency tapping and high frequency continuous modes of

deformations are both applied. Secondly, to test the homogeneity of different generators, same type of deformation is applied onto all the active crossing generators one by one. Their performance at the same deformation conditions is then compared. Thirdly, considering the potential application as a force/pressure sensor, the device's sensibility to a localized deformation and the ability to discriminate the neighboring deformation is tested by deforming one localized generator and measuring all the other non-deformed generators at the same time. The outputs of all the generators in the matrix in response to a localized deformation are recorded and further compared. Finally, the separated generators on the same device are connected in series and deformed all at the same time in order to explore the capacity of the whole device to harvest mechanical energy.

Different from the previous measurements carried out on the circular pad generator, the deformation of this prototype device was applied from the other side. I turned the prototype device upside-down, so that the shaker head taps on the bottom side of the microwire array, as illustrated in figure 5-16.b. The purpose of this change was to explore the more sensitive side of the device. Indeed, the thick cap layer of PDMS in the capacitive design damps the mechanical deformation and weakens the generator sensitivity to the external force. Although the bottom side of the microwires is also insulated from the bottom contact with a 1 µm PDMS layer, the thickness of this insulation layer is much less important than the cap layer on the wire-top side. However, for this prototype device this was not very important, since there are 65 μ m-thick Kapton films on both sides of the active membrane, which is only around 40 um thick. I tested the device's performance by adding the same deformation on both sides with the same external electrical connection, the output voltages were of a similar amplitude (still from the bottom side, the signals are slightly bigger). Therefore, I conclude that the Kapton films play a more important role than the PDMS cap layer for absorbing mechanical shocks. To be coherent, I present in the following parts all the results obtained when the device is deformed from the microwire-bottom side, as the case shown in figure 5-16.b.

Let's now give a look at the device's electrical performance.

A. Localized single generator measurement

Firstly, I have measured a single generator at one contact-line crossing. Figure 5-17 gives the voltage outputs of the generator at position c3 as an example. The generator

responds well to the external deformation of 10 Hz tapping (contact time 46 ms) and to the 1 kHz continuous compression. The characteristic decay time of the device can be estimated around several ms (the first peak decay time is 2 ms, while the releasing peak decay time is about 4 ms). In both conditions, this crossing-positioned generator bears a similar electric behavior as the previously described circular pad generator.



Figure 5-17. Typical voltage outputs of one generator (example of a generator c3) at 10 Hz (a) and 1 kHz (b) compression.

B. Generator matrix homogeneity test



Figure 5-18. Demonstration of the inhomogeneous response of generators at different positions (b2, c3 and d4) when experiencing the same external taping deformation of 20 Hz.

To test the device's in-plane homogeneity, all the separated generators are deformed and measured in the same conditions one after another. Figure 5-18 gives some output curves for comparison. Generators at b2, c3 and d4 positions are all tapped at 20 Hz with the same shaker control. They are supposed to be identical in response to external compression since all their constituting microwires come from the same growth (supposing that there is no density gradient or other growth inhomogeneities on the 2 inch wafer) and they experience the same device process flow. However, as we can see from the presented voltage output and force sensor output curves, the three generators at the three different positions receive different forces and give out different electrical outputs, though the external deformation conditions are nominally the same. From the force sensor output, we see that the deformation process for each localized generator is different. This can be a result of the differences of generators' thickness. Supposing that the Kapton films are homogeneous, it could be the thickness variation of the microwire-integrated membrane that plays the main role. The fabricated device has a surface area around 1 cm². The border effects after spin-coating of PDMS may be quite important. As a consequence, the membrane center, where the generator c3 is located, is the thinnest. Hence, it is this generator that feels best the outer deformation (because it experiences the smallest damping from the PDMS cap) and gives the best piezoelectric response compared to the other two.



Figure 5-19. Demonstration of the inhomogeneous responses of generators at different positions (b2, c3 and d4) when experiencing the same external continuous compression at 300 Hz.

Figure 5-19 gives the comparison between generators in face of a continuous compression at a higher deformation frequency, namely at 300 Hz. The same conclusion as in the case of a tapping deformation can be drawn. We conclude that with our fabrication procedure, all the generators at contact crossings demonstrate the same qualitative behavior, however their quantitative response to the external deformation fluctuates from one device to another.

The low repeatability of the generators in a matrix does not solely originate from the fluctuation of the polymer thickness, it may be due to the GaN microwire inhomogeneous growth as well. For auto-assembled microwires, the density of wires can vary on the substrate due to a temperature variation. Besides, the appearance of inversion domains in the wires is also random. Therefore, it is quite difficult to produce a homogeneous generator array. However, minimizing the fabrication border effect by using a larger growth surface or by improving growth homogeneity by applying selected area growth (SAG) can increase the macroscopic device homogeneity.

The observed inhomogeneity of the prototype is an important drawback for a deformation sensor matrix. For sensor application, this topological inhomogeneity can render the device calibration difficult and even impossible. However, for energy harvesting this is not that critical. As long as each generator reacts to external deformations, energy can be converted into electricity. The only issue is the required current matching between the individual generators to maximize the conversion efficiency when devices are connected in series.

C. Local deformation detection test

In addition to device homogeneity, the device's ability to distinguish localized deformation is also an important aspect to be taken into account, especially for sensor applications. Here I apply a compression at one localized generator and then measure at the same time the output voltage of all the other generators in the matrix. My expected ideal result is that only the deformed generator gives a distinct voltage output, whereas all the others remain inactive. If this is the case, it would be easy to localize the compression position and even calculate the force applied by analyzing the signal. However, in the experiment there are electric signals detected from every

generator, even from the non-deformed ones.

Figure 5-20 gives two examples when the tapping deformation is applied at the generator c3 at 50 Hz with different maximum forces. The two panels of the figure 5-20 plot the output voltages of every crossing generators in the matrix for two periods of deformation. The five different colors are used to mark generators in the five parallel lines. As we can see, all the localized generators are "active".

Only the generator c3 is deformed physically, it gives the maximum voltage output compared to the others. However, the other generators in line c, who are not deformed directly by the shaker head, give output voltages of a similar amplitude as c3. For all the five lines, in both cases of bigger or smaller compressing forces, the generators in the same line give similar voltage output values. Among different lines, there is no evident correlation between the voltage values and the line's distance from the compression source spot.



Figure 5-20. Output of each generator when only the generator c3 is compressed at 20 Hz with a maximum tapping force of 0.1 N (a) and 0.2 N (b).

The voltage output ratio between the maximum and the second maximum value can be considered as a parameter that helps to discriminate between a deformed and a non-deformed spot. In figure 5-20, this ratio is calculated as 2 (8.8 mV/4.4 mV) and 2.6 (33.6 mV/12.8 mV) for the two compression forces of 0.1 N and 0.2 N, respectively. These values show that with a higher deformation level, it is easier to localize the deformed position. Vice-versa, it is more difficult to detect the location of a small force.

I suppose that it is the Kapton film between the shaker head and the piezoelectric

membrane that spreads the mechanical deformation from the point where it is applied to the other generators. Getting rid of this Kapton film could be a solution to enhance the electric response contrast between generators. I will come back to this point at the end of the chapter, when discussing about the signal differentiation for sensor applications.

Figure 5-21 presents the results of the same test performed at a higher frequency of 1 kHz in a continuous compression mode. It is still the generator c3 in the center of the device that receives a localized continuous compression. As plotted, the continuous voltage output is detected from all the generators in the matrix. However, compared with the previous results in tapping mode, the outputs of generators differ stronger between the deformed and the non-deformed ones.



Figure 5-21. Output of each generator when only the generator c3 is compressed at 1 kHz (continuous compression mode).

Taking a closer look at the outputs of the generators in different lines, we can observe some discernible phase change among them. The outputs coming from a, b, d and e lines, where no shaker-induced compression happens, show a different time delay in comparison with the output of line c. I presume, apart from the possible mechanical wave propagation effects, that the electric crosstalk between the contact lines contributes to the output of the generators in non-deformed places. Besides, the non-deformed generators are capacitors. When the deformed piezogenerator is generating, it may charge the passive capacitors around, thus causing signals from the non-deformed places.

D. Voltage output addition

As the last part of the electrical measurements, the separated generators in the matrix are connected in series to demonstrate the overall energy harvesting capability of the prototype device. By design, one top contact line and one bottom contact line is used to have access to one separated generator. However in practice, the different generators on the same top line behave quite similarly under deformation. I connected the five top contact lines in series and used a shared bottom line for the mass. The device overall output is then the sum of the outputs of the five generators.

Firstly, I explore the generation of the device when only one spot on it is deformed. Then, the whole flexible device is homogeneously compressed by a glass block. The sum of the outputs of the five lines of generators is recorded. Finally, the device's peak and average output power density is estimated, based on the results obtained under the 1 M Ω external load of the oscilloscope.



Figure 5-22. Voltage outputs of the prototype generator when it is compressed at spot c3 at 50 Hz with a maximum tapping force of 3.38 N.



Figure 5-23. Voltage outputs of the prototype generator when it is continuously compressed at spot c3 at 500 Hz.

Figures 5-22 and 5-23 display the prototype generator overall output (sum of the voltages extracted from the five lines) when it is deformed at spot c3 under 50 Hz tapping and 500 Hz continuous compression, respectively. In both cases, the voltage output of line c contributes most to the final value, since the deformed generator belongs to this line.



Figure 5-24. (a) Schematic explanation of the way in which a homogeneous compression is added onto the whole generator surface by using a glass block. (b) Device voltage output at 50 Hz tapping deformation under a glass block. The maximum tapping force is 2.8 N, corresponding to a maximum compressing pressure of only 28 kPa.

Then, a glass block is used to deform simultaneously all the separated generators presented on the device to demonstrate its energy harvesting capacity. The glass block

is placed on top of the device (on the Kapton layer), and the shaker head taps in the center of the block, as indicated in figure 5-24.a. Thanks to the high rigidity of the glass layer, a uniform compression can be transferred to the whole surface of the matrix of generators. Figure 5-24.b selects one voltage output curve of the device at 50 Hz tapping deformation, with a maximum tapping force of 2.8 N and a deformation duration of 2.5 ms. The maximum force applied corresponds to a compression of only 28 kPa on the device.

As shown in the figure, the peak-to-peak overall voltage output of the device reaches 220 mV (from 154 mV to -66 mV). The less pronounced output peak value at releasing should be explained by the active membrane/device softness. The deformation recovery rate of the embedded piezoelectric wires has been slowed down by the viscous PDMS environment. Therefore, with the accumulation of several serial device signals, the total output bears a more distinct asymmetry.

Another point to notice is that the first positive peak does not show a progressive decay after the device compression, which indicates a longer device decay time τ than the contact time t_c . Meanwhile, the negative voltage peaks at releasing experience a regular exponential decay. This decay time is then estimated as 1.8 ms by fitting the presented curves. As mentioned before, the output signal decay after releasing is linked with the external circuit condition. In our case, the external circuit is a resistive load of 1 M Ω . Since this load forms a RC circuit with the capacitive device, the fitted decay time τ is the RC constant for the capacitor discharge. The capacitance of this prototype generator when connected in the previously described way can be calculated as 1.8 nF.

To analyze the linearity of the generator response, I kept the same compression duration, while the maximum applied tapping force has been increased and the device response has been recorded. The generated positive voltage output peak values have been traced as a function of the maximum applied force. As demonstrated in figure 5-25, a linear increase of the output voltage with the increasing tapping deformation is observed. We may also notice that the linear fitting (pink dashed line) of the positive peak values does not pass through (0,0). This strange behavior is an artefact related to the low precision of the used force sensor in our setup. As discussed in the previous section (refer to figure 5-7), the integrated force sensor is less sensitive to small forces than the analyzed generator. It may give a smaller maximum force value than the real one. Hence, I depicted in figure 5-25 with a green dashed-dotted line a linear relation

having the same slope, which possibly corresponds to the real maximum tapping force values.



Figure 5-25. Positive voltage output of the prototype generator under a homogeneous deformation applied by a glass block as a function of the maximum force/compression. Square dots are experimental values of the positive maximum voltage output. The pink dashed line and the green dash-dotted line show the linear fitting before and after correction.

Finally, considering the load resistance of 1 M Ω from the oscilloscope and the 154 mV maximum voltage output demonstrated in figure 5-24, the peak instantaneous power output of the generator matrix is calculated as 23.7 nW. Its average power output is calculated as 1.22 nW and the energy harvested from each tapping cycle is 24.4 pJ. Considering the flexible generator volume (which is overestimated because the active membrane is smaller than 1 cm²) V = 1 cm*1 cm*40 μ m = 0.004 cm³, the peak power output density and the average power output density of the device can be further calculated as 5.93 μ W/cm³ and 0.31 μ W/cm³.

After performing extensive characterization of this first matrix of generators, which can operate both as an energy harvester and a force sensor, I realized that it is necessary to uncouple these two functions in order to optimize the device performance in view of a single application. For each application, the performance indicators are different and require a specific structure, although a matrix design of generators can be applied in both cases.

From the characterization of the prototype device described above, we have seen that for a force/pressure sensor the cross talk between different points should be reduced and the mechanical wave propagation should be prohibited. In this way, a better signal localization can be achieved. As for the energy harvesting application, the cross talk and the mechanical vibration propagation seems less unfavorable.

New devices have been fabricated to improve the energy harvesting of the prototype generator. I will present the one that has the best generation output in the next section. Besides, a description of a generator made of stacking multiple wire membranes, which has been less successful, will be given in appendix. Though this device is less efficient in terms of energy conversion, it still shows an interesting design possibility. Finally, at the end of this chapter, the adaptation of the prototype device for sensor application will be discussed.

4. Improved piezogenerator for better energy harvesting

In this section, I will first describe the fabrication and the measurements of the piezogenerator with a reduced PDMS thickness (referred to as "piezogenerator A"). Then I will compare its electrical performance with the prototype generator with crossing contacts and make some further discussions.

4.1 Fabrication of the piezogenerator A

The piezogenerator A integrates the microwire array from the same wafer as the prototype generator discussed previously. The same fabrication process (refer to figure 5-12) has been applied. However, for the new generator A, the device active membrane thickness has been reduced. Instead of keeping the thickness of the microwire-integrated membrane around 40 μ m, the targeted active layer is thinned down to around 20 μ m (figure 5-26). The aim is to decrease the damping effect of the PDMS insulating top layer and to increase the generator sensitivity to the external deformation. As a drawback, the leakage current of the membrane is more prominent due to the increased number of long wires passing through the membrane top. In order to prohibit this effect, a plasma oxidation of the microwire-integrated membrane surface has been performed to form an insulating Ga₂O₃ layer on the wires tips. With this oxidation step, a capacitive design of the device is maintained.



Figure 5-26. 10 degree tilted cross section SEM image of the thinned microwire-embedded membrane.

Similar to the prototype device, the piezogenerator A uses a crossed contact design. On its rectangular surface of 1.2 cm*0.9 cm, 20 localized piezogenerators are realized. The contact lines have a 1 mm width and are separated by 1 mm spacing.

4.2 Electrical characterization of the piezogenerator A





Figure 5-27. Typical voltage outputs (black curves) of one generator from device A at 10 Hz tapping deformation (a) and 300 Hz continuous compression (b). The force sensor readings are reported in blue curves.

Each piezogenerator at the crossing positions in device A is evaluated with the help of the vertical compression setup. All the devices demonstrate an electrical behavior similar to the one of the prototype device. Figure 5-27.a and b show respectively the voltage output trace of one separate generator from device A under 10 Hz tapping (38 ms contact time) and under 300 Hz continuous compression.



Figure 5-28. Best recorded voltage outputs (black curves) of one separated generator from device A under 20 Hz tapping deformation (compression duration $t_c = 2.5$ ms). The force sensor readings are reported in blue curves.



Figure 5-29. Open circuit voltage (a, pink curve) and short circuit current (b, green curve) of one generator from device A under 20 Hz tapping deformation. The force sensor readings are reported in blue curves.

Figure 5-28 displays the voltage output signal from one individual generator of device A. The presented voltage trace recorded under 20 Hz tapping deformation is one of the best results obtained from this device. As can be clearly seen, with a tapping force as small as 1 N, the piezogenerator can deliver a peak-to-peak voltage output of 348 mV (from -188 mV to 160 mV). This value is obtained when the device is connected to an oscilloscope with an internal impedance of 1 M Ω . To evaluate the impact of the load resistance, here I further explore the open circuit voltage of this generator by

using a 100 M Ω external load (voltage amplifier with a unity gain, Stanford research systems SR560). Its short circuit current has also been measured under the same deformation condition by using a current amplifier (Stanford research systems SR570). The obtained results are traced in figure 5-29. The open circuit voltage and the short circuit current of the generator have a peak-to-peak value of 1.48 V (from -0.68 V to 0.8 V) and 440 nA (from - 240 nA to 200 nA), respectively.

As we can observe from the figures 5-28.a and 5-29.a, the decay time of the signal at device releasing is different for different load conditions. For the 100 M Ω load, the decay time is much longer. In fact, as discussed previously, for the capacitive design device, the signal decay time is governed by the RC constant of the circuit. When the load resistance is increased by 100 times, the signal decay becomes 100 times slower. The measurements shown here once again confirm the previously proposed device operation mechanism.

Using the standard formulas (given in chapter 4), I calculated the power output of a single piezogenerator at contact crossing from the results presented above. When the generator is operated with a 1 M Ω external load, its average power output is 0.33 nW. From each cycle of deformation, it delivers an energy of 16.4 pJ. When the external load is changed to 100 M Ω , the average power output of the generator increases to 0.87 nW and the energy delivered per tapping reaches 43.5 pJ. If considering the actual volume of the active layer, which is 0.00002 cm³ (1 mm*1 mm surface defined by the contact line, 20 µm-thick active membrane), the average power output density can be calculated as 16.5 µW/cm³ (with a 1 M Ω load) and 43.5 µW/cm³ (with a 100 M Ω load).

4.2.2 Tests of the device A under ambient deformation conditions

To characterize the device electrical performance as a whole, I connected all the generators in series for the measurements. In order to imitate the natural environmental deformation conditions, instead of using the controlled shaker head, I chose to deform the generator by index finger tapping. The tapping is done in a comfortable way at low frequency (around 3 Hz), the maximum applied force is less than 1 N (which is easily attainable in our daily life from other sources). The device is then connected to the oscilloscope (1 M Ω load) for output observation.



Figure 5-30. (a) The transient voltage output of the piezogenerator A under 20 seconds of direct finger tapping deformation. (b) Voltage output trace under six cycles of deformation.

Figure 5-30.a traces the transient voltage output of the piezogenerator A under 20 seconds of finger tapping deformation. Some randomness can be observed from the output in terms of its value and symmetry. In average, the voltage output peak reaches 89 mV in absolute value, indicating a good response of the piezogenerator under ambient vibrations.

Figure 5-30.b gives a zoomed view of the device output under six cycles of finger tapping. With this closer look, we can assume that the randomness of the device output may come from the varied finger tapping conditions. Each tapping deformation from finger movement has its proper character. The tapping force as well as the device deformed area may vary from time to time. During each effective contact duration, we can also see different signal fluctuations, which may be due to an unstable contact.



Figure 5-31. (a) The transient voltage output of the piezogenerator A for 20 seconds of finger tapping deformation with a glass layer as inter-medium. (b) Voltage output trace under six cycles of deformation.

To improve the repeatability, I placed a 1 cm^2 glass layer on the top of the generator. The finger now taps on the glass inter-medium instead of the device Kapton top. The generator still reacts to the finger movement, and its voltage output for 20 seconds of tapping cycles is shown in figure 5-31.a.

As we can see from the figure 5-31.a, under this new deformation condition, namely, finger tapping on a glass top inter-medium, the piezogenerator gives out a more reproducible voltage output. The average voltage output absolute peak value increases to 126 mV. From the zoomed six cycles of voltage output shown in figure 5-31.b, we can notice a more regular form of the output signal. A prominent positive peak marks the beginning of the tapping deformation. Then the signal drops to zero during constant contact. Finally, at releasing, negative voltage peak appears.

As we may notice, the voltage peak at tapping releasing shows some oscillations. It is not a single negative peak as has been observed in the previous study with a shaker head, but it is followed with a positive peak in a repeatable way. Most probably, the second positive peak is caused by the relative movement of the cap glass block, since it is not sticked to the device Kapton top, so it can bounce back. Despite this observation, the introduction of the rigid glass inter-medium cap layer makes the tapping deformation less random. Indeed, it is evident from the device output shape that, a compressing deformation can be applied onto the generator surface in a more uniform and reproducible way with the use of the glass block. The human finger tip with a certain curvature (though deformable) cannot ensure a homogeneous level of deformation on the whole piezogenerator surface.

We can evaluate the piezogenerator's performance under finger tapping in terms of its average power output. When the tapping is performed directly on the device top, the generator delivers an average power of 0.28 nW and an energy of 93.3 pJ per tapping deformation. When the glass cap is used, the average power output slightly increases to 0.29 nW and the energy delivered per tapping deformation increases to 96.7 pJ. These values are obtained after averaging the values recorded from 60 tapping cycles. In this way, the influence of the human-induced finger tapping variations is expected to be minimized. (The input total mechanical energy for the two measurement is supposed to be the same). The calculated output values of the device don't change with the application of the glass top layer. In fact, they are quite similar. Therefore, the main effect of the glass block on the device performance is to make the

deformation condition more regular in time and thus ensure the device generation in a more repeatable way. This observation may give us a hint to further improve the generator performance by design. While keeping the general flexibility of the device, a more rigid supporting layer of the membrane could be used to homogenize the device mechanical deformation in face of ambient random vibration.

4.3 Electrical performance comparison between the prototype generator and the new generator A

In this part, I will compare the electrical performance of the updated generator A with the prototype generator presented in section 3. I will first compare them in terms of their individual crossing-positioned generator performance. Then a comparison of the devices as a whole (with series connected individual generators) will be made.

Here I evaluate the device performance by taking into account their average power output. Indeed, the instantaneous peak power output values are always higher and look more promising. However, for the device application as an energy harvester, it is the average power output that matters. Hence, for the latter comparison, focus will be made on the device average output values, such as average power output and average power output density.

4.3.1 Comparison of the individual generators at the contact crossing positions

In figure 5-32, I trace together the voltage outputs of one individual generator defined by the contact crossing from each of the compared devices. The tapping deformations are performed at 20 Hz, with a device effective deformed duration of 2.5 ms. The maximum applied force is the same (0.86 N) for both generators from the two devices. This means that the deformation conditions are the same (implying the same strain rate of the embedded microwires).



Figure 5-32. The voltage outputs of individual crossing-positioned generators from the prototype device (a) and from the generator A (b), respectively. The measurements are done under 20 Hz tapping deformation and with a 1 M Ω external load. The deformation force received by the generator is reported in blue curves.

	Prototype	Piezogenerator A
	piezogenerator	
Peak-to-peak voltage output per	150 mV	348 mV
tapping	(78 to -72 mV)	(160 to-188mV)
Average power output	0.08 nW	0.33nW
Average power output density	$0.47 \ \mu W/cm^3$	$2.2 \ \mu W/cm^3$
(with Kapton film)		
Average power output density	$2 \mu W/cm^3$	16.5 µW/cm ³
(without Kapton film)		
Active layer thickness	40 µm	20 µm
Max applied force	0.86 N	0.86 N

Table 5-1 Comparison of one individual piezogenerator in device matrix

* Deformed surface is actually defined by 1 mm circular shaker head shape (calculated as 0.785 mm^2). Here it is overestimated as 1 mm² – the size of the contact line crossing area. The Kapton layer

thickness is 65 µm.

The table 5-1 gives a comparison of the two devices. We can see that under the same deformation condition, the individual generator in device A gives a higher voltage output (348 mV peak-to-peak) than the one from the prototype device (150 mV peak-to-peak). Correspondingly, the average output power of the individual generator from device A is higher (0.33 nW). From each tapping deformation cycle, it can

deliver an energy of 16.5 pJ. While for the individual generator from the prototype device, the average power output is 0.08 nW and the energy delivered per tapping is 4.1 pJ. By taking into account the deformed device volume (1 mm*1 mm surface area, thickness equals twice the Kapton thickness plus the active layer thickness), the average power output density of each individual generator can be calculated. For the generator from device A, the value is 2.2 μ W/cm³. While for the generator from the prototype device, the average power output density is only 0.47 μ W/cm³. In fact, if we only consider the electric performance of the active material, the device volume taken by Kapton layer need not be counted. In this way, the average output power density of the two devices increases to 16.5 μ W/cm³ and 2 μ W/cm³, respectively.

From the above comparison, we can conclude that the device A is more efficient in converting mechanical energy into electricity. Its improved performance is related to the device design, more precisely, to the active microwire-integrated membrane thickness. Thinning of the active membrane by getting rid of the excessive PDMS damping layer can greatly increase device's sensitivity to the outside deformation.

4.3.2 Comparison of the devices under ambient deformation conditions

As a second step, I wanted to compare the two generators in terms of their whole device electrical performance (with individual generators connected in series). The finger tapping experiment has been carried out the same day with the utilization of the 1 cm² glass cap. Unfortunately, the prototype device did not deliver clear electric signals in response to the finger tapping. While the outputs obtained from the device A has been previously presented in figure 5-31.

The average power output of the device A reaches 0.29 nW and its energy delivered under each tapping deformation attains 96.7 pJ. If we consider the whole device volume, which is $1 \text{ cm}^2 * 150 \mu \text{m}$ (20 μm active layer thickness plus twice the Kapton thickness), the device average power output density under finger tapping can be calculated as 19.3 nW/cm³. Otherwise, if we take into account only the active layer volume of the device, the average power output density goes up to 145 nW/cm³.

Finally, I'd like to make a remark on the device output power density calculation. For the generator A, its power output density is calculated as 2.2 μ W/cm³ (or 16.5

 μ W/cm³) and 19.3 nW/cm³ (or 145 nW/cm³) in terms of the individual generator and the device itself as a whole. These values differ by two orders of magnitude. To understand this difference, we note that the initial deformation conditions of the two measurements are different. The maximum pressure applied on the individual generator is in the order of MPa (1 N/1 mm²), while on the whole device is in the order of tens of kPa (1 N/1 cm²). In addition, there exists a spacing between the contact lines so that not all the microwires in the device volume are contributing to the piezogeneration. On the contrary, the passive microwires between the contact lines contribute to decrease the device power output density. Therefore, in order to achieve a better device performance, the passive non-connected volume of the device should be reduced. Reducing the contact line spacing is thus a good approach to further improve the device electrical power output.

In the following part, I will discuss the device further improvement.

4.4 Perspectives : new architectures to improve the piezogeneration

Based on my experience, I'd like to propose below some other possible ways to improve the piezoelectric harvester performance. These improvements address the following two aspects concerning the crossing-contact device design and the material choice.

4.4.1 Improvement of the design

- If we want to increase the voltage output from a given device volume, the device area should be divided into independent generators, which need to be connected in series. In comparison to the above-described contact design, the increase of the crossing contact line density would enhance the energy conversion. By reducing the contact line inter-spacing, the number of connected effective separated generators will increase and higher series output can be obtained. The power output density will also increase since the device will become more compact.
- If instead of a high output voltage we need a high output current, a large area device design should be used. By covering the whole active membrane surface with a unique broad metallic contact the current output of the device will be maximized. However, the active membrane quality should be good to avoid short

circuits between its top and bottom contacts due to membrane imperfections.

Another approach is to change the supporting Kapton substrate. The new substrate should be flexible, but when compared with the active membrane, it should have a higher rigidity. An enhanced rigidity contrast between the piezoelectric membrane and the supporting film is expected to better couple to the active membrane the mechanical deformation from a random vibration. If the chosen film is thin, that would be an additional advantage to improve the device compactness.

4.4.2 Improvement of the active material

- Integrating a denser piezoelectric microwire array seems a direct way for improving the device output. With the same device design, a higher density of the active material (which still does not degrade the membrane mechanical flexibility) would guarantee a higher transducing performance.
- Longer micro-scale piezoelectric wires have been reported to be more sensitive to external forces [88]. I propose to compare piezogenerators with the same design but based on wires with different lengths (but the same density) to see if the higher length indeed brings an improvement.
- Using microwires with a low inner free carriers concentration should also lead to a higher output voltage. Indeed, the screening of the generated piezoelectric charges by free carriers reduces the peak voltage. Therefore, microwires with a smaller doping level should be analyzed. Besides, microwires with an artificially created depleted region (e.g. with a pn junction) would also be interesting to test.
- Other types of micro-wires or nanowires with a high piezoelectric coefficient could be used. In the III-nitride material family, Al(Ga)N and In(Ga)N compounds both present high piezoelectric coefficients. It would be interesting to make a comparison between the GaN-based generators and devices made from these types of wires or from wires containing heterostructures.

The improved device design in combination with a proper material choice would enable compact and efficient energy sources based on these piezoelectric microwires.

5. Modifying the device architecture for force/pressure sensing applications

5.1 Design of the proposed piezo-sensor

Regarding the force sensor application of the previously described prototype device, the propagation of the mechanical deformation due to the top Kapton layer is detrimental for localizing the deformation position. Therefore, I propose to remove this layer in order to adapt the prototype device design for piezo-sensing. The same microwire growth has been used for the fabrication. In the absence of the top Kapton film with pre-patterned contacts, the top contact lines for the sensor need to be deposited directly onto the microwire-integrated membrane. This deposition is done prior to the membrane peel-off. Then the peeled-off ensemble is sticked using a PDMS adhesion layer to the pre-patterned bottom Kapton film, while keeping the perpendicular orientation of the top and bottom contact lines. Every line crossing forms an individual generator, and each of them now serves as a sensing node to locate the deformation.



Figure 5-33 (a) Structure of one separated sensing-node piezogenerator. (b) Top-view photo of the fabricated device.

Figure 5-33.a shows the side-view schematic of one separated sensing-node piezogenerator. It follows a capacitive design. The top-view photo of the fabricated sensor is displayed in figure 5-33.b. As can be counted, the number of effective sensing nodes on the device is 14. Each of them has a surface of 1 mm*1 mm.

5.2 Electrical characterization of the piezo-sensor

As the first step, the I-V curve of each sensing node is checked. They display similar hysteresis characteristics as shown in figure 5-14, confirming the capacitive design of each individual sensing node.

Then, a systematic evaluation of the device as described in the previous section 3.2.2 should be carried out. The characterization should be made on single piezogenerator performance (as in section 3.2.2.A), and then on the device 2D homogeneity (section 3.2.2.B) and further on the device local deformation sensitivity (section 3.2.2.C). Unfortunately, with the fabricated device shown in figure 5-33.b, no distinct electrical signals have been achieved. I attribute this failure to the device bad mechanical coupling condition. For the piezoelectric conversion measurement, the piezo-sensor is fixed on the support of the vertical compression setup via its Kapton substrate. Several extended conducting copper wires are used to connect the top contact lines of the device and the shaker is compressing one crossing-positioned sensing-node piezogenerator. Since the microwire-integrated membrane is fixed on the Kapton bottom layer by a soft PDMS adhesion layer and the membrane borders are free, the whole membrane moves under shaker tapping and absorbs the mechanical shock when the shaker head taps one spot. Therefore, the deformation of microwires under the tapped spot is strongly reduced and no distinct piezoelectric conversion takes place.

Although this experiment has failed to realize an improved piezo-sensor, it inspired some ideas to further adapt the prototype device for piezo-sensing applications.

5.3 Perspectives : other approaches for piezo-sensing

Experimental results have shown that removing the top Kapton layer with contact lines deteriorates the mechanical coupling of the deformation to the active part of the piezo-sensor. When the active membrane has many degrees of freedom, the mechanical deformation of the microwires in their growth direction is not favored. From this point of view, the top layer having a higher rigidity than the membrane should be maintained.

While the presence of the top cap is needed to couple the external deformation to the microwires, it is also necessary to suppress the membrane in-plane deformation

propagation. To this end, a patterning of the active membrane may be the right approach to increase the device local sensitivity to deformation.



Figure 5-34. Illustration of the mechanically decoupled piezogenerator matrix for force sensing applications.

The design idea is illustrated in figure 5-34. Based on the crossing contact design of the prototype device, each individual sensing node (each separated piezogenerator) should be mechanically isolated from one another. In our case, the piezoelectric wires are homogeneously present in the active membrane. PDMS etching in the regions not covered by the contact lines should be performed to cut off the membrane continuity. In this way, the local deformation will not be easily transferred through Kapton top to other places, and the detection of the external force localization should be improved. Although there are still microwires under the non-connected regions, they are now free-standing (without the PDMS encapsulation) and therefore they will not participate in the piezogeneration.

The technological challenge for this proposed architecture is the localized etching and the following contact lines aligning. When the contact lines themselves and their inter spacing are of 1 mm (as in the present case), the etching of the encapsulation material and the subsequent device integration might be easy. However, when the contact line width as well as the line spacing decreases for higher spatial resolution, the aligning of the patterned membrane with contacts would become difficult.

Based on this proposed design, other possible modifications can be added to further improve the device performance. For example, the individual sensing nodes which are of capacitive design here can be changed to the Schottky diode design. From the previous discussion, we know that the piezoelectric signal transient decay is faster for Schottky designed piezogenerators. Therefore, in view of high frequency deformation detection, the piezo-sensor with individual Schottky diode sensing-nodes will show a higher cut-off frequency.

At the same time, different active microwires can be used. Longer wires can be favorable to increase the device local sensitivity. Denser wire growth can help to increase the local signal intensity. Selective area growth (SAG) of microwires is nowadays under intense research and development. If the sensor is made with the homogeneous SAG wires, the sensor calibration will be easier and the detection would be more precise. As we can see, there are many approaches for improvement of the piezo-sensors based on nitride microwires.

5.4 On the piezo-sensor calibration.

Before concluding this chapter, I'd like to talk about the future piezo-sensor calibration. In the published works related to nanowire or microwire based sensing devices, the device calibration is rarely mentioned [62], [64]. Indeed, demonstrating the sensing principle is the first step. However, to make an operational sensor from those low-dimensional structures, there are still many steps and they are not easy.

Let's take the proposed force sensor illustrated in figure 5-34 as an example. In order to functionalize it as a 2D force/pressure sensor, the following points would be critical in terms of the device performance and calibration:

- Firstly, the spatial inhomogeneity of the piezo-sensor should be minimized. All its sensing nodes should be the same with negligible variation. The homogeneous material growth is the most important prerequisite for that. Selective area growth is a promising approach. Then, the sensing nodes need to have the same sensitivity after device integration. The durability of the contact lines and their aligning with desired sensing node positions are also critical in view of signal reading and transfer. The fabrication of the sensor itself is a big challenge.
- Secondly, in terms of single sensing node calibration, a good knowledge of the relation between the deformation and the detectable signal is mandatory. In the case of the presently discussed piezo-sensing, the relation between the deformation and the piezoelectric output should be established for each sensing node and at different frequencies. Usually, a linear relationship is required for signal analysis. While for the piezo-sensor discussed here, the linear relation exists between the device deformation change rate (or to say force change rate)

and the piezoelectric output. Therefore, the effect of time needs to be taken into account. As has been discussed in detail in chapter 4, the present piezogenerator reacts differently to different deformation types (tapping mode or continuous mode), which complicates the device calibration.

Finally, a powerful signal analysis program is indispensable. For single sensing node, there are already many possibilities to think of when relating one obtained electrical signal with the deformation. When the number of individual sensor nodes increases and a 2D detection matrix is formed, the possible deformation conditions may become more complex and the signal processing is more challenging. A well-developed signal reading system is needed to guarantee a good interpretation of the obtained signals.

Although its development is challenging, the main advantage of this piezoelectric wire based sensor is that it is self-powered. Compared with the traditional force sensors (based on resistance or capacitor changing effect), the piezo-sensor demands no power supply. Its only power consumption comes from the signal reading system. Besides, with the small footprint of the microwires, small size and more compact sensors can be made. A higher sensing resolution can also be expected. With the fast development of material engineering, I believe that piezo-sensors based on the micro/nanowires with a high resolution will be soon achieved [66].

Conclusion of the chapter

This chapter is dedicated to the flexible piezogenerating devices based on MOCVD-grown GaN microwires. At the beginning, the piezogeneration potential of this type of wires is demonstrated with a round contact pad generator on a copper film. Then, a prototype piezogenerator with a crossing-contact design is proposed and fully characterized. It shows the possibility of being further adapted to make more efficient energy harvesters or force/pressure sensors. Then, one successfully improved piezogenerator is reported, with its electrical performances compared in detail with the prototype device. It shows a high sensitivity to external force, and responds to gentle finger tapping movements. After that, some further propositions to improve the prototype device as energy harvester have been made. Finally, an attempt to make a piezo-sensor with GaN microwires has been presented. Some discussions and propositions have been made in terms of future device realization and calibration.

Chapter 6

Conclusion and prospective

The aim of this PhD work is to fabricate compact piezogenerators based on GaN 1D nanostructures and to study them systemically in order to have a better understanding of their operational mechanism.

The well-mastered material growth techniques of MBE and MOCVD in C2N and CEA-INAC laboratories have laid the foundation for this research work. The previous PhD work of N. Jamond [25] has analyzed in detail the GaN nanowire PAMBE growth for mechanical energy conversion application and has experimentally demonstrated the piezogeneration potential of individual GaN nanowire by AFM measurements. A promising piezogenerator prototype has also been proposed in [63]. As for the MOCVD GaN microwires, their growth has been much studied in the laboratory CEA-INAC for many years. Some microwire-based force sensor prototypes have been demonstrated and the related simulations have been done in the PhD work of A. El Kacimi [88].

For the current PhD work, its original aims can be considered accomplished. Some further progresses have also been made in terms of device improvement and innovation. I'd like to sum up the following points as the main contributions of this thesis work to the field of piezoelectric nanowire energy harvesting:

 \blacktriangleright Firstly, a well-controllable mechanical setup has been built and validated to characterize nanowire-based piezogenerators with a specific design (nanowire vertical integration) - the vertical compression setup. For similar piezogenerators based on other types of nanowires, or even thin films, the as-proposed setup can be directly applied for electrical measurements. It can serve to excite different devices under the same conditions in order to compare different device conversion efficiency in a more rigorous way.

 \succ Secondly, different deformation modes have been distinguished in view of piezogenerator characterization. As has been demonstrated experimentally in chapter 4, the tapping mode deformation widely applied in the literature to

characterize piezogenerators is not suitable for frequency-dependency study.

➤ Thirdly, the Schottky diode design and the capacitive design of nanowire-based piezogenerators have been compared. The equivalent circuits for both designs have been proposed, discussed and further tested by new device characterizations. A better understanding of the device physics has been achieved. The proposed device working mechanism is applicable to other piezoelectric nanowire-based generators.

➤ In terms of flexible device fabrication, some processes have been proposed and tested to be feasible. For ultra-short PAMBE-grown nanowire array transfer, a delicate procedure is detailed at the end of chapter 4. For MOCVD micro-wires, the flexible device process is much simpler and guarantees a good robustness of the final device (chapter 5).

➤ An innovative crossing-contact device design, which enables an easy series connection of individual piezogenerators for increasing the output voltage, has been proposed for making either an energy harvester or a force/pressure sensor.

> Then, a more reasonable estimation of device electric performance has been done during the study. Under different device deformation conditions, instead of using the instantaneous peak values (as have been done in most of the works reported in literature), the average power output related values have been adopted here as the standard to present the device generation capacity. Besides, for each result reported, an emphasis has been made on clarifying its measurement conditions. (For many reported works in literature, measurement conditions are not clearly described.)

➤ Last but not least, this PhD work has demonstrated experimentally the good potential of using GaN nanowires/microwires to make compact energy harvesters or high resolution force/pressure sensors. For the MBE-grown nanowire-based piezogenerators, the reported average output power density is in the order of mW/cm³(best recorded value reaches 22.1 mW/cm³, chapter 4). For the MOCVD GaN microwire-based devices, although their output power density is lower (~ μ W/cm³), they respond to ambient vibrations as gentle as the finger tapping and deliver an energy in the order of pJ per tap (highest recorded values is 96.7 pJ per tapping). In addition, despite the different growth techniques, the explored devices can response quickly enough to follow the deformation. This is a remarkable advantage in making sensors with a large frequency span.

The following of this work

I'd like to divide the perspectives of this thesis into two parts. One part aims to further complete the presented study and to perfect the characterization system, while another part targets to improve device performance by new experimental exploration.

Part one

 \succ For the vertical compression setup, it would be useful to add an accelerometer to enrich the information about the shaker movement and the device deformation. Although the force sensor can help to link the device output with its strain rate, the correlation is not direct. The acceleration of the deformed surface may show a more direct output trend, hence it would be interesting to explore this parameter in the future studies.

For the different piezogenerators characterized in this work, the device voltage output is obtained either at 1 M Ω load or at 100 M Ω load. No impedance matching has been performed. To complete the electrical characterization, looking for the optimal load of the generator is a necessary step. It may deepen our insight about the device operation mechanism and help to improve the device modeling.

➢ Until present, most of the simulation works about nanowire-based piezogenerators have been done with multi-physics softwares, such as COMSOL [89]. Much less work has been done to develop the electrical model of this type of devices. However, it would be useful to have an elaborated electrical model to mimic the piezogenerating device behavior.

Part two

> In terms of piezogenerator improvement, the crossing-contact design device can be further explored by using nanowires with other characteristics. As mentioned in chapter 5, longer, denser or even selective-area-grown nanowires can be tried. Nanowires with different doping or heterostructures can also be tested.

➢ If we want to change the piezogenerator design, the lateral integration of nanowires can be tried. In order to achieve a better device electrical performance, a good nanowire aligning technique should be employed. Some techniques already exist, but further improvements are needed to align the wires while preserving the orientation of their polarity.

> In view of the self-powered piezo-sensors, it would be interesting to first try the device proposed in chapter 5, figure 5-34. If a better location distinction can be achieved in comparison with the prototype device, further improvement could be made in terms of the detection resolution and calibration.

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Appendix

Piezogenerator B based on a stack of multiple active layers

 \diamond Device fabrication



Figure A. (a) Schematic of the multi-layer generator design. (b) Optical image of the device after depositing the first layer and the second layer of the active membrane.

Figure A.a shows the side-view structure of the device B. For its fabrication, the same microwire wafer has been used as for the prototype device and the piezogenerator A. The device is made by sandwiching a thicker active piezoelectric layer in-between the Kapton films. This thicker active layer is obtained by stacking three 20 μ m-thick microwire-integrated membranes. A diluted 1 μ m-thick PDMS adhesion layer is used to glue together the individual layers. Special care has been taken to make sure that the polarity of all the piezoelectric layers (determined by the polarity of the integrated microwires) is aligned. The optical photos taken during the fabrication process, showing the staking of one and two layers of piezoelectric membranes on the bottom Kapton film is shown in figure A.b.

The final device has an active surface area of about 0.4 cm*0.8 cm (the effective three layer overlapping area). The active layer thickness is estimated to be 60 μ m. A matrix of 2*4 separated piezogenerators was defined using the crossed contacts geometry.



♦ Characterization of the individual piezogenerators at crossing positions

Figure B. Best recorded voltage output (black curves) and a representative trace for one deformation cycle of one generator from device B with 3 layers of piezoelectric membrane under 20 Hz tapping deformation (compression duration $t_c = 2.5$ ms). The force sensor readings are recorded in blue curves.

Figure B displays one of the highest voltage outputs obtained when one crossing-positioned generator in device B is tapped at 20 Hz (measured with a 1 M Ω impedance oscilloscope). We can see that under a maximum applied tapping force of 5.4 N, one separated generator in device B gives a peak-to-peak voltage output of 136 mV (from 112 mV to -24 mV). However, compared with the prototype device and the generator A who are measured under a similar but less favorable condition (results shown in figure 5-32), the device B is much less sensitive to the external deformation. Though there are piezoelectric microwires integrated in each of the overlapped membranes, the softness of the overall thick membrane hinders the transfer of the mechanical deformation to the piezoelectric microwires. Besides, the soft PDMS environment may slow down the microwire deformation changing rate: the smaller voltage output peak of the device at releasing with respect to the peak at the compression is a direct demonstration of this slow-down effect.

♦ Tests of the device B under ambient deformation conditions

The voltage output of the device B during 10 seconds of finger tapping is illustrated in figure C (with a 1 M Ω load). One 1 cm² glass layer is posed on top of the device to guarantee a stable and repeatable deformation during the measurement. The average voltage peak value is 110 mV. The average power output of the device can be further calculated as 0.11 nW. For each tapping gesture, an energy delivery of 35.8 pJ can be estimated. As for its average output power density, the value calculated with and

without the consideration of Kapton films are respectively 18.1 nW/cm³ and 61.1 nW/cm^{3} .



Figure C. (a) The transient voltage output of the piezogenerator B for 10 seconds of finger tapping with a glass layer as inter-medium. (b) Voltage output trace of seven cycles of deformation.

I'd like to note at last that, although the device B suffers from a lower sensitivity to external deformation than the device A due to its increased soft membrane thickness, it can still respond to gentle finger tapping. This positive reaction should be attributed to its small device surface (estimated to be around 0.3 cm²) which may induce a relatively higher level of deformation (higher pressure received).

Résumé en français

La collecte d'énergie ambiante (également appelée récupération d'énergie) a beaucoup attiré l'attention ces dernières années. Contrairement aux batteries traditionnelles, qui doivent être rechargées ou remplacées après un certain temps d'utilisation, les récupérateurs d'énergie ambiante peuvent fournir de l'énergie tant que la source d'alimentation est présente. Grâce à la réduction de la consommation d'énergie des appareils électroniques (aussi bas que μ J ou μ W/cm2), en choisissant une méthode de transduction adaptée, il est maintenant possible de convertir l'énergie ambiante en énergie électrique afin de rendre ces appareils indépendants énergétiquement.

L'énergie ambiante existe en abondance sous de nombreuses formes, telles que l'énergie solaire, l'énergie thermique, le rayonnement électromagnétique à haute fréquence (RF) et l'énergie mécanique. L'énergie cinétique (par exemple, les vibrations mécaniques) est une forme d'énergie ambiante omniprésente, qui constitue une source d'énergie idéale pour alimenter des nœuds de capteurs localisés ou d'autres dispositifs nomades et portables. Étant donné que les vibrations environnementales ou les mouvements humains sont généralement des signaux aléatoires caractérisés par des basses fréquences et une large bande passante, la plupart des récupérateurs d'énergie cinétique classiques basés sur des systèmes microélectromécaniques (MEMS) se heurtent aux difficultés de l'application des basses fréquences. En outre, la miniaturisation des appareils est également compliquée et difficile.

Dans ce contexte, l'utilisation de structures 1D piézoélectriques de faible dimension (nanofils) est devenue une alternative prometteuse pour la récupération de l'énergie cinétique. Grâce à leur petite taille et à leur grande flexibilité mécanique [18], des générateur plus compactes et plus légèrs devraient être réalisées. De plus, il a été rapporté que les nanostructures d'un matériau donné partagent un coefficient piézoélectrique plus élevé par rapport à leur équivalent en bulk [19]. En 2006, la première démonstration expérimentale de la génération piézoélectrique des nanofils de ZnO unique a été rapportée. Depuis, le concept de «nanogénérateur» a été largement accepté. Au cours de la dernière décennie, divers générateurs piézo-électriques ont été fabriqués en intégrant différents types de nanofils. Néanmoins, une évaluation systématique des dispositifs fabriqués n'est pas une tâche facile car les résultats de la littérature ne sont pas présentés de manière normative commune, mais varient fortement en termes de conditions expérimentales et d'indicateurs de performance.

Cette thèse porte sur la fabrication et la caractérisation de piézogénérateurs à base de nanofils de GaN. Comparés à d'autres nanofils piézoélectriques largement explorés, tels que les nanofils de ZnO, les nanofils de GaN ont montré des propriétés piézoélectriques intéressantes, qui ont été prédites théoriquement [20] et démontrées expérimentalement [21]. Les nanostructures de GaN utilisées sont synthétisées par épitaxie par jet moléculaire assistée par plasma (EJM) ou par épitaxie en phase vapeur aux organométalliques(EPVOM). Les deux techniques peuvent offrir une bonne qualité cristalline du matériau, ce qui est important pour l'application de la génération piézoélectrique. Selon la morphologie de ces deux types de nanofils de GaN, des générateurs piézo-électriques rigides et flexibles ont été fabriqués. Des mesures systématiques ont ensuite été effectuées pour évaluer les performances électriques des générateurs fabriqués dans des différentes conditions de déformation externe. Des efforts ont été déployés pour tester les dispositifs dans une large bande de fréquences allant de 1 Hz à 3 kHz. L'analyse des résultats expérimentaux obtenus a permis de comprendre parfaitement le mécanisme de fonctionnement du dispositif. Différentes conceptions de dispositifs ont été élaborées et comparées, et les circuits électriques correspondants correspondants ont également été proposés.

La thèse comprend 6 chapitres. Dans le premier chapitre, une brève introduction de divers nanofils piézoélectriques et de leurs méthodes de croissance correspondantes est présentée. Ensuite, les nanofils de GaN et leurs propriétés piézoélectriques sont discutés en détail. Certains résultats de piézégénération des nanofils uniques sont repris des études précédentes du groupe. Comme montré dans la figure 1, le réseau de nanofils de GaN réagit bien au balayage de la pointe de l'AFM et fournit des signaux électriques distincts. Ces résultats expérimentaux confirment le potentiel des nanofils de GaN à être utilisés comme matériau de conversion d'énergie mécanique. À la fin du chapitre, certains générateurs piézoélectriques à la pointe de la technologie basés sur des nanofils sont répertoriés et comparés.



Figure 1. Mesures AFM de la tension de sortie d'un réseau de nanofils de GaN de 20 μm * 10 μm de surface. (a) Présentation 3D des sorties de tension d'un réseau de nanofils dopé-n sous une force normale de 98 nN appliquées par la balayage de la pointe de l'AFM. (b) Présentation 3D des sorties de tension d'un réseau de nanofils dopé-p sous une force normale de 149 nN appliquées par la pointe de l'AFM [25]



Figure 2. Schéma de la configuration de compression verticale utilisée pour caractériser les dispositifs à base de nanofils.

Le chapitre 2 décrit en détail les trois configurations mécaniques utilisées pour caractériser les générateurs piézoélectriques fabriqués, à savoir l'indentateur, la configuration de flexion à trois roues et la configuration de compression verticale. Parmi ceux-ci, la configuration de la compression verticale est récemment proposée au cours de cette thèse afin d'avoir un meilleur contrôle des conditions de mesure des dispositifs. La figure 2 donne une présentation schématique de cette configuration. En utilisant une platine porte-échantillon mobile et un capteur de force intégré sur le secoueur vibratoire, cette configuration peut assurer un contrôle précis de la

déformation ajoutée au dispositif caractérisé. Par conséquent, une bonne corrélation entre les performances électriques du dispositif et ses conditions de déformation peut être établie.

Les chapitres 3 et 4 se concentrent sur les dispositifs à base de nanofils GaN sythétisés par EJM technique. Le chapitre 3 présente les générateurs piézoélectriques à matrice rigide. Le processus de fabrication du dispositif se trouve à la figure 3. Une image optique du dispositif final se trouve dans le figure 3.c. Ce type de dispositif a été caractérisé par les trois configurations présentées. Bien qu'ils puissent donner des signaux électriques distincts, les performances doivent encore être améliorées.



Figure 3. Schéma du processus de fabrication du piézogénérateur à matrice rigide.

Par conséquent, au chapitre 4, les générateurs piézo-électriques à matrice molle sont étudiés de manière plus approfondie en utilisant la configuration de compression verticale adaptée. La fabrication de ce type de dispositifs partage le même flux de processus que celui illustré à la figure 3, mais avec le remplacement de l'encapsulation rigide HSQ par l'enrobage de polymère souple PDMS. De cette manière, les dispositifs deviennent plus sensibles à la force externe et plus robustes aux chocs méchanique. En exécutant différentes déformations, le mécanisme de fonctionnement du dispositif a été bien compris. La figure 4 présente la meilleure tension générée lorsque le dispositif est soumis au compression de coute durée. La densité de puissance maximale et efficace calculée à partir de ces mesures atteint respectivement 0,43W/cm³ et 22mW/cm³, établissant les nouvelles valeurs de l'état de l'art. De plus, les performances de dispositif analysé ont été explorées sous déformation en mode continu. Comme le montre la figure 5, sous 2kHz de vibrations

continues, la tension générée atteint des centaines de mV. C'est la première démonstration de la piezogénération d'un dispositif à base de nanofils sous deformation continue.



Figure 4. Meilleure performance enregistrée du générateur piézo-électrique à matrice molle sous une déformation coute durée à 300 Hz. La tension générée est tracé en courbe rouge, atteint une valeur crête à crête de 1,216 V.



Figure 5. Meilleure tension enregistrée du générateur piézoélectrique à matrice molle sous une déformation continue à 2 kHz. La tension alternative tracée en rouge atteint une valeur crête à crête de 260 mV.

Ensuite, plusieurs types de générateurs piézoélectriques conçus de manière capacitive ont été fabriqués, testés expérimentalement et comparés aux dispositifs de conception Schottky classiques. Les circuits équivalents des deux types de dispositifs ont été proposés, comme le montre la figure 6. À la fin de ce chapitre, quelques tentatives pour rendre les dispositifs souple ont également été présentées.



Figure 6. Schéma et circuit équivalent du générateur piézoélectrique à diode Schottky (a) et de manière capacitive (b). R_{NWS} représente la résistance interne de la source d'énergie, C_s la capacité du condensateur équivalent en série avec le générateur.



Figure 7. (a) 5 * 5 matrice de générateurs sur une surface 2D. Une compression homogène est ajoutée sur toute la surface du dispositf en utilisant un bloc de verre. (b) La tension générée par ce dispositif à 50 Hz coute-durée compression. La maximum force appliquée est de 2,8 N, ce qui correspond à une pression maximale de 28 kPa.

Le chapitre 5 présente les études sur les dispositifs à base de microfils de GaN sythétisés par EPVOM. Dans ce cas, les dispositifs flexibles sont fabriqués à l'aide d'une encapsulation des microfils par du PDMS et d'un pelage de membrane active.

La propriété piézoelectrique de tels dispositifs a été d'abord démontrée. Ensuite, un dispositif prototype basé sur la conception de croisement des ligne des contact a été proposé (figure 7.a). Avec une matrice (5 * 5) de piezogénérateur sur une surface 2D, ce prototype peut être utilisé comme récupérateur d'énergie ou comme une capteur de force. La figure 7.b donne une trace de génération de tension lorsque tout le dispositif est connecté et déformé de manière homogène par un lame verre. Comme on peut le constater, le dispositif génère des centaines de mV sous une compression douce, ce qui montre sa bonne capacité à réagir rapidement à la déformation externe. Des discussions sur l'utilisation de ce dispositif en tant que capteur de force ou de pression ont été présentées à la fin du chapitre.

Enfin, une conclusion générale a été tirée au chapitre 6.

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