

Study and design of MEMS microbalances for bioaerosol detection in indoor environments

Uğur Soysal

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by

Uğur Soysal

Doctoral school: Science, Engineering and Environment

Study and design of MEMS microbalances for aerosol and bioaerosol detection in indoor environments

This thesis was conducted between Université Paris-Est Creteil (UPEC, France), École Supérieure d'Ingénieurs en Électrotechnique et Électronique (ESIEE, France) and Centre Scientifique et Technique du Bâtiment (CSTB, France) and defended on **12 February 2019** in front of the thesis committee composed of:

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Nomenclature

S-Distributed mass sensitivity Δf – Frequency shift Δm – Added mass f_o - Resonance frequency Δm – Added mass m_{min} – Minimum detectable mass E_p - Stored energy in the resonator in each cycle μ_{pz} - Elastic constant ρ_{pz} - Density of the piezoelectric material A_{pz} - Piezoelectrically active surface area ρ_d - Density of the added mass ho_{pz} - Density of the piezoelectric material l_d - Thickness of the added mass l_{pz} - Thickness of piezoelectric material m_{eff} – Effective mass of oscillating material k_{eff} - Effective stiffness/spring constant $\Delta f_{3dB} - Q$ factor from 3dB m_{min} - Minimum detectable mass Q – Quality factor x_v – Vibration amplitude TCF - Temperature Coefficient of Frequency ΔT – Temperature change St_{50} – Stokes number

- d_{ae} Aerodynamic diameter
- Re Reynolds number
- ρ_p Density of particle
- ρ Density of air
- V_0 Average air velocity in the nozzle
- *W* Nozzle diameter
- μ Air viscosity
- n Number of nozzles
- C Cunningham slip correction
- P_2 Static pressure at the impaction plate
- P_1 Static pressure at the impactor stage
- S_d Distance between the plate and the nozzle
- T Nozzle throat
- D_c Nozzle cluster diameter
- Q_p Flow rate
- T_t Tapered inlet throat
- N_{in} APS particle concentration measurement without impactor
- N_{out} APS particle concentration measurement with impactor
- GCE Global collection efficiency
- MAD Mean median aerodynamic diameter
- d_d Diameter of the generated droplet
- d_{ve} Volume equivalent diameter
- C_v Volumetric concentration of the sodium fluorescein
- I_v Volumetric concentration of the nonvolatile impurities in the solution
- d_{me} Mass equivalent diameter
- Cu_{me} Cunningham correction factor for the d_{me}

- Cu_{ae} Cunningham correction factor for the d_{ae}
- ρ_r Solid residues density
- ρ_o Reference density
- γ Aerodynamic form factor
- φ Porosity term
- ρ_r Sodium fluorescein density
- $\sigma_{\rm g}$ Geometric standard deviation
- $\#_p$ Total number of VOAG generated particles
- Δt APS sampling time
- E_{Pi} Initial potential energy
- E_{Ki} Initial kinetic energy
- E_L Energy loss due to the collision
- E_R Rebound energy
- E_{Kf} Final kinetic energy
- E_{pf} Final potential energy
- V_p Applied polarization DC voltage
- V_{in} Applied alternating voltage
- ω Angular frequency
- $W_{electrostatic}$ Electrostatic energy
- U Applied voltage between the two electrodes
- F-Electrostatic force
- \mathcal{E}_0 Permittivity of space
- \mathcal{E}_r Permittivity of the gap
- W_e Width of the electrode
- h Thickness of the electrode
- d_o Gap distance between the resonator and electrode

- x Small displacement between the resonator and the air-gap
- i_m Motional current
- C Capacitance between the resonator and the electrode
- η Electrostatic transduction coefficient
- R_m Motional resistance
- L_m Motional inductance
- C_m Motional capacitance
- f_n Resonance frequency nth mode
- γ Amount of damping
- $\sigma_{max \ stress}$ Maximum stress
- M_y Bending moment of neutral axis,
- L Distance from the neutral axis
- I Moment of inertia
- b Width of the silicon beam
- R_Q Resistance to flow rate
- $P_{pressure} Maximum pressure$
- ρ_o Density of air-resistance
- Sb Surface area of the beam
- L Length of the resonator
- *G* Shear modulus
- *E* Young's modulus
- ν Poisson's ratio
- ρ Density of silicon
- A_e Effective area of the resonator
- Z Impedance
- R-Resistivity

X-Reactance

 Δf_{noise} – Frequency variation

 $d\mathcal{O}_{noise}$ - Phase variation

 M_m – Total mass of VOAG-generated particles

 f_{nb_d} - Mean resonance frequency before an impaction of a device

 f_{na_d} - Mean resonance frequency after an impaction of a device

 $\Delta f_{n,d}$ – Mean resonance frequency shift (before and after an impaction of a device)

 $\Delta m_n d$ – Corresponding added mass

 $\Delta f_{nbna d}$ – Mean resonance frequency difference before the next impaction after the previous impaction

ABSTRACT

Microfabrication methods are an emerging technology which enables to build micro scale airborne particle mass concentration measurement systems. A personal airborne particle monitoring system can be achieved by combining an appropriate sampling method with inertial microelectromechanical systems (MEMS) mass sensors. While aerosol sampling methods can take airborne particles from ambient air and transport to a detector in the most efficient way, MEMS provide the detection and estimation of the mass based on a shift in the resonance frequency of oscillating sensors.

In this context, an extensive literature review is proposed in order to examine the mass concentration measurement methods from past to present. The methodological tendencies for advanced real-time aerosol mass concentration measurement are evaluated. Finally, bulk-mode silicon-based MEMS mass sensor is chosen to be coupled with an appropriate aerosol sampler.

Following that the miniaturization possibilities of aerosol sampling methods are discussed and inertial impactor is chosen as a suitable aerosol sampling method. Then, the impactor is designed, fabricated, and characterized based on the classical impaction theory. The latter, the deposition characteristics of monodisperse aerosol (fluorescent) and bioaerosols (Aspergillus niger, Staphylococcus epidermidis, Pseudomonas fluorescens) are explored by inertial impaction on silicon and nanostructured silicon (i.e. black silicon). The empirical results show that the size of airborne particles plays a key role to determine the deposition characteristics of the impaction by the mechanism of rebound and reentrainment (i.e. bounce effect) of the particles.

In the context of developing an inertial mass sensor, sub-µm air gap MEMS mass sensors have been successfully fabricated based on the thick oxide as a mask layer method. This method enables to fabricate high-aspect-ratio air-gap MEMS resonators. Then, the devices are electrically characterized and the mass resolution is investigated. As a result, high-aspect-ratio MEMS sensors are operated in two different bulk modes (Lamé and extensional modes) and the mass resolution of the sensors is found to be as sub-ng.

Finally, the fabricated MEMS mass sensors are integrated into the developed impactor and monodisperse fluorescent particles are successively impacted on the sensors. The shift in the resonance frequency of MEMS mass sensors are evaluated based on Sauerbrey's principle. Ultimately, MEMS mass sensors have achieved to detect and perform mass measurements of the impacted fluorescent particles with a promising precision. Although more impactions are needed to calibrate the sensors, the theoretical mass sensitivity of the device is matched with the experimental mass sensitivity obtained from successive impactions. Therefore, the developed airborne particle detection system paves the way for real-time detection and mass measurements of aerosol and bioaerosols.

RÈSUMÈ

Grâce au développement des techniques de micro-fabrication, il devient désormais possible de réaliser des systèmes miniatures de mesure de la concentration en particules polluantes dans l'air. Ainsi, l'utilisation conjointe d'un système d'échantillonnage adéquat et d'un microsystème électromécanique (MEMS), comme capteur inertiel de masse, permet de former un dispositif individuel de contrôle de pollution particulaire. La méthode d'échantillonnage permet de prélever puis d'emmener les aérosols de l'air ambiant au capteur, alors que le MEMS permet de détecter puis d'estimer la masse déposée à partir d'un décalage de sa fréquence de résonance.

Dans ce contexte, une revue bibliographique approfondie a été menée sur les méthodes de mesure de masse traditionnelles et actuelles. Notamment, les avancées concernant les différentes méthodes émergeantes permettant une analyse en temps réel ont été examinées. Les MEMS en silicium à déformation de volume ont alors été choisi comme capteur de masse, couplé à système d'échantillonnage approprié.

La possibilité de miniaturiser les méthodes d'échantillonnage a ensuite été étudiée et l'impacteur inertiel a été choisi comme la plus appropriée des méthodes. En accord avec la théorie classique d'impaction, l'impacteur a été dimensionné et conçu puis fabriqué et caractérisé. Des dépôts d'aérosols monodispersés (fluorescéine) et de bioaérosols (Aspergillus niger, Staphylococcus epidermidis, Pseudomonas fluorescens) ont été réalisés, à l'aide du micro-impacteur, sur des surfaces de silicium poli et sur des surfaces de silicium nanostructuré (Silicium noir) et leurs propriétés ont été étudiées. Les résultats expérimentaux ont mis en évidence que la taille des particules joue un rôle déterminant dans les caractéristiques de dépôt, du fait des mécanismes de rebond et de réentrainement.

Afin de développer un détecteur inertiel de masse, des capteurs MEMS, ont été fabriqués avec succès, par microfabrication en utilisant un oxyde épais pour réduire la taille des gaps électrostatique à des dimensions sub-microniques. Cette méthode permet alors de réaliser des résonateurs MEMS à gap d'air avec de très fort rapport d'aspect. Les dispositifs réalisés ont ensuite été caractérisés électriquement et la résolution en mesure de masse a été étudiée. Ces capteurs MEMS à fort rapport d'aspect ont été actionnés suivant deux modes de déformation de volume (Lamé et mode extensionnel), et une résolution en masse inférieure au nanogramme a pu être démontrée.

Finalement, les capteurs MEMS ont été intégrés au microimpacteur et des particules monodispersées de fluorescéine ont été successivement impactées sur les capteurs. Le décalage de la fréquence de résonance des capteurs MEMS a été mesurée et la masse déposée a été évaluée à l'aide du principe de Sauerbrey. Les capteurs MEMS ont permis de détecter et de mesurer la masse de particules de fluorescéine avec une précision très prometteuse. Bien que de nouvelles impactions soient nécessaires pour calibrer les capteurs, la sensibilité en masse théorique est en accord avec celle mesurée pour les différentes impactions. Le système de détection de particules, développé dans le cadre de cette thèse, ouvre donc la voie à la détection et la mesure de masse d'aérosols et de bioaérosols en temps réel.

INTRODUCTION

An aerosol is an assembly of liquid or solid suspended particles in a gaseous ambient such as air and can be referred as an airborne particle. According to the definition of the World Health Organization (WHO), particulate matter (PM) is referred as a complex mixture of solid and liquid particles of organic and inorganic contents suspended in the air. The need to study aerosols has mostly arisen for the health and environment due to their significant role in both areas. These airborne particles can be found in a large diversity of shape, size, chemical composition, and origin.

Airborne particles can also be biological in origins such as fungal spores or fragments, pollen, virus, bacteria or their derivatives like allergens, endotoxin, mycotoxins, etc., and such referred as bioaerosols. Many of these biological airborne particles can be transmitted from one place to another and can remain viable during this transmission. Indeed, these particles can also be found nonviable in the environment, which means that these are either dead or unable to reproduce, unlike viable ones. Bioaerosols can be mainly found with the following features; (*i*) Single spores, pollen grains, bacterial cells or viruses. (*ii*) Aggregates of several spores or cells or other biological material. (*iii*) Fragments of spores and cells. (*iv*) Biological particle carried by other non-biological particles (Baron & Willeke, 1993).

In the context of human exposure and health effects of the aerosols, the toxicity of airborne particles depends on their size and their composition such as bulk chemical or trace element content, acid and sulfate content, etc. (Harrison & Yin, 2000). Indeed, the particle size is of major importance. Particles which have diameters greater than 2.5 μ m and less than 2.5 μ m are usually referred as "coarse particles" and "fine particles" respectively. Thus, particles smaller than 100 nm are referred as ''ultrafine particles'' or ''nanoparticles''. The fine and ultrafine particles can penetrate deeper in the human respiratory tract, and particle toxicity increases with high surface to volume ratio (see **Figure 1**). It has been documented that the ultrafine particles trigger alveolar inflammation, and may lead to cardiovascular diseases and deaths (Seaton, MacNee, Donaldson, & Godden, 1995). Long-term exposures to PM_{2.5} (Particle matter with an aerodynamic equivalent diameter below 2.5 μ m, which can be defined as the diameter of a sphere with the standard density of 1000kg/m³ that has the same terminal velocity when it settles under gravity as the particle of interest) were correlated with many types of cancers in the upper digestive tract, accessory digestive organs, lung in males and breast in females (Wong et al., 2016). In contrast, short-term exposures to PM_{2.5} induce DNA hypo methylation which leads to activate inflammatory, vascular



Figure 1 – An inhalation experiment with baboons' respiratory tract in vivo. Aerosol depositions (%) for the extrathoracic (ET) and thoracic (TH) regions are indicated. The fine particles effectively penetrated to the lungs (TH region) as opposed to the coarse particles, which effectively accumulated within the head airways (ET region) (Albuquerque-Silva et al., 2014).

responses, and increase blood pressure (Bellavia et al., 2013). According to WHO ("WHO | Air pollution levels rising in many of the world's poorest cities," 2016), the critical limit for yearlong and daylong exposure to $PM_{2.5}$ has been estimated at 10 µg/m³ and 25 µg/m³ respectively. Likewise, for PM_{10} , the critical limits were at 20 µg/m³ and 50 µg/m³ respectively.

Exposure to airborne biological particles such as pollen, viruses, bacteria and fungal spores has been one of the main concerns due to their adverse health effects on human being. The impact of bioaerosols on human health is influenced by their nature, their immunogenicity, their mass concentration, their size, and thereby their penetration in the respiratory tract (Lecours, Duchaine, Thibaudon, & Marsolais, 2017). Nowadays, clear evidences for bioaerosols exposure-related health issues have been widely recognized and the exposures have been associated with contagious infectious diseases, acute toxic effects, allergies, and cancer (Douwes, Thorne, Pearce, & Heederik, 2003) (Fiegel, Clarke, & Edwards, 2006) (Bush & Portnoy, 2001) (Lindsley et al., 2010). Infectious diseases linked to bioaerosols are essentially caused by viruses (e.g. influenza, measles), bacteria (e.g. tuberculosis, Legionnaire's disease) or fungal spores (e.g. aspergillosis, blastomycosis) (Jonsson et al., 2014). Non-infectious agents are usually associated with toxic or hypersensitivity conditions and lead to asthma, chronic bronchitis, hypersensitivity pneumonitis, and organic dust toxic syndrome (Lecours et al., 2017). Although it is

believed and referred as to the hygiene hypothesis that the exposures of infectious agents during childhood evaluate the immune system and ultimately reduce the risks of consequences (Okada, Kuhn, Feillet, & Bach, 2010), all these airborne particles are not beneficial and this hypothesis is still yet to be clarified. Ultimately, lack of quantitative bioaerosols exposure assessment methods leads difficulties to define exposure limits.

Usually, the exposure guideline depends on the mass concentration, particle aerodynamic diameter, and exposure time. The mass concentration measurement is usually carried out by offline or real-time mass concentration measurement tools such as standard gravimetric measurement, inertial impactors or Tapered Element Oscillating Microbalance (TEOM). Among these tools, for example, inertial impactors can classify the particles by their aerodynamic diameter. Finally, the exposure time can be determined by in-vivo studies. The latter, the dose of related health effects can be defined. However, prerequisite for reliable airborne particles mass concentration and size measurements are the efficient sampling and accurate detection of airborne agents. The sampling can be defined as an ability of extraction of airborne particles from ambient air and transport them to a detector in the most efficient way. The detection may be defined as a system that is capable of perceiving a specific airborne particle from a surrounding environment and provides a useful signal such as optical, electrical, and electrochemical. Then, the signal can ultimately be used to deduce the physical or chemical properties of the detected particles.

Aerosol sampling consists of several fundamental methods such as filtration, inertial impaction, thermal precipitation, and electrostatic precipitation. Each of those methods have been adapted to an appropriate detection technique using optics or spectroscopy (e.g. Fluorescent, Raman) (Jonsson, Olofsson, & Tjärnhage, 2014), impedance (M. Carminati et al., 2014), radioactivity (Husar, 1974) or electromechanical mass measurements (Paprotny, Doering, Solomon, White, & Gundel, 2013). The latter can be applied to determine the mass concentration of PM in ambient air. Besides, collection of a reliable and representative amount of bioaerosols has been realized by traditional aerosol sampling methods, including gravitational sedimentation, inertial impaction, centrifugation, electrostatic precipitation, and filtration. The latter, detection techniques such as polymerase chain reaction (PCR) (Pyankov et al., 2007), enzyme-linked immunosorbent assay (ELISA) (Speight, Hallis, Bennett, & Benbough, 1997), traditional colony counting (Han et al., 2018), optics or spectroscopy (e.g. Fluorescent, Raman) (Jonsson et al., 2014) have been used for qualitative and quantitative analysis of the collected bioaerosols. Most of the efforts have been recently given to real-time fluorescent-based relatively miniature optical systems, due to the intrinsic fluorescent of most of bioaerosols, either using microfluidic approaches (Choi, Kang, & Jung, 2015) or integrating it with a sampling method (Choi, Kang, Hong, Bae, & Jung, 2017). Although some of the proposed systems achieved real-time detection, none of them have demonstrated a

miniature, integrable (to integrated circuits, thus daily used electronic devices), low-cost and real-time bioaerosol concentration measurement system.

Today, measuring a mass can be actualized with (*i*) traditional balances (e.g. spring balance, beam balance etc.) and (*ii*) the change in the resonance frequency of an oscillating material (e.g. quartz, silicon etc.) in inertial mass sensors (e.g. QCM, TEOM, FBAR, SAW and MEMS). The latter was discovered by Sauerbrey in 1959 (Sauerbrey, 1959). As documented previously, three fundamental principles are required for any mass measurements: (*i*) the mass can be measured by placing it to a field, which is gravitational field for the traditional balances and inertial field for the inertial mass sensors, (*ii*) the mass sensitivity of any balances is proportional to the intensity of the field that acts on the mass, (*iii*) the measured mass in gravitational field or in time independent inertial field should be equal to the measured mass in time dependent-inertial field (Mecea, 2006). In recent years, the nano/microfabrication techniques have garnered considerable attention because they offer the possibility to realize inertial micro/nano mass sensors, and therefore enable to build chip-scale real-time aerosols mass concentration measurement systems.

As in microelectronics, the development of instrumentation for aerosol mass-concentration has followed Moore's law: over the past decade, devices are getting smaller and smaller. Unlike traditional cumbersome methods, Nano scale (devices that have nanoscale structures $<1\mu$ m) or Micro scale (devices ranging from 1 to 100 µm) Electromechanical Systems referred as NEMS/MEMS have revolutionized the capacities for measuring the mass down to a single airborne particle. NEMS/MEMS inertial mass sensors allow the realization of integrable, inexpensive, portable, and low power consumption sensors.

This manuscript consists of four chapters which are designated to build a reliable and accurate MEMS-based airborne particles (regardless of their origin) mass concentration measurement system. The goal of the proposed detection system is to sample aerosols and bioaerosols to a micro sensor in the most efficient way and then perform an accurate mass measurement of the detected airborne particles.

In **Chapter 1**, different types of mass measurement methods are presented. Particular attention is paid to the potential uses of systems of which airborne particles mass concentration measurement can be achieved. An extensive literature review is proposed in order to examine the mass concentration measurement methods from past, present and future. Ultimately, the methodological tendencies for advanced real-time aerosol mass concentration measurement are evaluated. Finally, a type of silicon-based MEMS mass sensor is chosen to be coupled with an appropriate aerosol sampler.

In Chapter 2, the miniaturization possibilities of aerosol sampling methods are discussed with pros and cons, which are followed by the decision of a suitable aerosol sampling method. Then, the sampler is designed, fabricated, and characterized. The latter, aerosol test particles and bioaerosols are generated, sampled, and characterized in terms of their physical deposition behaviour on two different

surfaces. This chapter does not only elaborate a relatively efficient sampler that is to be combined with a selected MEMS mass sensor, but also explores some similarities in the deposition behaviour of aerosol test particles and bioaerosols.

Chapter 3 is dedicated to the elaboration of the selected silicon-based MEMS mass sensor. The proposed MEMS sensors are designed, simulated, microfabricated, electrically characterized, and proof of concept mass measurements are exhibited. This chapter demonstrates the realization of a high-performance MEMS mass sensor which is fabricated based on a distinctive microfabrication technique to be integrated to the proposed sampler in order to perform real-time airborne particles mass concentration measurements in the near future.

In Chapter 4, the developed MEMS sensors are integrated to the developed sampler. Aerosol test particles with known size, mass, and origin are sampled on MEMS mass sensors, thus a reliable mass measurement is conducted. Although sensors could not be fully mass-calibrated yet, the mass estimation of aerosol test particles is highly promising. Therefore, the proposed detection system proves the capability of efficient sampling and accurate mass measurement of airborne particles.

Under the framework of developing a real-time MEMS-based aerosol and bioaerosol detection system, this thesis follows the work of Brice Berthelot (Berthelot, PhD thesis, Study and design of sensors dedicated to surveillance biological particulate indoor environments, University of Paris-Est, 2015) whose thesis is confidential until 2020. His work had mainly focused on adhesion properties of different fungi species by impaction on different surfaces, simulations of the mass sensitivity of different shape and size bulk-mode MEMS membranes, and chemical identification of different fungi groups by pyrolysis. One of the main analytical findings which highly concerning this work is the selective attachment and detachment of specific fungi on the resonator that is operating within a specific resonance frequency range (Berthelot, Algré, Moularat, Robine, & Gehin, 2015). Following that work, this thesis has aimed to develop a sampler and a MEMS resonator with a certain operational frequency range. Ultimately, this thesis contributes to the goal of specific aerosol and bioaerosol detection with the realization of MEMS integrated inertial impactor airborne particles mass measurement system.

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CHAPTER 1 - Aerosol mass concentration measurements: Recent advancements of real-time nano/micro systems

As excessive exposure to airborne particulate matter (PM) results in adverse health effects, the development of real-time airborne particles monitoring is highly relevant. The objective of this chapter is to broadly review the current state-of-the-art on aerosol mass-concentration measurement, and on realtime monitoring systems (Soysal et al., 2017). Widely used systems are bulky, time-consuming or expensive to maintain. Over the past decade, sensor developments have shown the following features: portable, inexpensive, and suitable for monitoring real-time measurements. PM monitoring systems can be easily accessed through the development of nano or micro scale systems. These sensors can be integrated into conventional electronic devices in order to demonstrate their capabilities to provide realtime and ultra-sensitive measurements. With respect to mass concentration measurements, we distinguish a generation of "first" and "second" systems based on their different sizes. We examine the main characteristics of PM systems as follows: type of instrument devices (either bulky or nano/microfabricated), sampling method, real-time monitoring measurement capability, sensitivity, and reliability of the new generation of sensors. Acoustic mass sensors are compared to nano and micro scale electromechanical sensors. While the miniature sensors still need to be matured and integrated into appropriate aerosols sampling methods, the physical constraints and the mass measurement capability of these sensors are investigated. Nano and micro sensors can be promising tools for aerosol mass concentration measurement systems, particularly in terms of sensitivity. A PM monitoring system can be achieved by combining an appropriate sampling method with nano or micro sensors. This review suggests different types of sensors that can be used as an appropriate option for airborne particles monitoring and suggests that fixed and reliable bulky systems are soon to be replaced by nano and micro scale sensors. Nevertheless, the latter systems should be further optimized in order to exhibit more accurate measurements.

1.1 First generation aerosol mass concentration measurement systems: Bulky structures

Table 1 shows the best-known aerosols mass measurement systems and their related studies. Whereas these systems provide sufficient sensitivity for environmental monitoring, they remain expensive, labor-intensive, time-consuming, and bulky. In this chapter, we refer to these types of methods as first generation mass measurement methods. At the present time, most of these methods are used for PM mass concentration measurements, PM classification, and composition analysis.

The first generation of mass measurement methods has been well-documented in the scientific literature. The methods have been classified in line with their ability to real-time monitoring mass measurement, an essential distinguishing feature for aerosols characterization (Watson et al., 1998) (Chow et al., 2002); (Wilson et al., 2002); (Amaral, de Carvalho, Costa, & Pinheiro, 2015).

The gravimetric method used for the mass measurement of PM₁₀ and PM_{2.5} has been described and validated as a reference method by the European Committee for Standardization (CEN). As shown in Table 1, this type of method is described in terms of flow rate and sensitivity. The measurement procedure consists of selecting particles by inertial separation at the inlet, followed by filtration and gravimetric analysis of collected particles on the filter. Despite this method is used as a standard method, it remains difficult to carry out accurate measurements because of a possible increase in particle-bound water and the loss of semi-volatile compounds during the filtering process. As a result, the measured mass can be over/underestimated as compared with the real mass deposited on the filter. In addition, this method requires a long time for sampling a sufficient amount of particles, and mass cannot be real-time monitored. However, the filtration method allows all of the particles below the given PM dimension to be collected. Another method, as referred to as the tapered element oscillating microbalance (TEOM), has been proposed and widely used internationally for PM₁₀ and PM_{2.5} mass measurements (Patashnick & Rupprecht, 1991); (Allen et al., 1997); (Charron, Harrison, Moorcroft, & Booker, 2004). The principle of this method relies on the determination of the oscillation frequency change when the particles are deposited onto the filter. To overcome the issues related to the condensation and evaporation of water, the temperature at the inlet is maintained at 50°C while operating. However, it has been shown that the latter temperature of the TEOM induces the loss of semi-volatile compounds of which amount may vary according to the seasons, and ultimately causes false mass measurements (Charron et al., 2004); (Allen et al., 1997);(K. Zhu, Zhang, & Lioy, 2007). Alternatively, systems such as TEOM-FDMS (filter dynamics measurement system) have been developed (Grover et al., 2005). It has been reported extensively that the TEOM-FDMS technique improved the measurement accuracy (Favez, Cachier, Sciare, & Le Moullec, 2007); (Schwab, Felton, Rattigan, & Demerjian, 2006). Whereas the latter method ensures real-time,

Table 1 – First generation aerosol mass concentration measurement systems: Bulky

Particulate mass measurement methods	Sampling method	Flow rate (L/min)	PM/Particle size separation	Real- time	Sensitivity	Ref.
Standard gravimetric measurement	Filtration	38.3	PM ₁₀ , PM _{2.5} /No	No	1 μ g/m ³ to 150 μ g/m ³ for PM ₁₀ , 120 μ g/m ³ for PM _{2.5} .	("CEN - European Committee for Standardization," 2014)(Rees, Robinson, Khlystov, Stanier, & Pandis, 2004)
Beta Gauge	Filtration	-	PM ₁₀ / No	Yes	$\sim 3 \ \mu g/m^3$	(Wedding & Weigand, 1993)
TEOM	Filtration	16.7	PM ₁₀ / No	Yes	$\sim 5 \ \mu g/m^3$	(Ruppecht, Meyer, & Patashnick, 1992)
Berner Low Pressure Impactor	Impaction	30	60 nm to 10 μm/Yes	No	-	(Wang & John, 1988)
QCM Cascade Impactor	Impaction	0.1	50 nm to 50 μm/Yes	Yes	50 to 100 µg/m ³	(Chuan, 1976)
Electrical Low Pressure Impactor	Impaction	9.73	16.7 nm to 10 μm /Yes	Yes	-	(Yli-Ojanperä, 2010)
DMA-APM	-	0.53	PM ₁ /Yes	Yes	$\sim 10 \ \mu g/m^3$	(Kihong Park, Kittelson, & McMurry, 2003)
Nephelometric	-	-	PM _{2.5} /No	Yes	13 μg/m ³	(Shendrikar & Steinmetz, 2003)

highly sensitive, and relatively fast measurements, the instrument remains bulky and expensive. Likewise, the beta gauge method has been used for real-time mass measurements. Its principle is based on a correlation between the intensity of the β radiation and the deposited mass of particles on a filter. Therefore, the relative change in the β –particle (electrons or positrons) intensity before and after the deposition is measured. This instrument comprises a radioactive emitter, which can be a limitation for practical use (Chueinta & Hopke, 2001). Despite this method can successfully determine the mass concentration of PM₁₀ (S. S. Park et al., 2001), the presence of natural or artificial radioactivity can modify the beta count, and leads to inaccurate mass concentrations (Sohirripa Spagnolo, 1987a).

Another method referred to as Berner low-pressure impactor is presented in Table 1. Such type of cascade impactor has been widely used for ultrafine particles size separation and post-collection analysis of the collected particles (Chow & Watson, 2007). Based on the principle of inertial impaction, a cascade impactor typically consists in a succession of nozzles and multi-stages of collection plates on which particles are deposited (Marple & Willeke, 1976);(Newton, Raabe, & Mokler, 1977). While sampling is operating, and whenever the particle's diameter is larger than the cut-off diameter of the stage, which is determined by the Stokes number, its inertia will be sufficient for the deposition on the plate. If not, the particle will follow the air stream until it is deposited onto one of the stages below. After the sampling time has elapsed, the plate is weighed manually, and the mass of collected particles is determined. This system is bulky and requires large vacuum pumps to maintain the appropriate air flow rate. Likewise, it involves long sampling time, and labor-intensive post-collection process to analyze the deposited particles. Unlike the filtration method, the impaction method does not allow for the collection of particles smaller than the defined cut-off diameters. It has also been documented that the inlet loss, the interstage loss, and the particle re-entrainment are main limiting factors while sampling (Marple & Willeke, 1976). As shown in Table 1, (Wang & John, 1988) reported that the Berner cascade impactors were more reliable in separating ultrafine particles by size rather than measuring the mass concentration of particles. Indeed, since mass measurements are carried out manually, the mass sensitivity is limited.

As reported by (Chuan, 1976), quartz crystal microbalance (QCM) sensors have been placed into each stage of the cascade impactor. A QCM sensor consists of a quartz crystal (piezoelectric material) which is sandwiched between two opposite metallic electrodes. The working principle of a QCM sensor is based on a relation between the natural vibration frequency of the quartz crystal, the mass of the crystal, and the electrodes. The total mass will change whenever the particle is collected on the crystal, due to a shift in the frequency (which is proportional to the added mass). The resulting impactor has shown likely higher ability to real-time sensitive mass measurements. This increase was attributed to the piezoelectric material which can produce a voltage when compressed across its faces. It should be noted that the material can also physically change its shape when an external electric field is applied. In a QCM cascade impactor, which uses the inertial impaction principle, poor adhesion properties of metallic electrodes can result in bounce or re-entrainment of the collected particles. However, the frequency shift is highly dependent on the location where particles are deposited, and non-uniform mass measurements might therefore occur (Baron & Willeke, 1993);(Daley & Lundgren, 1975). It has been stated that thinner electrodes lead to relatively more uniform mass measurement, but it decreases the mass sensitivity (L. Yang & Huang, 2015). Another type of system known as the electrical low-pressure impactor (ELPI) has been used to assess the particle size distribution and the concentration in real-time simultaneously (Keskinen, Pietarinen, & Lehtimäki, 1992). Unlike the cascade impactor, the particles are primarily charged and impacted onto electrically isolated collection plates. Once the induced current (generated by the charged particles) has been measured using an electrometer, the concentration and size distribution of the particles can be deduced in real-time. Nevertheless, the ELPI does not provide real-time mass concentration measurements because the effective density of the particles (which can be estimated through the particle mobility size and the aerodynamic size) should be priorly known. If known, a correlation between the measured current and particle mass concentration can be obtained (Giechaskiel et al., 2014). It should be mentioned that the effects of particle bounce and re-entrainment are one of the main encountered issues while sampling is operating. Alternatively, a virtual impactor has been designed in order to overcome the issues related to particle loss. Unlike the inertial impactor, the particles are separated in two different streamlines referred to as major and minor flows. While the large particles follow the minor flow to enter the collection probe instead of impacting on the collection plate, small particles follow the major flow (Marple & Chien, 1980). Despite the system cannot carry out mass measurements, it can separate the particles by size. Therefore, other instruments can be added for further analysis of collected particles (e.g. continuous particles monitoring (Jianwen, Kun, Zewen, & Yanwu, 2015).

Unlike the above-mentioned filter and impaction-based methods, the differential mobility analyzer-aerosol particle mass analyzer method (DMA-APM) can be used. The DMA has been developed using different working and sampling principles (McMurry, Wang, Park, & Ehara, 2002) in order to select particles of a given mobility size. Alternatively, the APM is used to classify particles according to their mass, and regardless of their shape or density (Kihong Park et al., 2003). The APM consists of two electrodes which are rotating at the same angular velocity. Once the equilibrium between the electrostatic and centrifugal force on the particle is maintained at a constant level, the particle passes through the electrodes (Ehara, Hagwood, & Coakley, 1996). The particles can, therefore, be classified regarding their charge-to-mass ratio. In contrast, the Couette centrifugal particle mass analyzer (CPMA) has been proposed to improve the AMP method. The CPMA uses rotating electrodes at different angular velocities to obtain a uniform mass distribution of the transmitted particles (Olfert & Collings, 2005). Both the CPMA and APM methods have significant advantages over the mass measurement methods using filters. Indeed, they can separate the particles by size and no artifacts such as volatilization of semi-volatile compounds or vapor absorption can be observed. Whereas these methods are relatively rapid and likely sensitive to PM₁ mass concentration, the CPMA and APM are considered as aerosol classifiers and are not reliable for measuring the mass concentration of particles.

Lastly, the nephelometer method can be mentioned. This system consists in providing a proportional relationship between the intensity of a scattered light and the mass of particles. The correlation depends on several variables such as the particle diameter and shape, and the real and imaginary parts of the refractive index (Watson et al., 1998). Complex algorithms have to be built in order to extract these parameters appropriately. In the case of high particles concentration, the complexity can be more severe because of multiple scattering. Unlike the Beta Gauge and the TEOM, the nephelometric method is not certified as an equivalent method by the CEN. It should also be emphasized that optical counters based on the principle of light scattering from the particles (Mie scattering) are miniature instruments that can size and count the particles in real-time. These types of instruments show wireless sensor networking capabilities that may be used to monitor dynamic PM movements in indoor environments (Hall et al., 2012).

Finally, the main methods gathered in **Table 1** suffer from the same pitfalls: they are bulky and expensive to maintain.

1.2 Second generation aerosol mass concentration measurement systems: Miniature structures

In recent years, the nano/microfabrication techniques have garnered considerable attention because they offer the possibility to build chip-scale real-time aerosols mass concentration measurement systems. Usually, a method for aerosol sampling is associated with a nano/micro sensor to assess the mass of particles. In this section, different types of miniature mass sensors are presented. Particular attention is paid to the potential uses of miniature systems of which aerosol mass concentration measurement can be achieved. An extensive literature survey is proposed in order to examine and compare the methods from past, present, and future. Ultimately, the methodological tendencies for advanced real-time aerosol mass-concentration measurement are evaluated.

Table 2 shows different types of miniature sensors associated with sampling methods such as

inertial impaction, thermal precipitation, and electrostatic precipitation. Unlike the methods are shown in **Table 1**, the size of the miniature devices has been dramatically scaled down, and such devices have demonstrated their ability to real-time sensitive mass concentration measurements. Thus, nano/microfabrication techniques enable batch and relatively simple manufacturing processes. **Table 2** shows, typical acoustic waves mass sensors such as the Surface Acoustic Wave (SAW), the Film Bulk Acoustic Resonator (FBAR), the QCM, and resonant mass sensors such as the NEMS/MEMS. All acoustic wave mass sensors are composed of a piezoelectric material which is used to generate the acoustic wave that can propagate either through or on the surface of the material. The changes in the velocity or the amplitude of the wave are of great interest to deduce the resonance frequency. In the case of NEMS/MEMS sensors, resonating nano/microstructures act like a mechanical damped harmonic oscillator, in which the resonance frequency can be further deduced by using the Hooke's law (**Eq. 4**). The NEMS/MEMS resonators can be excited at frequencies corresponding to the induction of acoustic wave propagation. It results in the deformation of the resonator in different ways such as bending, twisting, or expanding. In all cases, the deformations of the typical acoustic wave resonators are negligible (Campanella, 2010).

The mass measurement principle used with miniature sensors is based on similar approaches. The detection mechanism depends on the resonance frequency shift upon the mass load, and the shift can be correlated with the added mass by the Sauerbrey equation (Sauerbrey, 1959). Though this latter equation was derived for the QCM to deduce the oscillating frequency of a piezoelectric material, it can also be applied for the SAW (Thomas, Cole, Villa-López, & Gardner, 2016). The distributed mass sensitivity ($S = \frac{\Delta f}{\Delta m}$) of these types of miniature sensors can be calculated as follows:

$$\frac{\Delta f}{\Delta m} = -\frac{2f_o^2}{\sqrt{\mu\rho}}\frac{1}{A} \tag{1}$$

Where Δf and Δm are the frequency shift and mass change, respectively, f_o is the resonance frequency, μ and ρ are the elastic constant and the density of the piezoelectric material, respectively, and A is the piezoelectrically active surface area.

The sensitivity of an FBAR can be estimated with a form of the Sauerbrey equation as follows (Zhang & Kim, 2005); (Kim, 2010):

$$\frac{\Delta f}{\Delta m} = -\frac{f_o}{2m} \quad \text{with} \quad \frac{\Delta f}{f} \approx -\frac{\rho_d \Delta l_d}{\rho_p \Delta l_p} \tag{2}$$
Where ρ_d , ρ_p are density of the added mass and the piezoelectric material, respectively. l_d and l_p are thickness of the added mass and the piezoelectric material, respectively, while *m* is the mass of the piezoelectric material.

The sensitivity and the resonance frequency of a NEMS/MEMS resonant mass sensor can be defined as follows (Hajjam, Wilson, & Pourkamali, 2011):

$$\frac{\Delta f}{\Delta m} = -\frac{f_o}{2m_{eff}} \tag{3}$$

$$f = 1/2\pi\sqrt{k_{eff}/m_{eff}} \tag{4}$$

Where k_{eff} and m_{eff} are the effective stiffness/spring constant, and the effective mass of the resonator, respectively.

The minimum detectable mass (m_{min}) can be reduced by minimizing the frequency shift, which depends on the quality factor (Q-factor) of the sensor. Q-factor qualitatively determines the behavior of damped resonators and it can be defined by the following ratio: $\frac{f}{\Delta f_{3dB}}$, where f is divided by the peak width (the resonance width) at half maximum. For example, the minimum detectable mass for a NEMS/MEMS sensor can be shown as:

$$m_{min} = S^{-1} \frac{f}{2Q} \text{, thus } m_{min} = \frac{m_{eff}}{Q}$$
(5)

Where S is the distributed mass sensitivity and Q is the quality factor. It should be noted that the effective mass of a resonator at a specific location is a function of the vibration amplitude of the structure at the same location (Amir Rahafrooz & Pourkamali, 2010). The stored energy in the resonator in each cycle can be defined as:

$$E_p = \frac{1}{2}k_{eff}x^2\tag{6}$$

Where x is the vibration amplitude at a specific location on the resonating body. When identical particles are simultaneously added onto a resonator at different positions, the vibration amplitude will be differently experienced by each particle. Thus, different effective masses for each particle can be perceived by the sensor. This phenomenon results in non-uniform mass measurements and therefore can lead to non-reliable aerosols mass concentration. Additionally, it should be noted that abovementioned **Eq. (1-5)** are actually derived for the case of uniform added mass and do not necessarily apply to randomly localized particles. Moreover, these derivations are only valid if m_{eff} and k_{eff} of an added

mass is considerably smaller than m_{eff} and k_{eff} of the resonator. As shown in **Table 2**, typical acoustic wave and sophisticated nano/micro mass sensors have been designed and have successfully been coupled with appropriate sampling methods. In **Table 3**, acoustic wave and NEMS/MEMS resonant mass sensors are compared in terms of the resonance frequency, mass sensitivity, and minimum detectable mass capability. Tremendous efforts have recently been made for the use of miniature sensors in the field of aerosol metrology. Nonetheless, as respect to miniature sensors, the poor sampling efficiency of the articles as well as the sensing properties of NEMS/MEMS remains a challenge that is yet to be explored. So far, recent advances should be addressed to the aerosol scientific community.

1.2.1 Acoustic wave mass sensors

In the case of SAW sensors, an oscillating electric field is applied between two interdigitated electrodes which are placed on a piezoelectric material. When the acoustic wave propagates over the surface of the material from one electrode towards another (input transducer to output transducer), the path of the propagated wave can be perturbed by different parameters such as deposited particles or humidity and temperature fluctuations. This modified velocity of the wave can be monitored in order to deduce the mass of particles. The ability of SAW for PM_{2.5} monitoring was studied theoretically (W. Hao et al., 2014). In their study, authors attributed the deposition of the particles, which occurred on the sensing surface area located between the electrodes, to the phenomenon of thermophoresis. This phenomenon is driven by the so-called thermophoretic force resulting from a thermal gradient (from high to low temperature) on the particles, which therefore move from one region to another in a surrounding gas. While submicron particles with large Knudsen numbers have enough momentum from gas molecules, larger particles with small Knudsen numbers are subjected to thermal or diffusion slip at the particle surface (Leong, 1984). In this case, it has been stated that the thermal conductivity and shape of the particle have a significant influence on the thermophoretic force (Zheng, 2002); (Li, Liang, & Ye, 2013); (Sagot, 2013). This leads to an insufficient collection efficiency of micron size particles.

A sophisticated work has been recently carried out to detect deposited particles in the range from $30 \ \mu m$ to $0.75 \ \mu m$ by a SAW sensor (Thomas et al., 2016) (see **Table 3**). In this work, the particle mass is measured and the penetration depth of the acoustic wave is used to separate particles by size. The acoustic wave is characterized by mechanical and electrical penetration depths which are inversely proportional to the resonant frequency. The sensitivity increases when the particle's diameter is smaller than the penetration depth. Changing the resonant frequency may, therefore, allow one to determine the size of the

Particulate mass measurement methods	Sampling method	Flow rate (L/min)	PM/Particle size separation	Real- time	Sensitivity/Mass concentration	Ref.
SAW	Thermophoresis	-	PM _{2.5} /No	Yes	0.17 ng (resolution)	(Hao, Liu, Liu, & He, 2014)
FBAR	Thermophoresis	0.006	PM _{2.5} /Yes	Yes	$2 \ \mu g/m^3$	(Paprotny et al., 2013)
QCM	-	0.1	>3.2µm and ~2.82µm /Yes	Yes	$208 \; \mu g/m^3$	(Liang, Shih, Chen, & Dai, 2010)
MEMS resonator (In-plane electrothermal actuation)	Impaction	0.017	~1µm to 140nm for the first stage and 140nm-40nm for the second stage /Yes	Yes 1	29.4ng/m ³ for the first stage and 6.2ng/m ³ for the second stage	(Maldonado- Garcia, Wilson, & Pourkamali, 2016)
Bulk mode MEMS resonator	Impaction	0.7	296nm/No	Yes	29.5 Hz/ng	(Zielinski, Kalberer, Jones, Prasad, & Seshia, 2016)
MEMS (CANTOR-2)	Electrostatic precipitation	0.3	Nanoparticles No	s/ Yes	5 µg/m ³	(H. S. Wasisto, Merzsch, Uhde, Waag, & Peiner, 2015)
NEMS (Vertical Silicon nanowire)	Electrostatic precipitation	0.68	Nanoparticles No	s/ No	7.1 MHz/ng	(H. S. Wasisto et al., 2013)
NEMS (Filter-fiber)	Impaction and Brownian diffusion	0.2	Nanoparticles No	s/ Yes	740 ag	(Schmid, Kurek, Adolphsen, & Boisen, 2013)

Table 2 - Second generation aerosol mass concentration measurement systems: Miniature.

Micro-fabricated mass measurement methods	Resonator dimensions (L×W×h)	Frequency	Sensitivity	Minimum detectable mass	Ref.
SAW	Active surface area $(L \times W)=1 \text{ cm}^2$	200 MHz	904 Hz/ng	3 pg	(Bowers, Chuan, & Duong, 1991)
SAW	1764 μm×720 μm	262 MHz	275 Hz/ng	210 pg	(Thomas et al., 2016)
FBAR	50 μm×70 μm×0.18 μm	2.6 GHz	10 kHz/ng	1 pg	(Campanella et al., 2008)
QCM	-	5 MHz	1 Hz/ng	3000 pg	(J. Leskinen, 2009)
CANTOR-1	2750 μm×100 μm×50 μm	43.9 kHz	10 Hz/ng	1 pg	(Hutomo Suryo Wasisto, Merzsch, Waag, et al., 2013a)
CANTOR-2	1000 μm×170 μm×19 μm	201.8-202.1 kHz	-	-	(Wasisto et al., 2015)
MEMS –Piezoelectric actuation	114.8 μm×76.5 μm×30μm	27-54 GHz	4 kHz/ng	0.25 pg	(Harrington, Abdolvand, Hajjam, Wilson, & Pourkamali, 2010)
MEMS-thermal actuation	17.6 μm×5 μm×15 μm	61 MHz	1.5MHz/ng	0.01 pg	(Hajjam et al., 2011)
MEMS–electrostatic actuation	Diameter=30 μm h= ~3 μm	132 MHz	131.5 kHz/ng	0.059 fg	(A. Cagliani et al., 2011)
NEMS–Vertical Silicon nanowire	Diameter= 0.65 μm h= 40 μm	0.325 MHz	7.1 MHz/ng	0.031 pg	(H. S. Wasisto et al., 2013)
NEMS-Filter-fiber	138 μm×3 μm×0.22 μm	-	-	740 ag	(Schmid et al., 2013)

Table 3 - Comparison of the acoustic wave and NEMS/MEMS resonant mass sensors: Representative studies.

detected particles. But then, it has been observed that the sensor suffered from non-uniform mass measurements as mentioned above for QCM sensors. Whereas a SAW sensor shows good sensitivity to detect airborne particles, it can be highly affected by the ambient conditions because of its excellent sensitivity for temperature, humidity, and pressure (Bo et al., 2016). SAW sensors can a priori be inappropriate for airborne particle mass measurements, but a reference SAW sensor is often used to compensate the effects of ambient conditions (Thomas et al., 2016). Nonetheless, the sensitivity of SAW sensors remains likely lower than with other methods such as those provided in Table 3.

Another microfabricated mass measurement system, referred as a mass sensitive FBAR sensor, was combined with an air-microfluidic circuit in order to separate the particles by size (Paprotny et al., 2013) (see Table 2). An FBAR consists of a sandwiched thin piezoelectric film between top and bottom metal electrodes. When an electric field is created, the acoustic wave propagates towards the top electrode-air interface, where it is reflected. In order to maximize the reflection, the structure is suspended (from the bottom contact side) over an air gap. As a result, the sensor can reach high frequency and becomes mass sensitive. In the same study, the particles smaller than 2.5 µm were separated by a microfabricated virtual impactor. Size-selected particles were then deposited onto the FBAR sensor using a thermal precipitation method. Although the sensor shows good sensitivity, the effects of temperature and humidity on the sensitivity were neglected.

It has been shown that an FBAR sensor can measure a localized mass (Campanella et al., 2008). However, the sensitivity depends on the location where the mass is deposited. The best sensitivity was obtained when the deposited mass was located at the center of the resonator because the vertical geometry of the FBAR induces greater longitudinal resonance mode at the center. Alternatively, the QCM-based miniature particle mass sensor is shown in **Table 2**. Despite the sensor has poor sensitivity and the QCM is not compatible with integrated circuits, this type of miniature system successfully combines a virtual impactor with the sensor, and ensures the separation of particles by size prior to mass measurement (Liang et al., 2010). The QCM mass sensor has been extensively used in many applications including PM monitoring. As shown in **Table 3**, QCM is characterized by poor mass sensitivity, non-uniform mass measurements, and limited frequency range, which makes unable to compete with the performance of a SAW or an FBAR sensor (Bowers & Chuan, 1989); (Campanella et al., 2006) (see **Table 3**).

The second generation mass measurement methods are promising options for practical applications in the field of airborne particle mass measurements. Based on the particle detection capacities of micro sensors, SAW and FBAR sensors are good candidates to achieve this task among existing systems. But, other miniature devices, known as the NEMS/MEMS devices, show a very good sensitivity and could also be relevant alternatives to typical acoustic wave mass sensors, in particular for

low mass measurements. In addition, NEMS/MEMS sensors are compatible with a variety of daily used electronic devices.

1.2.2 NEMS/MEMS resonant mass sensors

Miniaturized sensors are characterized by low production costs due to batch-operated manufacturing processes. They offer a large panel of applications because an array of the sensor array can be placed on a single silicon chip. Basically, a NEMS/MEMS mass sensor should be able to detect a specific substance from a surrounding environment as well as to provide mechanical displacement. The latter is ultimately transduced into an electrical signal. As shown from equations (3-6), high frequency, low weight, and high *Q*-factor (for a good limit of detection) resonators are needed to demonstrate ultrasensitive mass measurements. So far, various types of nano/micro resonator structures were investigated, among the widely studied systems using a flexural vibrating structure (cantilever). It consists of a beam of one-end rigidly fixed and the other end suspended and bendable, of which a mass can be loaded along its length (Davila et al., 2007). In order to obtain high resonance frequency and Q-factor, studies on micromechanical resonators have focused on different geometries, size and deformation modes of the resonators such as flexural modes of beam or beam-like structures (Bannon, Clark, & Nguyen, 2000), counter mode of disk-shaped resonators (Clark, Hsu, & Nguyen, 2000), bulk resonant mode of disk-shaped resonators (Z. Hao, Pourkamali, & Ayazi, 2004), and square shaped resonators (Khine & Palaniapan, 2009); (Lin, Yan, & Seshia, 2010).

Among MEMS devices, bulk mode MEMS resonant devices come to the forefront due to their superior Q-factor, resonance frequency, and tunable surface area (Z. Hao, Abdolvand, & Ayazi, 2006)(Lee, Zhu, & Seshia, 2008). In bulk mode, both shear and longitudinal elastic waves propagate in the bulk. When shear waves are predominant, face shear or lame mode can be observed. By contrast, extensional mode or breathing mode can be realized (H. Zhu & Lee, 2014); (Abdolvand, Bahreyni, Lee, & Nabki, 2016). The deformation mode reveals the location of nodes and antinodes of the resonator surface. Therefore, the modes exhibit the most sensitive parts of the sensor surface, which is critical for mass sensing applications.

So far, there are only a few studies which have reported the ability of NEMS/MEMS sensors to aerosols mass concentration measurement (see Table 2). However, with respect to aerosols detection, NEMS/MEMS can be divided into two categories: cantilever-based and bulk mode resonant based mass sensors.

Nano and micro-scaled devices are characterized by a high surface area to volume ratio;

therefore, surface effects dominate volume effects. These types of devices have the following features: immediate change of the angular momentum, low energy consumption, rigidness, rapid heating-andcooling properties, superior adhesive and electrostatic forces. Over the past two decades, new designs of sensors were proposed. The novelty was the ability to replace the thin plate by a microfabricated cantilever (Butt, 1996), and once loaded, the ability to measure its bending in gas medium (Berger et al., 1997) or in an aqueous medium (Raiteri, Nelles, Butt, Knoll, & Skladal, 1999). In another study, the microfabricated cantilever arrays were functionalized with anti-Aspergillus niger polyclonal antibodies to maintain a specific detection of Aspergillus niger fungal spores. The mass of spores and their growth which resulted in additional mass on the cantilevers were measured by the resonance frequency shift. The mass sensitivity of the sensor accounted for ~53 pg/Hz (Nugaeva et al., 2007). In another study dedicated to the detection of an immobilized single virus, authors used a microcantilever (but its thickness was at the nanoscale), and the detected mass of the virus was 9.5 fg (A. Gupta, Akin, & Bashir, 2004). Additionally, a series of different lengths (20 µm to 100 µm) and uniform width and thickness (9 µm and 200 nm, respectively) of microcantilevers have been studied theoretically and experimentally for the detection of Bacillus anthracis Sterne spores in air and water. In water, the minimum detectable mass of ~50 spores (~140 pg) and the sensitivity was 0.1 Hz/fg. In the air (by sedimentation sampling), the minimum detected mass corresponded to 2 spores (~740 fg) and the sensitivity was 9.23 Hz/fg. Some discrepancies observed between the theoretical and the experimental mass of the spores in the air were attributed to the sedimentation of the spores onto the cantilever surface. This sampling method therefore induced accumulation of a different number of spores on the top and bottom of the cantilever. In addition, the authors stated that longer cantilevers were likely less sensitive than smaller ones (Davila et al., 2007). This could be due to the non-uniform mass sensitivity of the cantilever-based MEMS sensors. Indeed, this assumption was latterly confirmed by (K. Park, Kim, Morisette, Aluru, & Bashir, 2012) whose sensors were using MEMS resonant based mass sensors instead of using microcantilevers. These studies regarding cantilever-based mass measurement show lack of an efficient aerosol sampling method, but exhibit the important proof of concept for the development of future aerosol mass measurements.

Piezoresistive silicon resonant MEMS cantilever-based sensors have been proposed for the detection of airborne ultrafine particles, and were called CANTOR-1 and CANTOR-2 (Hutomo Suryo Wasisto, Merzsch, Waag, et al., 2013b); Wasisto et al., 2015) (see **Table 2**, **3**). In these works, micro scale cantilevers were used as resonators. CANTOR-1 and CANTOR-2 were obtained by using an external piezoelectric actuator as well as an integrated electrothermal heater, respectively. An extensive review about piezoresistive cantilevers was proposed by (Bausells, 2015). The authors reported that a mechanical periodic thermal expansion can be induced by the electrical fluctuation due to the alternating

ohmic loss (actuation). The mechanical expansion induces a change in the resistance because of the piezoresistive effect. Thus, the output current can be modulated (detection). Both CANTORS used electrostatic precipitation as a sampling method. Unlike other studies, the particles were not initially charged, but their natural charges were used for sampling. The cantilever was polarized and only particles with opposite charges were significantly attracted towards the surface. The resulting efficiency of the sampling was low. Since the CANTOR-2 performs higher frequency, high O-factor, and lower dimensions, the sensitivity of the CANTOR-2 was 5 μ g/m³, while it was measured as 25 μ g/m³ for the CANTOR-1 (Hutomo Suryo Wasisto, Uhde, & Peiner, 2016). As above-mentioned, the position of the deposited mass on the cantilever has an influence on sensitivity (Dohn, Svendsen, Boisen, & Hansen, 2007). In order to address lower mass concentration with a better uniformity, the size of the cantilever has to be reduced down to the nanoscale. (Ilic et al., 2004) reported that NEMS cantilever-based sensors can measure the mass of deposited gold dots with attogram sensitivity. In addition, using very high frequency NEMS sensors, clear evidences for sensitive mass measurement of adsorbed gaseous species at the zeptogram scale could be found (Y. T. Yang, Callegari, Feng, Ekinci, & Roukes, 2006). Cantilever-based NEMS resonators integrated on complementary metal-oxide-semiconductor (CMOS) chips and the resonators were also used to measure the mass of glycerine drops. The mass sensitivity was reported to account for 4 ag/Hz (Forsen et al., 2005). Other studies demonstrated that the integration of electrostatically actuated NEMS resonators reduced the parasitic capacitance. Though this type of NEMS sensors has not been developed to detect airborne particles, ultra-low mass measurement has been demonstrated.

The growing interest in the detection of nanoparticles has triggered the development of NEMS/MEMS sensors for measuring the mass concentration of nanoparticles. Considering that NEMS sensors are able to detect single particles due to their very small size and ultra-high frequency, it shows their potential for the detection of airborne nanoparticles. However, an efficient sampling method is of crucial importance. (Schmid et al., 2013) proposed a nanomechanical resonant fiber for nanoparticle sampling and detection system (see Table 2, 3). The authors used the Brownian motion based diffusion and inertial impaction principles for particle sampling and successfully detected nanoparticles with the mass resolution of 740 ag. The latter mass was deduced from the resonance frequency shift of the fiber (diameter <100nm), due to the particle deposition. Another study depicted vertical silicon nanowire (diameter <100nm) NEMS resonators as a nanobalance to measure the mass of aerosol nanoparticles (H. S. Wasisto et al., 2013) (see Table 2 and 3). Authors measured aerosol nano particles with a mass sensitivity of 7.1 Hz/fg and a mass resolution of 31.6 fg. Electrostatic precipitation was used to deposit aerosol nanoparticles on the nanowires. A portable miniature electrostatic precipitator was embedded in

the developed sensor instead of using a bulky commercial nanometer aerosol sampler (NAS, TSI 3089). The sampling efficiency was three times higher as compared to the commercial sampler. But, the efficiency remained low (10.8%) in comparison to the efficiency of the NEMS filter-fiber mass measurement system ($65 \pm 31\%$).

Cantilever-based or other NEMS mass sensors can be used for a single airborne nanoparticle detector. Their small dimension, low weight, and ultra-high frequency would ensure the detection of a single nanoparticle with an extreme mass sensitivity. However, it is crucial to take the active area of the sensor into consideration when detecting micron size airborne particles such as fungi. Since NEMS mass sensors consist of the nanoscale active area, they cannot be used for this purpose. Although cantilever-based MEMS mass sensors can be utilized for the detection of micron size particles, their mass resolution, and mass measurement uniformity are poor. Therefore, highly sensitive bulk mode MEMS resonant based mass sensors have been developed in order to detect micron or nano size single airborne particle with relatively uniform mass sensitivity.

Some authors documented that individual airborne particle mass measurement could be performed by using thermally actuated high frequency MEMS resonators with piezoresistive readout (Hajjam et al., 2011) (see Table 3). Authors showed that the thermal piezoresistive resonators can reach very high frequencies and high Q-factor values. In the case of shrunk devices, it significantly enhances thermal actuation properties while reducing power consumption (Amir Rahafrooz & Pourkamali, 2010); (A. Rahafrooz & Pourkamali, 2011). Moreover, it has been noted that the thermal actuation results in more uniform mass sensitivity than others, such as electrostatic actuation. As shown in table 3, electrostatically actuated bulk mode MEMS resonator demonstrated a good performance in terms of both frequency range and sensitivity. However, due to a lack of sampling method in the system, a microscope was used to align the deposition of particles onto the micro resonator. A single aerosol particle of ~ 200 nm in diameter (with 1.5 MHz/pg sensitivity) could be measured, while the minimum detectable mass accounted for ~10 fg. Latterly, a chip-scale aerosol cascade impactor has been integrated to thermalpiezoresistive MEMS resonators (Maldonado-Garcia et al., 2016) (see Table 2). The cascade impactor consisted of 2 stages and the flow rate was adjusted at 0.017 L/m. It was shown that the size of the deposited particles was in the range to 1 µm from 140 nm and 140 nm from 40 nm for the first and second stage respectively. The mass concentration accounted for 29.4 ng/m³ and 6.2 ng/m³, respectively. Another recent study provided in Table 2 has also combined a bulk mode MEMS resonator with an impactor to demonstrate the feasibility of the aerosol mass concentration measurement system (Zielinski et al., 2016). Authors have collected 296 nm particles with a 70% impactor sampling-efficiency (this global collection efficiency has been experimentally estimated by using two condensation particle counters (CPC) for the

inlet and outlet of the impactor. Therefore, it clearly overestimates the efficiency by avoiding the particles that are not deposited on the sensor surface but deposited around the chip) and no saturation of the sensor was noticed within 60 min of sampling. Moreover, the extensional mode has been used for a piezoelectric square-shaped resonator ($1.4 \text{ mm}^2 \times 1.4 \text{ mm}^2$). Thereby, the location of the collection pattern was correlated with a sensitive area of the resonator.

Apart from extremely sensitive aerosol particle detection capabilities obtained with the previously described MEMS resonators, NEMS/MEMS mass sensors are sensitive to the ambient conditions such as pressure, temperature, and relative humidity. The changes in the ambient conditions can cause undesirable frequency shift which leads to inaccurate mass determination. The effects of the ambient conditions on silicon cantilever MEMS have been studied extensively (Hutomo Suryo Wasisto, Merzsch, Waag, et al., 2013a). It was shown that Young's modulus of silicon-made resonators is affected by the variations of ambient temperatures (-28.6 ppm / °C). This is due to the thermal effects that cause an undesirable change in the resonance frequency and represented by the Temperature Coefficient of Frequency (TCF = $\frac{1}{f_0}\frac{\Delta f}{\Delta T}$). The changes in relative humidity induce water molecules to be absorbed onto the cantilever, which acts as an additional mass; therefore, undesirable resonance frequency shift was observed (Low rH (-1.4±0.1) ppm / %, high rH (-2.3±0.1) ppm / %). Thus, pressure also induces a decrease in the resonance frequency ((-5.9 ± 1.5) ppm / kPa), and it has been suggested that the short sampling time can be beneficial to reduce the effects. However, the sampling efficiency should be maintained as high as possible in order to collect representative and reliable amounts of particles. In the case of thermally actuated silicon resonator (Hajjam et al., 2011), the influence of temperature was reduced by doping the resonator with boron (-2.72 ppm / °C), boron-assisted aluminum (-1.5 ppm / °C) (Samarao & Ayazi, 2009), and phosphorous associated with bias voltage to the resonator (-0.05ppm / °C) (Hajjam, Rahafrooz, & Pourkamali, 2010, p. 100).

1.2.3 Regeneration of the MEMS sensors

The above-mentioned NEMS/MEMS sensors can be exposed to a wide range of aerosol concentrations, from a few seconds up to several minutes, but prolonged exposures can fully load the small active surface of the sensors. Indeed, the surface area of the resonators can be increased to enhance maximum detectable mass. In contrast, the sensitivity will be reduced due to the increased dimensions of the resonators (see **Table 3**). Consequently, the regeneration of sensors using wet and dry cleaning techniques have been investigated and documented in **Table 4**. Though the sensors are easily disposable and demountable, it would be a breakthrough of having a technique that allows real-time particle removal

from the surface without necessarily demounting all the system. The studies provided in **Table 4** show that this goal is only partially achieved because the saturated sensors have to be taken out of the system to be specifically treated. One of the wet cleaning techniques used currently is based on photoresist deposition onto the cantilever prior to the particle deposition. The photoresist is a light-sensitive polymer material used in the photolithography process in microfabrication that can be dissolved in a solution. Thus, its removal also lift-off the deposited particles from the sensor surface (Merzsch et al., 2012). The cleaning efficiency can be determined through the detection of resonance frequency before and after treatment. Another study documented the use of dry and wet cleaning methods consecutively. Firstly, the loaded cantilever was purged using Nitrogen flow. Only particles with a diameter larger than 2.5 μ m were removed from the surface. Then, the sensor was immersed in a solution and an ultrasonic cleaner was used to remove the remaining particles (Hutomo Suryo Wasisto, Merzsch, Waag, et al., 2013b).

Particle detachment techniques	Method	Sensor	Real-time detachment	Efficiency	Ref.
Wet cleaning	Lift-off (Photoresist)	A cantilever type-MEMS	No	99.68 %	(Merzsch et al., 2012)
Wet cleaning	Ultrasonic cleaner	A cantilever type-MEMS	No	90–99 %	(Hutomo Suryo Wasisto, Merzsch, Waag, et al., 2013b)
Dry cleaning	Nitrogen purging	A cantilever type-MEMS	No	All particles dia > 2.5 μm	(Hutomo Suryo Wasisto, Merzsch, Stranz, et al., 2013)
Dry cleaning	CO ₂ snow jet	A resonant type-MEMS	No	99.9 %	(Mehdizadeh et al., 2017)
Dry cleaning	PDMS cleaning	Nanopillar- NEMS	No	99 %	(Hutomo Suryo Wasisto, Merzsch, Stranz, et al., 2013)

Table 4 - Comparison of available aerosol particle detachment techniques.

(Mehdizadeh, Kumar, Wilson, & Pourkamali, 2017) have recently proposed a carbon dioxide (CO₂) snow jet as a dry cleaning technique in which solid CO₂ particles were targeted at high velocity towards the loaded resonator. The mechanical impact of the CO₂ particles removed submicron particles from the loaded surface and did not damage the resonator. Another cleaning method using Polydimethylsiloxane (PDMS) was proposed. PDMS was deposited on the loaded cantilever, and removed from the particleloaded surface. Due to the high cohesion strength of the mold in comparison to the binding forces between the particles and the sensor surface, particles could also be removed (Hutomo Suryo Wasisto, Merzsch, Stranz, et al., 2013). Apart from all these cleaning methods, a novel approach to manipulate particles has been recently proposed by (Johnson & Mutharasan, 2016). In this study, millimeter-scale cantilevers have been used to detect, manipulate, and release of suspended particles in a liquid. The polyethylene microparticles have been trapped at the regions of highest surface vibration amplitude. Thus, the particle trapping zones exhibited a dependence on the mode shape. Moreover, when the fundamental mode (n=1) was switched to a noise signal that simultaneously excites multiple high-order modes across the frequency spectrum, the trapped particles have been rapidly released. When the moment of inertia of the sensor is greater than the adhesion moment of the particles, detachment has occurred and particles are released due to the buoyancy of water since the study is carried out in liquid. Analogously, this approach may be applied to the particles in the air. But, an external repellent force (e.g. upward air flow) is needed to replace with the buoyancy in order to overcome possible sedimentation of the detached particles due to the gravity. Nevertheless, the particles can also be collected by inertial impaction into a liquid (i.e. liquid impingement) in which MEMS mass sensors can be operated with a poor performance.

1.3 Discussion and conclusion

First generation aerosol mass concentration measurement methods are being mostly used for the purpose of environmental monitoring. As reported by the CEN, the mass resolution of the first generation methods is appropriate to satisfy the critical threshold exposure concentration for people. However, the systems could be portable and easily accessible to people. Therefore, new generation of mass measurement systems should be considered. In order to realize a highly sensitive, inexpensive, integrable, and real-time detection system, a suitable sampling method has to be selected and adapted to a nano/micro detector. While nano/micro mass sensors have shown extremely sensitive feature to detect a single airborne particle, nano/microfabrication tools enable to facilitate CMOS compatible sensors on a silicon chip. Since conventional electronic devices are ubiquitously used in daily-life, integration of such

sensors on a silicon chip would ensure low-cost and low power consumption PM sensors ready-to-use in the pockets.

Aerosol sampling methods have been miniaturized in order to be adapted to nano/micro mass sensors. The developed systems are promising technologies, but the sensors need to be further improved, particularly as respect to active surface area, sensitivity or mass measurements uniformity. Unlike the filters, post-collection analysis of collected particles may be impractical for the sensors. Moreover, none of the proposed real-time mass measurement methods have overcome the limitation related to the postdeposition process. After a short time of exposure has elapsed, the deposited plate eventually saturates with particles; therefore, it has to be cleaned or replaced. Though dry and wet cleaning techniques have been proposed to fully unload the surfaces, it requires undesirable treatments. New cleaning techniques should be further investigated in order to ensure a real-time regeneration process. With respect to NEMS/MEMS sensors, the need of new cleaning techniques is even more crucial because of their small active surface area which can be rapidly saturated with particles. It results in a decrease of the Q-factor, and ultimately the performance of the device as that of the mass sensitivity. Although the development of miniature devices is mostly dedicated to detecting the very low concentration of airborne particles, revolutionary measurement techniques such as resonance frequency dependent inertial detachment has to be specifically addressed to NEMS/MEMS airborne particles mass sensors. Thus, the ambient parameters have great influence on the sensors, and the reliability and accuracy of the sensors can be questioned. Recent developments show promising outcomes, particularly those which compensate the temperature effects. Rapid heating and cooling properties of small structures can be beneficial to disrupt condensation of water molecules on the sensor surface, and therefore reducing the humidity effects. Sophisticatedly designed sensors show mechanical robustness to sustain pressure. Additionally it should be mentioned that the issues related to the condensation and evaporation of water during filter sampling also apply to NEMS/MEMS mass sensors. A possible increase in particle-bound with water, as well as the loss of semi-volatile compounds (due to abrupt changes in the ambient conditions), can affect adsorbed particles, and may ultimately lead to false measurements.

Lastly and as previously documented (Lewis & Edwards, 2016), rapidly developed, cheap, massproduced, and unmatured personal sensors, spark off low quality and insufficient sensors to people's life. These devices might be to achieve reliable PM measurements, but are still not sufficiently calibrated and tested in the field. Thus, there is a potential risk to release inaccurate and unconfirmed data to the public. The use of these newly developed sensors in daily life needs to be further investigated, and uncertainties are yet to be clarified. The promising NEMS/MEMS technology would be reliable for short-time measurement in indoor environments, in which meteorological conditions such as wind speed, temperature, and humidity are relatively stable. Based on these new developments, smart cities can be developed by replacing robust, fixed, and bulky official monitoring stations. Finally, pervasive integrated sensors would constitute a new monitoring paradigm based on dense networks (Snyder et al., 2013); (Marco Carminati, Ferrari, & Sampietro, 2017).

This chapter emphasizes micro-scale sensors; in particular MEMS sensors for mass measurements. According to this review, bulk mode MEMS mass sensors are favorable micro detectors in order to realize a real-time aerosol mass concentration measurement system. Therefore, bulk-mode MEMS sensors have been chosen as an appropriate option for a detector in this work (see Chapter 3). While there are only a few aerosol mass concentration measurements documented with MEMS sensors, MEMS-based bioaerosol mass concentration measurements have not been investigated yet. Although several MEMS-based biological material detection and mass measurement studies have been shown so far, these studies do not concern bioaerosols. Furthermore, all the proposed micro detection systems either lack of an aerosol sampling method or developed sampling methods have not characterized sufficiently which results in an overestimation of collection efficiency that ultimately leads incorrect mass measurements based on resonance frequency shifts.

In the next chapter, an efficient sampling of aerosol and bioaerosols will be the main concern by investigating the characteristics of a selected sampler.

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CHAPTER 2 - Exploring deposition characteristics of aerosol and bioaerosols by impaction for the development of black silicon-based MEMS mass sensors

With respect to Chapter 1, airborne particle monitoring systems can be accessed through the development of silicon-based micro scale systems and can be achieved by combining an appropriate sampling method with bulk-mode MEMS devices.

The objective of this chapter is to elaborate a sampling method that can possibly be combined with MEMS sensor(s). In this context, firstly, aerosol sampling methods have been examined and an inertial impactor is decided to be an appropriate sampler for the detection system. Secondly, a multiple round nozzle single-stage impactor has been designed, fabricated, and characterized based on classical impactor design criteria. The characterization of the impactor reveals the experimental collection efficiency (referred to as global efficiency in the manuscript). The latter, various type and size of aerosol and bioaerosols have been generated and impacted on two different surfaces, namely silicon (i.e. smooth silicon) and black silicon (i.e. nanostructured silicon). Thus, the deposition characteristics such as shape, size, and the collection efficiency (i.e. local collection efficiency) have been exploited. The empirical results show that the size of airborne particles plays a key role to determine the deposition characteristics of the impaction by the mechanism of rebound and re-entrainment (i.e. bounce effect) of the particles. Furthermore, the effect of different surfaces on the impactions has been emphasized.

2.1 Choice of an aerosol sampler technique

The major objective of the sampler is to extract aerosols from the air and efficiently bring them to the sensor surface. Aerosols detection system has been designed to be operated with a flow rate that simulates the human breath whose rate is around 10 LPM (liter per minute) (J. K. Gupta, Lin, & Chen, 2010). Thus, the main design consideration of the system is to maintain 10 LPM flow rate with reduced particles loss during the transport and efficient deposition on the micro sensor which should also show resistance to such flow rate. It should be mentioned that the active surface area of a bulk-mode MEMS sensor has been designed as 1 mm² and the corresponding details can be found in **Chapter 3**. As a consequence, cross-sectional area of microchannels which deliver the particles onto the active surface of the sensor by any means should be designed to be smaller than 1 mm² and feasible to 10 LPM flow rate to facilitate a laminar flow.

In **Chapter 1**, several sampling methods are presented. In the following, the pros and cons of possible miniaturization of aerosol sampling methods and bulky instruments have been evaluated.

2.1.1 Filtration

As the working principle of TEOM relies on the determination of the oscillation frequency change when the particles are deposited onto the filter, microfabrication tools would enable to fabricate filter-like MEMS resonators by etching holes on the resonators. The latter can be considered as a micro – TEOM and provide highly sensitive mass concentration measurements. Besides of inertial forces, it should be kept in mind that the interception, diffusion, and electrostatic attraction also contributes to the deposition of the particles on the filter (Baron & Willeke, 1993). MEMS resonators should be maintained at an optimum temperature to avoid condensation of water vapor while preventing loss of semi-volatiles. Although the filtration method has been used for the sampling and analysis of aerosols, post-collection analysis of collected particles may be impractical for the sensors. Furthermore, filter-like micro resonators may lead difficulties to alter the properties of the sensor surface. In particular, surface functionalization by the microfabrication techniques such as thin film coating or etching would be much challenging and could lead to impede sensitivity and selectivity improvements. Additionally it should be mentioned that etching holes to form a filter-like MEMS resonators results in a degradation of the sensor performance in terms of its quality factor, resonance frequency, and deformation mode characteristics such as vibration amplitude and distribution, and ultimately the mass sensitivity and uniformity (Shao & Palaniapan, 2008).

2.1.2 Sedimentation, thermophoresis, and electrostatic precipitation

Sedimentation may also be mentioned as another aerosol sampling method. When the settling velocity of a particle is sufficient to overcome the motion exerted by the air velocity, sedimentation can occur. However, it is very difficult to measure the volume of sampled air, and thus concentration of the collected particles. Besides, the collection efficiency highly depends on the size of particles.

As another force resulting from a thermal gradient, the thermophoretic force could be beneficial to build a micro thermophoresis sampling method (Paprotny et al., 2013). Although thermophoresis can be successfully adapted to a microsystem, it fails to collect micron size airborne particles as emphasized in Chapter 1, Section 1.2.1

Electrostatic precipitation method may come to the forefront due to its excellent adaptation to a micro system. As it has been shown in **Chapter 1**, **Section 1.2.1**, natural charges of the particles would not be enough to a sufficient particle collection, and therefore prior charging component (e.g. micro corona discharge) should be developed and integrated to the micro system. Besides the fabrication complexity, it is known that ozone is produced during bioaerosol charging and may affect microorganism viability (Amato et al., 2017). Moreover, a high sensitive MEMS mass sensor can absorb the produced ozone and provide a mass measurement that ultimately leads to a cross-sensitivity.

2.1.3 Inertial impaction

Lastly and as previously described in **Chapter 1**, inertial impactors have been utterly microfabricated and achieved to couple with a MEMS resonator. But, these representative studies have never demonstrated the deposition characteristics rather than the collection efficiency. As the size and shape of the deposits have never been investigated, the collection efficiency estimation is usually based on the difference between an amount of particles at the inlet and outlet of the sampler. Ultimately, the estimated collection efficiency is overestimated. Because the estimated collection efficiency usually consists of the particles which are not deposited on the sensor surface due to misalignments or large deposit sizes. Therefore, some of which cannot be analyzed by a micro sensor, but are included in the collection efficiency. Thus, we refer to this efficiency as global collection efficiency in this manuscript. Besides, the ratio of a number of collected particles on a micro sensor is referred to as local collection efficiency which leads to an accurate estimation of amount of particles perceived by a micro sensor. The miniaturized impactor-detection systems usually put efforts on reducing working flow rate below 1 LPM. Hence, these systems are usually designed and meant to detect nanoparticles. Clearly, if one aims to

sample aerosols or bioaerosols by 10 LPM with a micro scaled impactor based detection system, the design considerations should be adapted to the high operating flow rate. Therefore, all the proposed miniature systems ultimately would fail to achieve this goal. When the high flow rate handling capability of a micro scaled impactor is achieved, surface properties of a collection plate can also be improved in terms of its hydrophobicity, adhesion properties, and nano/micro structuration to increase the surface to volume ratio that would facilitate potential improvements of sensitivity, selectivity, and collection efficiency of the detection system. Besides, all the impactors commonly encounter inlet losses, interstage losses (in the case of cascade impactor), rebound and re-entrainment (i.e. bounce effect) of particles which lead to collection efficiency reductions as well as modification of impactor characteristics.

Among all the physical forces which can be effectively applied on airborne particles to constitute a sampling method, inertial impactors can be shrunk down to micro scales and facilitate nanometer to micrometer size of airborne particles collection regardless of their origin. In addition, this method provides one opportunity for further developments, compact packaging, and ease of handling. Therefore, this study has selected inertial impactor as a sampling method which intends to be coupled with a MEMS mass sensor(s).

2.2 Study, design, and realization of a lab-made single stage inertial impactor

The concept of the inertial cascade impaction has been proposed for the first time by (May, 1945) (see Figure 2). Subsequent to the first description, the impactors have been widely studied, used, and characterized over 50 years.

According to the classical impactor design theory, the performance of an impactor can be accurately predicted. The most important characteristic of an impactor is the collection efficiency curve that shows the fraction of particles of any size which are collected on the impaction plate as a function of the particle size (Marple & Willeke, 1976). The cut-off diameter is an aerodynamic diameter (d_{ae}) of particles which are collected with 50% collection efficiency. It can be shown as d_{50} and can be calculated as in Eq. 7. The efficiency curve is expected to have a sharp separation between the cut-off diameter of a stage, however, it is usually obtained as 'S' shape, which results in an excessive collection of particles whose aerodynamic diameter smaller than the cut-off diameter and lower collection efficiency of large particles (see Figure 3). The cut-off diameter, thus the efficiency curve is determined by the square root of Stokes number ($\sqrt{St_{50}}$). This dimensionless number predicts whether the particle impacts on the plate due to its large inertia or remain in the air flow by escaping the impaction, while Reynolds number (Re) determines the sharpness of the curve. (see Eq. 8 and Figure 3).

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Figure 2 - A schematic of a single stage, tapered inlet, and single round nozzle impactor which is combined with a MEMS sensor as an impaction plate.





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$$d_{50} = \sqrt{\frac{9W\mu nSt_{50}}{\rho_p CV_0}}$$
(7)

$$Re = \frac{\rho W V_0}{\mu n} \tag{8}$$

Where ρ_p is the particle density, ρ is the air density, V_0 is the average air velocity in the nozzle, W is the nozzle diameter, μ is the air viscosity, n is the number of nozzles, and C is the Cunningham slip correction and can be found using (Marple & Willeke, 1976):

$$C = 1 + \frac{0.163}{d_p P_2} + \frac{0.0549}{d_p P_2} \times e^{-6.66d_p P_2}$$
(9)

Where P_2 is static pressure at the impaction plate, which is the difference between static pressure at the impactor stage inlet (P_1) and $\frac{1}{2}\rho V_o^2$. Besides, several parameters have influence on the sharpness of the curve and suggested to design an impactor according to following considerations (for round nozzle) as follows (Marple & Willeke, 1976): (*i*) the ratio of the distance between the plate and the nozzle (S_d) and nozzle diameter (W) as $S/W \ge 1$, (*ii*) the ratio between the nozzle throat (T) and the nozzle diameter (W) as $T/W \ge 1$, (*iii*) Reynolds number should be between 500 < Re < 3000 that leads to theoretical value of $\sqrt{St_{50}}$ equals to 0.47, and (*iv*) Tapered inlet shape. Also, it has been suggested that when the impaction plate diameter is about three times larger than that of the nozzle, theoretical value of $\sqrt{St_{50}}$ agrees well with the computed results (Huang & Tsai, 2002). Additionally it should be mentioned that abovementioned considerations comprise a basis for single nozzle impactors. In the case of multiple round nozzles in a circular cluster, it has been suggested that when $W \times n / 4D_c > 1.2$, (where *n* is the number of nozzles, and D_c is the nozzle cluster diameter) multi-nozzle impactors operate satisfactorily (Fang, Marple, & Rubow, 1991). Otherwise, as referred as cross-flow, results in kidney-shaped deposits or even no deposition on the impaction plate.

In this study, a single stage multiple nozzle inertial impactor has been designed and elaborated. As shown in **Figure 4**, the impactor consists of a probe connection, a nozzle plate where 10 round nozzles with tapered inlet each of 500 μ m diameter located circularly, impaction chamber which exhibits a 1000 μ m separation between the nozzles and impaction plate on which silicon and black silicon surfaces are placed to simulate the impaction conditions of MEMS sensors. Finally, pump connection is to connect the pump to provide air flow. The impactor is made of Aluminum to ensure reduced electrostatic loss due to conductive walls. The design parameters can be found in **Table 5**. As this lab-made single-stage impactor with the calculated cut-off diameter of 0.39 μ m consists of 10 nozzles, Reynolds (Re) number has been kept below 3000, and each nozzle renders 1 LPM to corresponding MEMS sensors. Thereby, 10 nozzles

are meant to be aligned with 10 MEMS sensors. It has to be mentioned that the active surface area of the sensors is 1 mm² and each sensor chip has been designed as 6.4 mm × 6.4 mm in order to ease the handling of the chips. In this study, silicon and black silicon pieces are used as 10 individual impaction plates in order to mimic the impaction conditions of silicon-based MEMS sensors. Silicon pieces have been diced from p-type silicon wafers (Addison Engineering, Inc. San Jose, CA) whose thickness is (500 \pm 25) µm.

The realization of this impactor enables to sample bioaerosols and aerosols with 10 LPM by taking advantage of the batch-fabrication of MEMS sensors. Subsequent to an extraction of aerosols or bioaerosols from an ambient air with a given flow rate, the particles are accelerated along each nozzle (e.g. air-micro channels) in which flow-rate is divided to 1 LPM for each micro channels. The latter, each nozzle delivers the particles onto the corresponding ten MEMS sensors with 1 LPM flow rate. While this system avoids applying a high pressure on a single micro sensor due to the reduced flow rate, it also enables to investigate ten different impaction spots. Accordingly, the MEMS integrated inertial impactor can be operated for real-time mass concentration measurements of airborne particles with a theoretical cut-off diameter of 0.39µm.



Figure 4 - Single stage multiple nozzle impactor design. Distance from probe connection to pump connection is 11.8 cm and the diameter of plates is 8 cm.

Designed		Calculated			
Number of nozzles (<i>n</i>)	10	Average air velocity in the nozzle (V_0)	84 m/s		
The distance between the impaction plate and the nozzles (S_d)	1000 µm	Cunningham slip correction (<i>C</i>)	1.36		
Nozzle diameter (W)	500 µm	Theoretical cut-off diameter (d_{50})	0.39 µm		
Nozzle throat (<i>T</i>)	700 µm	Reynolds number (Re)	2825		
Flow rate (Q_p)	10 LPM	Static pressure at the impaction plate (P_2)	0.957 atm		
Tapered inlet throat (T_i)	350 µm				
Tapered inlet angle (°)	45°				

Table 5 - Designed and calculated lab-made single stage impactor parameters

2.2.1 Characterization of the impactor

To characterize the impactor in order to evaluate its global collection efficiency, an effective method has been used. Firstly, a circular Aluminum piece with a thickness of ~500 μ m which is identical to the impaction plate has been inserted on the impaction plate to reduce the distance between the impaction plate and the nozzles to 500 μ m. This additional piece has been used in impaction to simulate the impaction of particles on silicon surfaces as it is difficult to dice one circular silicon piece which is identical to the impaction plate. As shown in **Figure 5**, an aerodynamic particle sizer (APS) and a pump have been connected to downstream of the impactor. The flow rate of APS is 5 LPM as that of the pump. Thus, the operating flow rate of the impactor has been set to 10 LPM. Prior to the characterization measurements, a HEPA filter has been firstly connected to the inlet of the impactor, and then the inlet of the set-up to ensure no leakage either in the impactor or in the set-up. The latter, as shown in **Figure 5**, the successive measurements have been carried out by sampling the air in the laboratory. For the first 120

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Figure 5 - Schematic of the impactor characterization experimental set-up (left), and the measurement method (right).



Figure 6 - All aerodynamic size of total collected particle concentration with and without the impactor VS time.

seconds, only the APS sampled the air (N_{in}) , and then the next 120 seconds, the impactor has been started to sample the air with the APS (N_{out}) (see Figure 6). Each case repeated 10 times; therefore, the whole experiment has taken 2400 seconds, which provides repetitive coherent results. As it is expected and can be seen in Figure 6, the particle concentration in the laboratory is relatively stable which enables to carry out reliable successive measurements. Then, global collection efficiency for each 240sec can be calculated for each aerodynamic size of particles for ten times to deduce the mean global collection efficiency (*GCE*) for each size of particles as following:

$$GCE_{d_{ae}}(\%) = 100 - \left(\frac{N_{out}}{N_{in}} \times 100\right)$$
(10)

Where N_{in} is the total concentration of particles with a given aerodynamic size and measured when only the APS has been sampling airborne particles in the air. Nout is the particle concentration that represents the particles which have not been sampled by the impactor. It is measured when the impactor and APS are both under operation. Hence, the global collection efficiency can be calculated based on eq.10 for desired aerodynamic particle size as small as 0.5 µm due to the limitation of APS. As a result, the global collection efficiency has been obtained and the empirical cut-off diameter is deduced (see Figure 7). As it is mentioned previously, the actual collection efficiency curve often exhibits a tendency to form an 'S' shape. The lower portion of the S-shaped curve could not be demonstrated with this technique. However, in Figure 7, the 50% collection efficiency of particles relies on 0.8 μ m mean aerodynamic diameter, and therefore it can be considered as the empirical cut-off diameter of the impactor. Although the theoretical value of the cut-off diameter is 0.39 µm, the impactor parameters such as the distance between the nozzle and the plate, particle bounce from the collection plate or other factors related to the rough theoretical estimation could cause the differences between the experimental and theoretical cut-off diameters (Yao & Mainelis, 2006). Besides, collection efficiency of the particles which are larger than the cut-off diameter does not reach up to 100%. This deficiency could be originated from poor adhesion properties of the impaction plate that can effectively contribute to the particle loss, and therefore the global collection efficiency of the impactor can be defined as $(62.8 \pm 3.2)\%$ for the aerodynamic diameter of 1 µm particles. Furthermore, as shown in Figure 8, the Al-made impaction plate has been taken out of the system following the successive measurements. The impaction patterns have been observed as haloshaped deposits. It has been argued that the halo-shaped deposit may lead to obtaining lower collection efficiencies as well as it has an influence on the collection efficiency curve characteristic (Rocklage, Marple, & Olson, 2013). The shape of the deposits will be explained in the section of Results and discussion in details.


Figure 7 - The empirical collection efficiency curve of the impactor. The impaction has been done on an Al plate.



Figure 8 - The digital microscopy images of the different impaction spots after laboratory air sampling. Red arrows indicate halo-shaped deposits and scale bars are 2 mm.

Nevertheless, the use of this impactor can be beneficial and relatively efficient for $PM_{2.5-10}$, $PM_{1-2.5}$ and the most common individual bacteria whose diameter is 1 μ m or larger due to their tendency of aggregation and attaching to larger particles. Likewise, it can be an appropriate sampler for common fungal particles which can be usually found as large as 5 μ m in the air (Yao & Mainelis, 2006).

2.2.3 Black silicon as an impaction plate

The abovementioned major issue in inertial impactors is the bouncing particles off the impaction plate. This phenomenon may cause low collection efficiency, discrepancies between the theoretically and experimentally deduced cut-off diameters, and it can enlarge the size of the impaction spot. The common practice is to use sticky materials like oil/grease on the impaction plate to reduce this effect or fiber-porous like structures to enable penetration of the particles into the structures, thus reducing the bounce effect (Baron & Willeke, 1993). Practically, these solutions are not adaptable to build with microfabrication tools, and therefore not adaptable to MEMS sensors. However, microfabrication methods could also be beneficial to create unique attachment zones on the active surface area of a micro sensor where 3D micro/nano structures can be developed.

So far, there has been no study investigated a micro/nanofabricated surface as an impaction plate. Usually, the miniature methods use non-treated silicon as a gravimetric sensing material, and hence the deposition and impactor characteristics have not been highlighted. On the other hand, the mechanical bactericidal properties of emerging nanostructured silicon referred to as black silicon (bSi) have been recently reported (Ivanova et al., 2013). This material has shown to be highly bactericidal against Gramnegative and Gram-positive bacteria, and endospores. In fact, the discovery on this synthetic nanostructured silicon surface has been inspired by nature, by the wings of a species of cicada (Psaltoda claripennis) (Ivanova et al., 2012). It has been found out that the cicada wings consist of periodic high aspect nanostructures which serve as very sharp needle-like structures that are used to impale the organisms to rupture them. Moreover, the wings exhibit a superhydrophobic surface that is used to perform self-cleaning (e.g. Lotus effect) by sliding and rolling of the water droplets to sweep the foreign contaminants (dust, dirt, bacterial cells etc.). Otherwise, the insect would not be able to avoid possible infections due to the colonization of bacterial cells. Therefore, the discovery of synthetic mechanical bactericidal bSi does not only open new doors in the field of mechano-biology but also in the field of aerosol and bioaerosols detection.

Besides of its excellent technological compatibility with MEMS fabrication and the mechanical impaling properties, this material can be exploited as an impaction plate aiming to reduce the bouncing

effect as well as aiming to enhance the collection efficiency in the impactor. Thus, bSi has been used as an impaction plate in the impactor as an innovative solution to the encountered issues during impactor operation.

In this study, bSi has been fabricated using $O_2 - SF_6$ plasma-based (~ -110 C°) cryogenic deepreactive-ion etching (DRIE) method (see Figure 9). In this method, the plasma mixture produces SF_x^+ ions and F^{*} radicals that diffuse to the silicon and result in an isotropic chemical etching reaction, while oxygen produces O^{*} radicals that contributes to the diffusion and form a passivation layer as Si_xO_yF_z to impede the etching. Although this layer is sensitive to SF_x^+ , it cannot be removed by the F* radicals. Since the etching is more pronounced on horizontal surfaces than that of vertical walls due to ions' trajectory,



Figure 9 - SEM of bSi surface used in this study. A top view of the surface (Top left), a cross-sectional of the pillars (measured bar shows: \sim 3 µm), and another cross-sectional view of the surface where contaminants are impaled by the pillars.

the competition between two cycles (SF_6/O_2 gas flow ratio, time, temperature, voltage bias, and RF power) leads to obtaining high aspect anisotropic etching, and therefore bSi can be obtained (Nguyen et al., 2012). Additionally it should be mentioned that the fabrication of black silicon enables to produce this unique surface on a large-scale, however the formation of the structures such as density and length of pillars is not necessarily homogeneous across the wafer. Moreover, it is quite likely to obtain different topologies from one wafer to another, which may impede the utility of bSi surfaces. Nevertheless, development of bSi surfaces has been urging unprecedented advancements in silicon MEMS-based airborne particles detection technology.

2.3 Airborne particles generation and impaction on silicon and black silicon

To investigate the deposition characteristics of the impactor, a variety of experiments carried out to impact different size and origin of particles on smooth and black silicon surfaces with a thickness of $(500 \pm 50)\mu$ m. Practically, the main concern is to align the samples corresponding to the nozzles. To ensure a good alignment, double-sided tapes with a thickness of $(50 \pm 20)\mu$ m has been used. Prior to sticking the samples, a syringe with a 0.45 μ m diameter needle has been used to deposit blue ink through the nozzles, thus ink marks have been formed on the tapes. The latter has been used to align the samples. In **Figure 10**, silicon and black silicon pieces (arbitrarily cut by a diamond cutter), which are mimicking silicon-based MEMS sensors, have been glued by double sided tapes on the impaction plate where ink



Figure 10 - Si and bSi pieces as impaction plates are aligned corresponding to the nozzles on the impaction plate (Diameter of the plate shown as 8 cm).

marks are located. This method ensures to align each impaction plate underneath each nozzle. Circular formation of ten nozzles is expected to result in homogeneous deposition of particles on each impaction plate. As the distance between the nozzle plate and impaction plate is 1000 μ m, the samples at top of the tapes result in (550 ± 32) μ m distance that establish the condition of S/W ≥ 1.

Following the definition of the protocol that has been used in all experiments, it should be emphasized that various sizes of particles are generated such as $(0.92 \pm 0.02)\mu$ m, $(2.07 \pm 0.03)\mu$ m, $(2.53 \pm 0.05)\mu$ m, and (3.83 ± 0.01) µm mean median aerodynamic diameter (*MAD*) of fluorescent spherical particles by using Vibrating Orifice Aerosol Generator (VOAG), Aspergillus niger spores with *MAD* of $(3.04 \pm 0.05)\mu$ m by dry generation, Staphylococcus epidermidis, and Pseudomonas fluorescens with *MAD* of $(0.70 \pm 0.02)\mu$ m, and $(0.66 \pm 0.01)\mu$ m, respectively by Collison nebulizer method. These particles have been impacted on silicon (smooth) and black silicon surfaces (pillars ~ a few nm diameters and ~ 3.00 µm length) as impaction plates of the impactor.

2.3.1 Generation of airborne monodisperse fluorescent particles

Monodisperse solid particles of fluorescein were generated by a vibrating orifice aerosol generator (VOAG model 3450, TSI) and impacted via connecting the output of the VOAG and inlet of the impactor to a homogenization sphere (see **Figure 11**). The VOAG used a liquid solution of ultrapure water and sodium fluorescein ($C_{20}H_{10}Na_2O_5$, CAS 518-47-8, CI 45350). The solution is forced through a small orifice with a diameter of 20 µm by a syringe pump at a predetermined volume flow rate (Q = $(0.139 \pm 0.03) \text{ cm}^3/\text{min}$). The jet is then broken up into uniform droplets by a vibrating orifice with an operating disturbance frequency of (69.13 ± 0.06) kHz. The theoretical diameter of the generated droplet can be defined as follows and deduced as ($d_d = (40 \pm 3)$ µm).

$$d_d = \left(\frac{6Q}{\pi \times f}\right)^{1/3} \tag{11}$$

This generated initial droplet is conveyed by compressed filtered dry air (70 LPM) to ensure that water is completely evaporated from the generated droplet. The volume equivalent diameter (d_{ve}) of the dry particle of fluorescein depends on the initial sodium fluorescein and impurities in the solution. Thus, d_{ve} can be calculated with the following expression (Marple & Willeke, 1976):

$$d_{\nu e} = (C_{\nu} + I_{\nu})^{1/3} \times d_d \tag{12}$$

Where C_{ν} and I_{ν} are the volumetric concentration of the sodium fluorescein and the volumetric

concentration of the nonvolatile impurities in the solution, respectively. The aerodynamic equivalent diameter d_{ae} can be expressed by the following (Da et al., 2015):

$$d_{ae} = \sqrt{\frac{Cu_{me} \times \rho_r \times d_{me}^2}{Cu_{ae} \times \rho_o \times \gamma}}$$
(13)

$$Exhaust$$

$$Fxhaust$$

$$HEPA$$

$$Fump 10 LPM$$

$$HEPA$$

$$Fump 10 LPM$$

$$HEPA$$

Figure 11 - A schematic illustration of the VOAG - test bench.

$$d_{me} = \frac{d_{ve}}{\varphi} \tag{14}$$

Where d_{me} is the mass equivalent diameter, Cu_{me} and Cu_{ae} are the Cunningham correction factor for the d_{me} and d_{ae} diameter, respectively. ρ_r and ρ_o are the solid residues and reference density, respectively ($\rho_o=1000 \text{ kg m}^{-3}$). γ is the aerodynamic form factor which is 1 for a sphere. φ is a porosity term, and it is here assumed that the generated residues are spherical and not porous ($d_{me}=d_{ve}$). The sodium fluorescein density (ρ_r) is 1530 kg m⁻³. By using these equations, one can change the aerodynamic diameter of generated particles by either changing the volumetric concentration of the solution, the liquid flow rate, or the disturbance frequency. In this study, the volumetric concentration has been altered to produce different particle sizes. In Figure 12, typical APS data has been shown for each size of generated monodisperse fluorescent spherical particles which are subsequently impacted on Si and bSi surfaces. When monodisperse particles are intended to be generated, one of the most critical parameter is the geometric standard deviation (σ_g). It is generally believed that the σ_g should be lower than



Figure 12 - A typical APS data from the generation of fluorescent test particles. Generation and impaction parameters of $(0.92 \pm 0.02)\mu m \overline{MAD}$ (A), $(2.07 \pm 0.03)\mu m \overline{MAD}$ (B), $(2.53 \pm 0.05)\mu m \overline{MAD}$ (C), and $(3.83 \pm 0.01)\mu m \overline{MAD}$ (D) of fluorescent particles are shown.

1.2 in order for the generation to be considered as monodisperse. As seen in Figure 12, all size of generation can be considered as monodisperse. Besides, the impaction times (e.g. 60sec, 90sec, 100sec, 67sec in Figure 12) have been chosen randomly and three different impaction durations have been performed for each size of particles and impactions, however, 2 out of which is not shown herein. As a result, $(0.92 \pm 0.02)\mu m$, $(2.07 \pm 0.03)\mu m$, $(2.53 \pm 0.05)\mu m$, and $(3.830 \pm 0.007)\mu m$ of \overline{MAD} fluorescent test particles have been generated by 60sec, 90sec,100sec, and 67sec of impactions, respectively. It should be mentioned that Figure 12 is not demonstrating measurement of the whole generation, but only the impactions. Usually, all the impactions have been started when the generation is maintained stable. In all generations, APS is set to sample the particles in 1 second intervals, provide total concentration of particles as a function of aerodynamic size and recorded it. The recorded data are monitored in real-time with Aerosol Instrument Manager Software which allows adjusting APS parameters.

2.3.2 Generation of airborne bacteria: Staphylococcus epidermidis and Pseudomonas fluorescens generation

The Collison nebulizer (atomizer) method has been used as it is a recognized technique for the efficient aerosolization of various liquids. In principle, compressed filtered dry air used to aspirate the solution into the air jet where the fluid is broken into droplets. Then, the droplets are impacted on the internal wall of the nebulizer chamber in order to eliminate the larger fraction of droplets out of which smaller droplets entrained in the airstream and leave the nebulizer chamber (May, 1973). In this study, Staphylococcus epidimidis (CIP 81.55) and Pseudomonas fluorescens (CIP 56.90) have been cultivated on tryptic soja agar at 37 C° and 28 C°, respectively, prior to 48h of incubation at 29 °C before the generation (see Figure 13). Then, the suspension of spore solution has been prepared with ultra-pure water (1:10) in a nebulizer chamber. The latter, the droplets which are carrying one type of the bacteria have entered the dilution chamber with the compressed air (10 LPM) where the water is completely evaporated from the droplet carrying bacteria. Since then, airborne bacteria could be sampled by the impactor (see Figure 14) and the APS data is shown in Figure 15. The \overline{MAD} of Pseudomonas fluorescencs and Staphylococcus epidimidis is $(0.66 \pm 0.01)\mu m$ and $(0.70 \pm 0.02)\mu m$, respectively. The generation has resulted in a stable and monodisperse production of 2 different airborne bacteria. Namely, Pseudomonas fluorescencs (Gram-negative) and Staphylococcus epidimidis (Gram-positive) differ from each other. Gram-positive cells are usually more rigid and more resistant to mechanical lysis than Gramnegative cells due to their peptidoglycan cell wall which is about 5 times thicker than that of the Gramnegative bacteria (Ivanova et al., 2013). Besides, when most Gram-negative bacteria are ruptured, it

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Figure 13 - The cultivated Staphylococcus epidimidis (gram-positive) (left) and Pseudomonas fluorescencs (gram negative) (right) bacteria colonies.







Figure 15 – The APS data from the generation of bacteria, Pseudomonas fluorescens (Left) and Staphylococcus epidermidis (Right).

releases endotoxins (complex lipopolysaccharides) which are composed of three distinct regions: Ospecific antigen forming the surface antigen, core polysaccharide, and a non-polar lipid A. Besides, endotoxins are responsible for toxic effects causing variety of diseases, while there is a lack of rapid and low-cost quantitative detection system development (Das, Kumar, & Swain, 2014).

2.3.3 Generation of Aspergillus niger spores

A dry generation method has been used to generate airborne spores of Aspergillus niger. Aspergillus niger (400-150 L/cm³) has been cultivated on a petri dish for 15 days (see Figure 16). Then, the petri dish has been placed in a sealed glass chamber from where compressed filtered dry air uptakes the spores and delivers them to the homogenization spheres. The latter, aerosolized Aspergillus niger spores have been impacted via impactor. By contrast with the previous set-up for the generation of bacteria, there are 2 homogenization spheres used in this set-up to prevent unstable concentration of the



Figure 16 - The cultivated Aspergillus niger colonies.

spores at the inlet of the APS during the operation of the impactor (see **Figure 17**). Simultaneously, the impaction has been started and the valve between two spheres has been closed. From then on, the total concentration of Aspergillus niger spores has gradually decreased at the inlet of the APS, therefore the total concentration of the spores at the inlet of the impactor has been considered stable and estimated as that of the concentration at the beginning of impaction during the operation (see **Figure 18**) As it is seen in Figure 35, the generation can be considered as monodisperse and the \overline{MAD} of Aspergillus niger spores is $(3.04 \pm 0.05)\mu m$.



Figure 17 - An illustration of the test bench for the generation of Aspergillus niger used in this study.



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Figure 18 - The APS data from the generation of Aspergillus niger (Red circle indicates the total concentration when the valve between the APS and the homogeneous sphere is closed).

2.3.4 APS spectrometer measurements and calculations

The aerodynamic equivalent diameter of the generated bioaerosols and aerosols is measured with an aerodynamic particle sizer spectrometer (APS, TSI model 3321) in all experiments described in this manuscript. The APS sampling pump flow rate is 5 LPM. Data is recorded at 1 sec intervals. After each experiment, statistic parameters have been calculated for the interval defined by the upper and lower bounds selected from the graph distribution in Aerosol Instrument Manager Software. The number of particles impacted on the surfaces has been counted on images which are taken from optical and scanning electron microscopes (SEM). Then, the images have been treated to count the deposited particles with the ImageJ software. The number of counted particles on each impaction spot (10 nozzles = 10 spots) has been compared to theoretical total number of generated particles, in order to deduce the local collection efficiency, which can be obtained by the following:

$$\#_p = Q_p \times N_{in} \times \Delta t \tag{15}$$

Where Q_p is the sampling flow rate (m3/s), N_{in} is the particle number concentration measured by the APS (cm⁻³), and Δt (sec) is the APS sampling time. The theoretically generated number of particles per nozzle is then estimated as dividing the $\#_p$ by the number of nozzle (n=10).

2.4 Results and discussion: Micro-scale deposition characteristics of airborne particles

Subsequent to the impactions, the deposition characteristics have been inspected using a digital microscopy (Dino-Lite Digital), an optical microscopy, and SEM. Then, the images taken from those have been treated by applying a filter to denoise and to detect the particles with the MountainsMap Imaging Topography software or ImageJ software to be able to count the particles with reduced errors.

The generated monodisperse bioaerosols and aerosol test particles have been impacted on silicon and black silicon surfaces and their deposition characteristics such as deposition shape and size have been investigated in order to reveal the difference between global collection efficiency and local collection efficiency. Although the properties of the biological and non-biological test particles used in this study are different, their deposition characteristics show similarities and the deposition patterns correlated with the size of the particles.

2.4.1 Results

The results show that the halo-shaped, ring-shaped or only primary deposits (underneath the nozzle) have been observed on silicon and black silicon impaction plates (see Table 6). A halo type pattern consists of a primary deposit in the center that is surrounded by a ring-shaped (secondary) deposit. A ring-shaped pattern forms a particle-free area underneath the nozzle, thus the secondary deposit encloses this area and forms a ring shape deposit (see Figure 19).

The impaction characteristics of various sizes of monodisperse spherical fluorescent particles are shown in **Figure 20**. In this figure, digital microscopy images of deposition patterns of the fluorescent particles on silicon are shown in the first row. These patterns are magnified by the optical microscopy and shown in the second row (filtered images). Finally, the optical microscopy images of the fluorescent particles' deposition patterns on black silicon are shown in the last row. It has to be mentioned that deposition patterns in each column are classified by the particles of the same size.





It can be clearly seen in **Figure 20**, as the diameter of particles increased from d_{ae} of 0.92 µm to micron sizes, the deposits have gradually changed from the halo shape to ring shape. All d_{ae} of 0.92 µm size particles have demonstrated a halo type pattern regardless of the surface, which leads to an enlarged deposition area. Although the black silicon surface has not significantly affected the deposition characteristics of these particles by exhibiting halo-shaped deposits, it breaks all the micron size particles into fragments and provides a localized circular deposition pattern (diameter < 500µm) underneath the

nozzle which is smaller than the nozzle diameter (500 μ m) (see Figure 21).

SEM images in Figure 21 also prove that the impacted particles of the micron size have been broken into pieces on the black silicon surface. As the micro chips are meant to be placed right underneath the nozzles, measurement of the collection efficiency at the primary impaction zone is essential. In Figure 22, the local collection efficiency of the primary impaction zones of silicon has been estimated as $(17.9 \pm 1.8)\%$ for the impaction of d_{ae} of 0.92 µm fluorescent particles. It has been found < 1 % for particles with d_{ae} of 2.07, 2.53, and 3.83 µm sizes. Indeed, d_{ae} of 0.92 µm fluorescent particles have been largely deposited on the whole inspection zone (2470 µm × 1860 µm). But, the primary impaction zone has been considered ~ 0.75 mm² as the particles are highly concentrated in that area and the active surface area of the sensor is 1 mm². Although the primary zone and the ring are more distinguished on the black silicon, more experiments are needed to confirm this subtle difference. Apart from that, there is no exceptional difference observed between the behavior of Si and bSi against to d_{ae} of 0.92 µm particles.

In Figure 23, the digital microscopy images show the impaction patterns of Pseudomonas fluorescens with \overline{MAD} of $(0.66 \pm 0.01)\mu m$ and Staphylococcus epidimidis with \overline{MAD} of $(0.70 \pm 0.02)\mu m$ on the silicon surface. It can be clearly seen that the halo-shaped deposit has been formed for both bacteria. The bacteria are more concentrated in the primary collection zone (>500 μm diameter) than the ring. Indeed, the density and the diameter of the ring depending on the particle concentration and the impaction time. The black silicon surface appears black to the human eye due to its %90 of absorption at wavelengths ranging from 250 to 2500 nm (Ma et al., 2018). When the light of the digital microscope illuminates the surface, it still remains difficult to inspect the pattern. However, the SEM images inspection reveals that the bacteria are localized and concentrated in the primary deposition area (<500 μm) and it is encircled by a dispersed ring, which constitutes a halo-shaped pattern on the bSi surface.

Moreover, as it is shown in **Figure 24**, the aggregation of several bacterial cells on both surfaces makes them difficult to be counted. Therefore, the collection efficiency of bacteria has not been estimated for both surfaces. On the other hand, noticeable morphology changes in bacteria can be seen in **Figure 24**. As it has been mentioned previously, the mechanical bactericidal behavior of the black silicon surface is more likely played a role with the effect of the impaction of bacterial cells. Although this study has not been aiming to investigate the qualitative bactericidal-survival rate, some of bacterial cells on black silicon black silicon black silicon bacterial cells on black silicon black silicon

Interestingly, the impaction of Aspergillus niger spores \overline{MAD} of $(3.04 \pm 0.05)\mu m$ on the Si

surface has shown difficulties to be investigated because of the subtle visibility of the primary impaction zone. By contrast with the deposition shapes of the micron size fluorescent particles on silicon, the primary impaction zone has not exhibited a particle-free area. As seen in Figure 25, the primary impaction zone is formed by fragments of Aspergillus niger. It is clear to see that all fungi spores have left their fragments in the primary zone. Then, the particles have been found at the edge of the sample

		Silicon	Black Silicon
Fluorescent particles	(d _{ae} of 0.92 µm)	Halo	Halo
Fluorescent particles	(d _{ae} of 2.07 μm)	Halo	Primary deposit
Fluorescent particles	$(d_{ae} \text{ of } 2.53 \ \mu m)$	Ring	Primary deposit
Fluorescent particles	$(d_{ae} \text{ of } 3.83 \ \mu m)$	Ring	Primary deposit
Pseudomonas fluorescens	$(d_{ae}of0.66\;\mu\text{m})$	Halo	Halo
Staphylococcus epidimidis	$(d_{ae}of0.70\;\mu m)$	Halo	Halo
Aspergillus niger	$(d_{ae}of3.04~\mu m)$	Primary deposit (fragments)	Primary deposit

Table 6 - Deposition characteristics of the particles used in the impaction study.

(see Figure 25). Some of these particles are destroyed of which most likely contribute to the fragments in the primary impaction zone. Otherwise, non-destroyed of which probably escaped the impaction by following the air streamlines and eventually sedimented at the edge of the impaction plate. On the contrary, the impaction of fungi spores on the bSi has exhibited a localized circular deposition pattern (< 500μ m) by severely breaking the spores into fragments (see Figure 26).



Figure 20 - The impaction characteristics of fluorescent particles on silicon and black silicon surfaces



Figure 21 - SEM of the impacted fluorescent particles on silicon and black silicon surfaces.



Figure 22 - The (local) collection efficiency investigation of the various sizes of fluorescent particles on the primary impaction zone of silicon impaction surface.

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Figure 23 - Digital microscopy images of Pseudomonas fluorescens and Staphylococcus epidimidis impaction pattern clearly shows halo formations.



Figure 24 - SEM of the bacteria impaction on silicon and black silicon surfaces.





Figure 26 - SEM of Aspergillus niger impaction on black silicon reveals a localized deposition pattern and disintegrated fungi spores.



2.4.2 Discussion

There have been only a few studies discussing the reason for the deposit shapes, but it hasn't been achieved a consensus. Usually, the halo-shaped (primary deposit + ring deposit), only ring-shaped or only primary deposits (underneath the nozzle) have been observed in the impaction studies.

(May, 1975) has stated that the halo-shaped deposition patterns occur due to the hydrodynamic or Magnus effects when Reynolds number is higher than 2000 or the jet velocities exceed 60 m/s at low Reynolds number in the case of micron size test particles ($d_{50} = 3.5$ to 13 µm).

(Willeke & Pavlik, 1979) have reported ring and halo shaped deposits form as a result of vortex formations of test particles with d_{50} of ~ 2.6 µm at Reynolds number of 3140.

(Oodo, Takashima, & Hanzawa, 1981)'ve shown that the halo forms when Reynolds number is higher than 2000 in the case of micron size test particles for aerodynamic diameter of 1.10 μ m and 2.02 μ m. As they did not observe the halo when the impaction plate was coated with silicon grease at even high Reynolds numbers, the occurrence of the halo has been correlated with rebound and re-entrainment of the particles.

In another study, Stokes number variation was correlated with different deposition patterns in terms of shape and size by changing the flow rate, and therefore; by changing Reynolds number (Sethi & John, 1993). They've reported that the ring-shaped deposit forms when Stokes number is 0.47. The increase in Stokes number leads to form only primary deposits whose diameters can be as twice as smaller than the outer diameter of the ring deposits. This study has also used the aerodynamic diameter of $3.0 \,\mu\text{m}$ test particles.

(Michaud, Picard, & Baril, 1999) have observed the halo-shaped deposits in the lower stages of their impactor whose d_{50} changes from $(2.0 \pm 0.1)\mu m$ to $(0.07 \pm 0.01)\mu m$. They have stated that the halo is the reason of jet turbulence.

On the contrary, it has been documented that the impaction of aerodynamic diameter of 1.3 to 6.3 μ m test particles have exhibited a halo-shaped deposit at only lower Reynolds number of 1000, and disappeared above 1000. It has been stated that the sedimentation could be the reason of the halo-shaped deposits. Because, the impaction of larger particles formed ring deposits which are closer to the primary deposit than that of smaller particles due to the increased effect of gravity on the larger particles (Rocklage et al., 2013).

Latterly, the ring-shaped deposits in a small S/W of an impactor have been investigated for the aerodynamic diameter of 3 to 15 µm test particles (Fredericks & Saylor, 2018). The occurrence of the ring-shaped deposits has been correlated with particle inertia. Hence, internal diameter and thickness of

the rings have been stated as a function of the particle diameter.

In this study, we show that the halo-shaped and ring-shaped deposits occur due to rebound and reentrainment of the particles, depending on their size and regardless of their origin, in a lab-made single stage multiple nozzle impactor at Reynolds number of 2825 which meets the classical impactor criteria. The size (d_{ae}) of impacted test particles has varied from 0.92µm to 3.83µm, and accordingly, the deposit shapes have changed from the halo shape to the ring shape. The impaction of larger particles ultimately results in a fewer amount of deposited particles in the primary impaction zone. In the case of the largest test particles (\overline{MAD} of 3.8 µm) used in this study, almost no particle is deposited in the primary zone.

It is well known that particles can instantaneously rebound when they strike to flat and nontreated impaction surfaces. Also, they may strike to other previously collected particles, detached them from the surface, and follow the air-stream which is referred to as re-entrainment (see Figure 27). As a result, particles can bounce off either the primary impaction zone or the impaction plate.

A simplified theory of these mechanisms has been adapted from (Dahneke, 1971; Paw U, 1983) and are shown in **Figure 27**. When the particle which is accelerated along the nozzle throat, exits the nozzle, its initial kinetic energy comprises the particle mass and its initial velocity and can be shown as E_{Ki} . Then, the particle falls into the initial particle-surface potential energy well (E_{Pi}) by getting closer to the surface. If the kinetic energy of the particle before the impaction ($E_{Ki} + E_{Pi}$) is sufficient to overcome





the energy loss due to the collision (E_L) , the particle can escape the surface with the rebound energy of E_R . Otherwise it will be captured by the surface. The latter, final kinetic energy of the particle remains as E_{Kf} by climbing the final potential energy well which reaches to E_{pf} . The potential energy wells are the function of the adhesion force field between the particle and the surface which is created by Van der Waals forces. The energy dissipations originated from the compressed air layer squeezed between the particle and the surface has been suggested to be considered negligible either in a relative vacuum or in air (Paw U, 1983). Besides, the energy loss due to the collision E_L is originated from the followings: elastic and plastic deformation, internal friction, radiation of acoustic waves such as shear, compressive and Rayleigh surface waves, and flexural work (for the thin and flexible surfaces) (Dahneke, 1971). On the other hand, the particle may collide to the previously collected particle on the surface (see Figure 27). Subsequent to this collision, the impacted particle can be detached from the surface. Then, both particles can either rebound separately (in the case of large particles due to their high aerodynamic drag force) or together by attaching to each other. The latter occurs by the rolling, sliding or direct lift-off of the particles. Finally, the detached particle follows the air stream, thus it practices the re-entrainment. Besides, the re-entrainment can also occur due to turbulence that is created by the high velocity near the surface, which may overcome the adhesion force (Ibrahim, Dunn, & Brach, 2003; Ziskind et al., 1995). The rebound and re-entrainment are interactive mechanisms, thus it is difficult to assess them separately. Therefore, both mechanisms are usually referred to as the bounce effect.

In our study, the increase of the particle size leads to an increase in the initial kinetic energy E_{Ki} which more likely overcomes the energy loss due to the colision E_L . Thus, the larger particles tend to bounce off the primary zone and formed the ring shape. Although some of the large particles are also deposited in the primary zone, they can be also subjected to the re-entrainment by the following particles which impacts with a high kinetic energy. By contrast, the decrease of the particle size to d_{ae} of 0.92µm leads to a decrease in the E_{Ki} that is presumably insufficient for the particle to escape the potential well E_{Pi} which is characterized by Van der Waals forces. Thus, d_{ae} of 0.92µm particles have shown a relatively uniform deposition pattern in the primary impaction zone. But, in the case of halo, the re-entrainment mechanism may play a dominant role over the rebound mechanism due to the competition between the E_{Ki} of the incoming particle and Van der Waals force subjected previously attached particle on the smooth silicon surface. On the other hand, the sharp pillars of the black silicon surface have slowed down the impacted micron size particles by destroying them. In this case, it is difficult to distinguish which of the rebound or re-entrainment mechanism has played a more dominant role.

This study shows that the collection efficiency of the primary impaction zone is the particle of size-dependent due to the bounce effect. In the case of smooth silicon impaction surface, the local collection efficiency at the primary impaction zone (0.75 mm^2) is estimated as $(17.9 \pm 1.8)\%$ for d_{ae} of 0.92µm particles. This local collection efficiency at the primary impaction zone has been found to be less than 1% for the impaction of particles with d_{ae} of 2.07, 2.53, and 3.83 µm. Although the bounce effect looks like a serious disadvantage for the silicon-based impactor detection system at first glance, it may be utilized to separate the particles by size on the same impaction stage by placing multiple MEMS according to the deposition shapes and size.

In the present study, the black silicon surface has been used as an impaction plate to overcome the bounce effect by its nanostructured surface properties. It has not significantly changed the deposition characteristics of particles with d_{ae} of 0.92µm. However, preliminary experiments have shown that the black silicon enables to reduce the bounce effect of micron size particles used in this study and provide a confined circular deposition spot by breaking these particles into fragments. Therefore, the local collection efficiency from the particle counting cannot be demonstrated. Though porous substrates are often avoided in inertial impactors due to the penetration of the impinging jet that causes excess particle collection, which leads non-ideal collection efficiency curves, more experiments are needed to investigate this effect on the efficiency curve. Therefore, this study suggests that black silicon implemented MEMS mass sensor can be favorable for the detection of micron size particles like Aspergillus niger spores.

Next chapter focuses on the development of bulk-mode MEMS devices as mass sensing component of the developed impactor for an airborne particle detection system.

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CHAPTER 3 - Fabrication, electrical characterization, and sub-ng mass resolution of sub-µm air-gap bulk mode MEMS mass sensors for the detection of airborne particles

Among inertial mass sensors, Micro-Electro-Mechanical Systems/Nano Electro-Mechanical Systems (MEMS/NEMS) have shown unprecedented sensing performance. In recent years, bulk-mode MEMS devices have received a lot of attention, and their superior performance in comparison to their widely used counterparts such as flexural beams (i.e. cantilevers, beams) have been exploited. Usually, the microstructures (i.e. beams) have been excited to oscillate in the out-of-plane direction, and therefore the devices are subjected to severe air-damping and other loss mechanisms. Ultimately, such devices have demonstrated poor Q-factor in the air, which has led to poor signal-to-noise ratio and therefore low-performance mass sensors. Although a few attempts have been made to excite flexural beams in-plane direction in order to enhance Q-factor, it has not been achieved a remarkable outcome yet.

In order to enhance the performance and sensing properties of these structures, the approach has always been to reduce the size of the microstructures to the nanoscale. Hence, these oscillating nanostructures (so-called NEMS) have demonstrated exceptional sensing performances which have enabled the measurement of mass down to a single nanoparticle. As the goal of this work is to detect and perform uniform mass measurements of sub-µm and micron size airborne particles, the proposed ultrasensitive nano scale systems ultimately fail to achieve this task. On the other hand, longevity is a critical characteristic of an airborne particle sensor, which ultimately enables reliable and long-term exposures. To meet the requirements of aerosols and bioaerosols detection and real-time mass measurements; therefore, a highly sensitive, high signal-to-noise, and large surface area in-plane MEMS sensors are needed.

Bulk-mode MEMS sensors do not only successfully meet abovementioned criteria thanks to their unprecedented Q-factor, high resonance frequency, reasonable noise floor, and tunable surface area, but also provide different fundamental deformation modes such as Lamé mode, the extensional mode, and the shear mode. These specific deformation modes show the nodes and antinodes of the sensor surface which are indicating the minimum and maximum vibration amplitude distribution, respectively on the resonating

body. Unlike all the proposed inertial mass sensors, the deformation modes, and thus the vibration amplitude distribution of bulk-mode MEMS sensors is believed to be relatively homogeneous which ultimately separate this type of sensors from the others for accurate and uniform mass measurements. Likewise, bulk-mode MEMS sensors can be actuated in several ways such as electrostatically, piezoelectrically, or electrothermally. Owing to the fact that electrostatically actuated devices are less complex to fabricate, these devices can also be made by silicon, and therefore they are well-characterized. Furthermore, the tunable silicon surface of these devices allows one to accomplish functionalization which is utterly compatible with microfabrication tools and can tune the surface both chemically by changing the surface hydrophobicity and physically by creating micro/nanostructures such as black silicon. As a result, functionalized, highly sensitive, and bulk-mode MEMS sensors can be fabricated based on silicon technology, which makes them fully adaptable to the integrated circuits (IC) that leads to integrating the sensors into our daily used electronics.

A prerequisite to integrate MEMS sensors into IC, low-power consumption and low-motional resistance are needed. To achieve this challenging objective in electrostatically actuated MEMS, either the actuation gap between the electrode and resonator should be filled with a high k-dielectric material or the gap should be reduced. In this context, we propose to realize high-performance inertial bulk-mode MEMS mass sensors by the thick oxide as a mask layer fabrication technique. The objective of this chapter is to describe the elaboration of bulk-mode MEMS mass sensors which is to be coupled with the developed impactor for a real-time aerosol and bioaerosols detection and mass measurement system.

In this chapter, we first present the working principle of the electrostatic actuation, performance characteristics, and design considerations of the microbalance. Then, optimization of the microfabrication process will be followed by the electrical characterization and the proof-of-concept mass measurement.

3.1 Bulk-mode MEMS resonators: A high-performance nanobalance

Based on airborne particle detection capabilities of micro sensors, typical acoustic wave inertial mass sensors such as the Surface Acoustic Wave (SAW), the Film Bulk Acoustic Resonator (FBAR), and the Quartz Crystal Micro/nanobalance (QCM/N) sensors show lack of mass sensitivity and uniformity as described in Chapter 1. However, resonant MEMS inertial mass sensors show promising sensitivity and could be relevant alternatives to typical acoustic wave mass sensors for low and relatively uniform, and therefore accurate mass measurements.

Among MEMS devices (torsional modes, flexural modes etc.), bulk-mode single-crystal silicon (SCS) MEMS resonant devices have demonstrated unprecedented Q-factor, high resonance frequency, and tunable surface area (Hao, Abdolvand, & Ayazi, 2006) (J. E.-Y. Lee, Zhu, & Seshia, 2008) (Pourkamali & Ayazi, 2004). Moreover, electrostatically actuated and capacitively transduced bulk-mode SCS MEMS resonators show sensitive and relatively uniform mass measurements (Cagliani & Davis, 2011).

Unlike typical acoustic wave resonators, when MEMS resonators are excited at frequencies corresponding to the induction of acoustic wave propagation, they are subjected to the deformation in different ways such as bending, twisting, or expanding (Campanella, 2010). Particularly, bulk-mode MEMS resonators are characterized by in-plane deformation of the structure through symmetric planar expansions or contractions in their fundamental modes such as Lamé mode, extensional mode or shear mode. By contrast, flexural or torsional modes of MEMS structures are subjected to high loss mechanisms and ultimately demonstrating poor device performance. Furthermore, the deformation mode reveals the location of nodes and antinodes of the resonator surface. Therefore, the modes exhibit the most sensitive parts of the sensor surface, which is critical for mass sensing applications. These bulk-mode devices can be characterized by the developable large surface area that is vital for the longevity and sensitivity of an airborne particles micro sensor, without compromising on the device performance. For example, the resonant frequency of bulk mode resonators is not dependent on the thickness of the device. On the one hand, thick resonators result in an increased area for electrostatic transduction that ultimately reducing the motional resistance in capacitively-transduced resonators. On the other hand, relatively large and thick resonators should potentially show more resistivity against harsh ambient conditions such as high wind speed and pressure. Although MEMS sensors are meant to be encapsulated in the cleanroom conditions, the sensors are ultimately subjected to high flow rates in order for sampling. Thus, thicker resonators are required to enhance the resistivity against air-flow originated pressure. Therefore, the fabrication method of structures should facilitate high-aspect ratio sensors.

In electrostatically actuated and capacitively-transduced MEMS resonators, reducing

resonator-to-electrode gaps (i.e. air-gaps) lead to increase the capacitive electromechanical coupling. As a result, a high signal-to-noise ratio and low equivalent motional impedance can be obtained.

3.1.1 Electrostatic actuation and capacitive detection

The actuation and detection of MEMS inertial mass sensors have been performed electrostatically and capacitively, respectively. The theoretical actuation mechanism has been illustrated in Figure 28. A polarization DC voltage (V_p) and an alternating voltage (V_{in}) are applied to one of the electrodes facing the resonator. The frequency (ω) of applied alternating voltage $V_{in}(t) = V_{AC}sin(\omega t)$ is used to excite the resonator to a resonance frequency by matching ω and ω_o at mechanical resonance of the resonator. The applied voltages induce a periodic electrostatic force so-called the actuation force and can be defined as:





$$\vec{F} = -\overline{grad}(W_{electrostatic}) \tag{16}$$

Where $W_{electrostatic}$ is the electrostatic energy and can be shown as:

$$\vec{F} = -\overline{grad}(\frac{1}{2}CU^2) \tag{17}$$

Where U is the applied voltage between the two electrodes, which leads to:

$$F_x = -\frac{1}{2}\frac{dC}{dx}U^2$$
, and thus $F_x = \frac{1}{2}\frac{dC}{dx}(V_p + V_{in})^2$ (18)

Where V_p is the polarization DC voltage, V_{in} (t) is the alternating voltage and equals to $(V_{AC}sin(\omega t))$, and the $\frac{dC}{dx}$ can be defined as a change in the resonator-electrode capacitance per unit displacement. The capacitance between the resonator and the electrode can be presented by the parallel plate model which assumes a uniform generated electric field within the gap and shown as follows:

$$C(x) = \frac{\varepsilon_r \varepsilon_0 W_e h}{d_0 - x(t)} \tag{19}$$

Where \mathcal{E}_0 and \mathcal{E}_r are the permittivities of space and the gap, respectively, W_e is the width of the electrode, h is the thickness of the electrode, d_o is the gap distance between the resonator and electrode, and x is the small displacement (as a function of time) as a result of the actuation and can be avoided. When the partial derivative of $\frac{dC}{dx}$ is taken and substitute into Eq. 18 by taken the conditions of $V_{AC} << V_p$ and $x << d_o$ into the account, the electrostatic force can be assumed as follows:

$$F_x(t) \approx \frac{\varepsilon_r \varepsilon_0 W_e h}{d^2_0} V_p V_{in}(t)$$
⁽²⁰⁾

Thus, the transduction factor or electromechanical coefficient can be presented as follows:

$$\eta = \frac{\varepsilon_r \varepsilon_0 W_e h}{d^2_0} V_p \tag{21}$$

Where η represents electrostatic transduction coefficient. Hence, the electrostatic force F_x can be deduced as follows:

$$F_x = V_{in} \times \eta \tag{22}$$

As it is vital to increase the transduction factor to enhance the signal-to-noise ratio, several approaches such as reducing the air-gap or replacing the air-gap to a high-k dielectric material, and increasing the applied DC voltage have been typically used to enhance the transduction principle. As shown in **Figure 28**, while a combination of AC voltage (V_{in}) and DC voltage (V_p) has been applied on an excitation electrode, the resonator is statically charged due to the applied polarization voltage. When the electrostatic force is adequate to induce a periodic vibration of the resonator due to the applied AC voltage, the capacitive gap between the electrode and the oscillating resonator is changed, and results in modulation of the output capacitance which generates an output current as referred to motional current (i_m) that can be sensed through one of the anchors. The amplitude of this motional current is proportional to the displacement of the resonator which is altered by the quality factor.

Whereas the vibration amplitude of the resonator goes to the maximum at its mechanical resonance frequency, the motional current with the same resonance frequency and maximum amplitude is obtained. It should be noted that the electrostatic transduction coefficient can be increased by using two counter electrodes as excitation electrodes that results in a higher motional current. Indeed, the motional current flowing through the anchor can be defined as follows:

$$i_m = \frac{d}{dt} \left(C(t)U \right) = \frac{d(C(t)(V_P + V_{in}(t)))}{dt}, \text{ and thus } i_m(t) = \frac{dC}{dt}U + C\frac{dV_{in}}{dt}$$
(23)

When $V_{AC} << V_p$, the following can be obtained:

$$i_m(t) = \frac{dC}{dt} V_P + C \frac{dV_{in}}{dt}$$
(24)

The output current of the resonator comprises two contributors. The first one is $(C \frac{dV_{in}}{dt})$ capacitive current due to the presence of static and parasitic capacitances. The latter is the motional current and can be defined as follows:

$$i_m = \frac{dC}{dt} V_P = \left(\frac{dC}{dx}\frac{dx}{dt}\right) \times V_P \tag{25}$$

Which occurs due to the resonator displacement. Then, the motional current can be further defined as:

$$i_m = \frac{\varepsilon_r \varepsilon_0 W_e h}{d_o^2} V_P\left(\frac{dx}{dt}\right)$$
, and thus $\frac{dx}{dt} = \frac{i_m}{\eta}$ (26)

Analogously, this mechanism can be modeled as a classical damped Single-Degree-of-Freedom (SDOF) oscillator which is excited by a periodic harmonic force that is varying sinusoidally in time. The damped SDOF system can be solved by using Newton's second law of motion (see Figure 2) and can be derived as follows:



Figure 29 – A mechanical model of the MEMS resonator is shown as a damped spring-mass harmonic system (left) and simplified equivalent electrical RLC circuit of the resonator.
$$m_{eff}\left(\frac{d^2x}{d^2t}\right) + \gamma\left(\frac{dx}{dt}\right) + k_{eff}x = F(x)$$
⁽²⁷⁾

where m_{eff} is the effective mass, γ is the effective damping coefficient, and k_{eff} is the effective spring constant, under the time-varying effective force F(x) which is externally applied to the MEMS resonators and can be originated by piezoelectrically, electrothermally or electrostatically. In electrostatic actuation, the differential equation can be rewritten by using Eq. 22 and 26:

$$\frac{m_{eff}}{\eta}\frac{di_m}{dt} + \frac{\gamma}{\eta}i_m + \frac{k_{eff}}{\eta}\int i_m = \eta V_{in}$$
⁽²⁸⁾

$$\frac{m_{eff}}{\eta^2}\frac{d^2i_m}{dt^2} + \frac{\gamma}{\eta^2}\frac{di_m}{dt} + \frac{k_{eff}}{\eta^2}i_m = \frac{dV_{in}}{dt}$$
(29)

Then, the differential equation of a series RLC circuit can be written as follows:

$$L_m \frac{d^2 i_m}{dt^2} + R_m \frac{d i_m}{dt} + \frac{1}{c_m} i_m = \frac{d V_{in}}{dt}$$
(30)

The RLC circuit consists of a motional resistance (R_m) , a motional inductance (L_m) , and a motional capacitance (C_m) , which are defined as:

$$R_m = \frac{\gamma}{\eta^2} = \frac{\sqrt{k_{eff}m_{eff}}}{Q} \frac{d_0^4}{(\varepsilon_r \varepsilon_0 W_e h V p)^2}, \quad C_m = \frac{\eta^2}{k_{eff}} = \frac{(\varepsilon_r \varepsilon_0 W_e h V p)^2}{k_{eff} d_0^4}, \quad L_m = \frac{m_{eff}}{\eta^2} = \frac{m_{eff} d_0^4}{(\varepsilon_r \varepsilon_0 W_e h V p)^2}$$
(31)

In this model, the equivalence of the mechanical components is shown electrically as follows: the damper is the resistance, the mass is the inductor, and the spring is the capacitance. The latter leads to a time-varying electrostatic force and the electrical equivalence circuit (transformers have been excluded for the sake of simplicity) can be shown as in **Figure 29**. The basic resonating RLC electrical circuit is usually used in the most MEMS resonators in order to assess the mechanical resonance of the resonators. The applied V_P is to charge the electrode-resonator capacitance and therefore, its absence utterly impedes the output motional current.

Moreover, as it is depicted in **Figure 29**, the capacitive parasitic current (i_f) often significantly contributes to the total current (i_s), in turn, it can mask the motional current. As a result, the detection of the resonance signal essentially can be hindered. This current can be originated from the direct overlap capacitance of the transducer, capacitive coupling through the substrate interconnects, and the electrical package where the chip is mounted (J. E. -Y. Lee & Seshia, 2009b). Therefore, several approaches have been proposed to eliminate the feedthrough current by using different actuator and detection techniques such as one-port, two-port, 2^{nd} harmonic, mixing, piezoresistive sensing, and 2^{nd} harmonic drive with piezoresistive sensing that enable high motional signal to feedthrough current ratios (Lin, Lee, Yan, & Seshia, 2010). Otherwise, using a single-to-differential drive amplifier at the input of the resonator (+Vp, -Vp) which produce an anti-phase output signal in comparison to the input of the resonator. Then, the large feedthrough capacitor (C_f) builds a parallel

connection to the resonator, therefore the anti-phase output signal (i.e. feedthrough compensation) can eliminate the feedthrough current (i_f) (J. E.-Y. Lee et al., 2008). Thus, when the resonator vibrates at its resonance frequency where the vibration amplitude reaches its maximum, the pure motional AC current with the same resonance frequency can be detected. The motional current can be calculated by taking Eq. 30 and substitute into Eq. 31 and can be shown as:

$$i_m = \frac{V_{in}}{R_m} = \frac{d_0^4 \sqrt{k_{eff} m_{eff}}}{Q \ \varepsilon_0^2 \ \varepsilon_r^2 \ V^2_p \ A^2_e}$$
(32)

Where *A* is the effective area of the electrode and *Q* is the quality factor of the resonator. It is revealed in **Eq. 32** that the high motional current and the low motional resistance can be facilitated by adjusting the structural parameters of the MEMS resonator and strongly dependent (4th order) on the distance between the resonator-to-electrode (d_0). Also, the higher *Q* the lower the motional resistance.

3.1.2 Quality factor

The resonant behavior of the damped mass-spring system, and therefore the MEMS resonator can be solved in the permanent regime. When we also consider the RLC circuit and its equivalent mechanical model as described in Eq. 29 and 30, *Q*-factor can be then defined for the RLC circuit equal to $\frac{L_m \omega_0}{R_m}$, and it is defined as $Q = \frac{m_{eff} \omega_0}{\gamma}$ for the mechanical system. The latter, RLC circuit can be rewritten as follows:

$$(-L_m C_m \omega^2 + j R_m C_m \omega + 1)\underline{im} = j \omega C_m V_{AC}$$
(33)

Where ω the voltage pulsation (i.e. angular frequency) and i_m is the complex amplitude of the current and can be shown as:

$$i_m = \left|\underline{Im}\right| = \frac{V_{AC}}{R_m \sqrt{\left(\frac{\omega_o}{\omega} - \frac{\omega}{\omega_o}\right)^2 Q^2 + 1}}, \text{ and thus } \frac{V_{AC}}{R_m} = \frac{1}{R_m \sqrt{\left(\frac{\omega_o}{\omega} - \frac{\omega}{\omega_o}\right)^2 Q^2 + 1}}$$
(34)

Where we have used the natural pulsation as $\omega_0 = \sqrt{\frac{1}{L_m C_m}}$ and $Q = \frac{L_m \omega_0}{R_m}$ for corresponding replacements in Eq. 33. We may also define $\omega_0 = \sqrt{\frac{k_{eff}}{m_{eff}}}$ and $Q = \frac{\omega_0 m_{eff}}{\gamma}$ according to Eq. 31. When the pulsation is equal to the natural pulsation (see Figure 30), the motional current is maximum and equal to $\frac{V_{AC}}{R_m}$. Since $\omega_0 = 2\pi f_o$, the resonance frequency of the system can be defined as follows: $f_n = \frac{n}{2\pi} \sqrt{\frac{k_{eff}}{m_{eff}}}$ (35)

Where f_n is the *n*th mode resonance frequency. As seen in Eq. 35, a decrease in the effective mass of the moving body or adding a mass leads to an increase in the resonance frequency (i.e. resonance

frequency shift). On the other hand, γ implies the amount of damping that the system has been subjected and can be shown as:

$$\gamma = \frac{2\pi m_{eff} f_n}{Q} \tag{36}$$



Figure 30 - A measured resonance curve demonstration when $(\omega_0 = \omega)$ showing the full width at half maximum ω_{fwhm} is equal to γ .

Thus, when the resonator vibrates at the resonance frequency, the maximum energy is stored in the system. Due to losses, the oscillation amplitude is spread over a bandwidth at the half of the maximum $\gamma = |w_1 - w_2|$ around ω_o , and therefore *Q*-factor defines the sharpness of the resonance response (see Figure 30). Hence, it makes the definition of the Eq. 36 equivalent to the following as shown previoulsy:

$$Q = \frac{m_{eff}\omega_o}{\gamma} \tag{37}$$

Half power $\left(\frac{Pmax}{2}\right)$ bandwidth method (or $\frac{imax}{\sqrt{2}}$ in the case of i_{max} as $\left(\frac{imax}{\sqrt{2}}\right)^2 \times R = \frac{Pmax}{2}$) or can be referred to -3dB (i.e. $Q = f_0 / \Delta f_{-3dB}$) method as the output amplitude (unit of decibel) drops to its

peak value divided by $\sqrt{2}$ which approximately corresponds to -3dB (or 0.707 of i_{max}) is the most widely used method to determine the Q-factor in MEMS sensors. However, when the signal-to-noise ratio or the damping is low, the accuracy of the Q-factor estimation substantially reduces due to the difficulty to find the half power points at both sides of the resonance peak. Thus, there have been several alternatives approaches such as a peak in imaginary plot and zero in real plot, frequency response function-Lorentzian curve fit, frequency response function—resonance curve area method, and Nyquist plot circle fit method proposed (Logeeswaran, Tay, Chan, Chau, & Liang, 2003). Finally, the quality factor of the system can also be defined as follows:

$$Q = 2\pi \times \frac{\text{maximum energy stored in one cycle}}{\text{energy dissipated per cycle}}$$
(38)

In our study, we have obtained output signal as impedance versus resonance frequency. Then, the real part of the impedance value which is proportional to the motional resistance of the resonator has been extracted and mathematically compensated (nulling the capacitive parasitic current) as it is subjected to the feedthrough capacitance. The latter, maximum of the real part of the impedance has been used to estimate the Q-factor with the Δf_{3dB} method as shown in Figure 30 by using a script which automatizes quality factor extractions from the resonance peaks.

Several loss mechanisms have been identified to cause a reduction to the Q-factor in the MEMS sensors. The total loss is the sum of the individual loss mechanisms which are estimated individually. The total loss is shown as $\frac{1}{Q_{total}}$ because the lowest Q-factor represents the dominant loss mechanism and can be shown as follow:

$$\frac{1}{Q_{total}} = \frac{1}{Q_{air}} + \frac{1}{Q_{surface}} + \frac{1}{Q_{TED}} + \frac{1}{Q_{anchor}} + \frac{1}{Q_{others}}$$
(39)

Each loss mechanisms are shown in Eq. 39 has been widely studied for a variety of shape and mode of MEMS resonators. The losses due to the air damping (Q_{air}) are generated by the collision of the surrounding air with the vibrating resonator. The Q_{air} consists of viscous damping which removes the air around the resonator, acoustic radiation and squeezed-film damping which occur when the resonator vibrates out-of-plane. By operating the resonator under vacuum, the air damping can be avoidable. It also can be significantly reduced in the case of in-plane vibration of the resonators. The $Q_{surface}$ related losses are dependent on the surface-to-volume ratio. Therefore, it is negligible for bulk-mode MEMS resonators, but it can play a significant role to reduce the quality factor in NEMS resonators. Additionally, it should be mentioned that it can be also originated from the roughness, contaminates, and etching residues and contribute to the total loss in bulk-mode MEMS resonators. The thermo-elastic dissipation (Q_{TED}) occurs due to the intrinsic properties of the material by the coupling between the elastic field in the structure caused by deformation and the temperature. It has been shown that it is a dominant loss mechanism in thick and long cantilevers (i.e. flexural beams) as opposed to bulk-mode resonators since their volume is preserved during the in-plane vibration. Therefore, it has been widely studied and shown that the bulk-mode resonators have demonstrated Qfactors exceeding 1 million in vacuum (J. E. -Y. Lee & Seshia, 2009a). The losses due to the anchors (Q_{anchor}) have been proven to be a dominant loss mechanism for bulk-mode resonators operating in vacuum. The vibration energy of the resonators is dissipated through elastic propagation of waves through the anchors to the substrate and the environment. As this irreversible flow of the energy from the resonator causes a stress in the anchors where the structure is clamped by a beam to the substrate, there have been alternative designs such as t-shaped anchors instead of straight beams in order to split the stress aiming to enhance the Q-factor in the bulk-mode MEMS resonators (Campanella, 2010) (Xu & Lee, 2012) (Joshua E.-Y. Lee, Yan, & Seshia, 2011), (Khine & Palaniapan, 2009), (Khine, Palaniapan, & Wong, 2007).

Usually, the figure of merit for MEMS resonators is defined as the product of resonance frequency and the Q-factor (i.e. $f \times Q$). To realize a high performance MEMS resonator ultimately leads to a highly sensitive inertial MEMS mass sensor. As a matter of fact, this study has focused on reducing the air-gap to decrease the motional resistance and the operating voltage and increase the motional output current. Thereby, it aims to result in an improved signal-to-noise ratio which is essential to maintain a reasonable noise floor that leads to a highly sensitive MEMS mass sensor.

3.1.3 Design consideration

To achieve a highly sensitive and long-term exposure capability of a bulk-mode MEMS mass sensor, the designed sensor should enable to perform a mass measurement of a low concentration of aerosol and bioaerosols to a high concentration of airborne particles without the saturation of the sensor. Essentially, high-performance MEMS sensors are needed and can be attained by the realization of in-plane bulk-mode resonators which are capable of demonstrating high-Q factor in the air due to the reduced air damping.

Another characteristic of these MEMS is to be able to obtain high resonance frequencies (>MHz) which result in sensitive mass measurements. Moreover, the architecture of the MEMS can be designed in a way that the high signal-to-noise ratio can be obtained by reducing the air-gap and designing the electrodes all around the resonator in order to enhance the electrostatic transduction.

While the large active surface area $(\geq 1mm^2)$ of the resonators are suitable for long-term exposures in sensing applications, tuning the thickness of the resonator without compromising the device performance open the way for fabricating robust sensors against to high flow rate which is essential for an airborne particle detection system. In order to realize such a sensor, high-aspect-ratio

should be maintained between the resonator and the air-gap. However, the conventional optical photolithography has shown a critical resolution of $\geq 1 \mu m$ which hinders to achieve this goal. The following section demonstrates the effort to fabricate and develop high-aspect-ratio bulk-mode MEMS mass sensors with a thick oxide mask layer gap reduction method that aims to improve this critical limit down to sub- μm .

3.2 Thick oxide mask layer gap reduction method

The reducing the air-gap to sub-µm or sub-100 nm regime is essential to efficiently operate capacitively actuated MEMS resonators. However, the optical lithography method is limited to define the structures in sub-µm resolution. Therefore, several gap reduction methods have been extensively documented. Although some of which have successfully reduced the gaps even down to sub-100nm (i.e. nanogap), all the proposed methods either required the electron beam lithography (e-beam lithography) which has a sub-10nm resolution or multiple etching and deposition layers which lead to complex and high-cost fabrication processes. Single-mask thick oxide as a mask layer gap reduction technique has been previously proposed and enabled to reduce the resonator-to-electrode gaps to sub-µm with the optical lithography in capacitively transduced MEMS resonators (R. Abdolvand & Ayazi, 2006). Although this fabrication technique has not received a lot of attention in the literature yet, it substantially reduces the fabrication cost, complexity, and eliminates the need of removing sacrificial layer, whose thickness usually defines the size of the gaps (N. D. B. Ciressan, Hibert, Mazza, & Ionescu, 2007) (Pourkamali & Ayazi, 2003). The details of this fabrication method are explained hereinafter.

The thick oxide mask layer technique requires a well-characterized selective Deep-Reactive-Ion Etching method (DRIE) in order to achieve high-aspect ratio suspended structures. A method of anisotropic plasma etching of silicon to obtain high-aspect-ratio structures, as referred as Bosh process, has been developed and widely used in MEMS field (US5501893A, 1996). Typically, this method comprises physical-chemical etching and consecutive etching and passivation steps as shown in **Figure 31**. Sulfur hexafluoride (SF₆) ions are used to perform etching vertically which is followed by deposition of a passivation layer (i.e. Teflon) by oxygen plasma to prevent further etching and maintaining protection. Although the passivation layer prevents the sidewalls etching in the subsequent etching step, the passivation layer at the bottom is etched faster than the sidewalls due to the additional directional ions which lead to anisotropic etching (physical etching). However, the isotropic (chemical) etching is dominant at the bottom of the trench. As a result of numerous repetition of this cycle leads to deep vertical trenches all the way down in silicon wafer. Thus, a high-aspect ratio Bosh recipe should be defined for the DRIE method in order to attain deep vertical trench profiles and smooth sidewall roughness.

Ultimately, this gap reduction technique requires thick oxide as a mask layer to sustain durable and selective DRIE processes. Furthermore, a thick oxide layer also determines the final gap size by the openings of oxidized features. It has been shown that the gap aspect-ratio has been achieved as high as 60:1 with this proposed technique (R. Abdolvand & Ayazi, 2006). Nevertheless, 18 µm thick SCS bulk mode MEMS resonators with a gap aspect-ratio>130 have also been achieved by using high aspect-ratio combined poly and single-crystal silicon (HARPSS) technique (Pourkamali & Ayazi, 2004). In this method, a sacrificial oxide layer determines the gap size while the highly doped



Figure 31 – A schematic of the BOSH process is indicating the passivation of protection polymer layer and following etching step (Ertl & Selberherr, 2010).

polysilicon layer determines the electrodes (Ayazi & Najafi, 2000). However, relatively simple, single-mask, and low-cost thick oxide mask layer technique should be developed to employ high aspect-ratio resonators with reduced air-gaps. This study aims to reduce the air-gaps down to sub-µm with thick oxide mask layer technique which utilizes the conventional optical lithography for the fabrication of bulk-mode square-shaped MEMS mass sensors.

In the following, the fabrication and optimization of high aspect ratio test structures will be presented in order to emphasize the critical encountered issues in this fabrication method. Next; the design, the fabrication, the electrical characterization results, and the mass measurement as a proof of concept are presented.

3.2.1 High aspect ratio test structures optimization

Test structures have been used to optimize the relevant parameters of small gap fabrication. Firstly, a thin stoichiometric silicon nitride layer (~100 nm) has been deposited on a silicon wafer by Low-Pressure Chemical Vapor Deposition (LPCVD), which is followed by a polysilicon layer deposition (~1 μ m thick) by LPCVD (**Figure 32**). Subsequently, the designed test structures, whose feature sizes (distance between each pattern) vary from 1 μ m to 25 μ m, is defined by optical lithography. Then, the polysilicon layer is etched by Reactive Ion Etching (RIE) in order to reveal the patterns (**Figure 32**). The etched polysilicon features are thermally oxidized in an oxidation furnace at 1100°C for 3h to obtain a ~1.2 μ m thick oxide layer (**Figure 32** - III). Due to the silicon nitride layer,



Figure 32 – Schematic of the optimization process flow. SEM images show before and after ~1.2 μ m oxidation of an initially ~ 1.7 μ m spaced (after RIE etching) features.

only the sidewalls and top of the polysilicon patterns are oxidized, and therefore the gap between two subsequent features is reduced to sub- μ m. Finally, we have used a high-aspect ratio DRIE recipe (see **Table 7**) and performed the etching all the way down in the silicon wafer (**Figure 33**).

Following the RIE process, the initial opening size has been measured in the polysilicon layer in order to determine the required thickness of the grown oxide. Several openings from ~450 nm to ~750 nm have been obtained by growing ~1.2 μ m oxide on different polysilicon patterns whose initial width vary from 1 μ m to 25 μ m. The initial opening is measured as ~ 1.7 μ m from one of the 1 μ m consecutive gap features. The non-uniform openings across the wafer are due to the resolution limit of photolithography that leads to the variations in the oxidized gaps. As the DRIE rate depends on the opening size, the depths vary from one to another consecutive feature as shown in Figure 33-34.

The highest aspect ratio has been obtained as ~70:1 as shown in Figure 33. As the aspect ratio for the same openings is slightly different, the ~ 71:1 gap aspect ratio has been determined by taking the trench whose width ~ 466 nm and the ~ 33 μ m trench depth in Figure 33. When a high aspect ratio and vertical sidewall etching of DRIE recipe is well characterized, the aspect ratio is limited by the thickness of the oxide layer that serves as a mask layer for the selective DRIE process. As shown in Figure 33-34, the oxide layer has successfully resisted prolonged DRIE processes. In

Table 7 – DRIE silicon etching parameters

High-aspect-ratio DRIE parameters			
Parameter	Unit	Value	
Etching/Passivation	second	5/2	
Flow rate: SF_6/O_2	sccm	300/150	
Pressure	Pa	4	
Source Power	Watt	1800	
LF Platen Power	Watt	90	
Temperature	°C	20	



Figure 33 – SEM images of as small as ~ 465 nm wide trenches with an aspect ratio of ~70:1. The inset magnifies the bottom of the trenches.

order to obtain uniform structures across the wafer, it is crucial to take the limitations of optical lithography into the account. Therefore, the initial air-gaps have been designed as 2 μ m and 1.8 μ m which can be well defined by photolithography and uniformly patterned across the wafer for the fabrication of the MEMS. Although the large feature sizes result in uniform patterning, it requires longer oxidation processes for the gap reduction which increases the fabrication cost. However, the thick oxide layer can sustain longer to DRIE process, and the high aspect ratio can, therefore, be obtained. The trade-off between the oxide thickness and the required etching depth leads to optimization of the air-gap. As a result, this method should potentially enable high-yield batch fabrication of the designed sub- μ m air-gap resonators.



Figure 34 – SEM images of as small as \sim 484 nm wide trenches with aspect ratio \sim 42:1. The inset magnifies the bottom and the top of the trenches.

3.3 Elaboration of sub-µm air-gap bulk mode MEMS resonators

As the fabrication process (4-masks process) and the critical dimensions have been optimized, various type of MEMS resonators have been designed in Coventor software. The design of 1 mm² square-shaped resonators are differentiated and mainly focused on the initial electrode-to-resonator gap size, the anchor length, and the architecture of the electrodes one of which render only the 2nd modes of the desired deformation modes. The major goal of this study is to experimentally optimize the air-gap, electrical measurement set-up, and deformation modes, and to determine the minimum mass sensing capability of the fabricated bulk-mode resonators operating different deformation modes.

3.3.1 Design and simulations

As highlighted in Chapter 2, the design of a bulk-mode MEMS mass sensor is not only depending on its performance criteria but also design considerations of the impactor which constructs a detection system altogether with MEMS. The impactor consists of 10 circular nozzles each of which is 500 μ m diameters due to the fact that the surface area of the MEMS resonator has been priorly suggested as 1 mm². The length is the only dimensional parameter for a bulk-mode MEMS resonator

to determine its fundamental bulk-mode resonance frequencies. Hence, $1 \text{ mm} \times 1 \text{ mm}$ sized resonators ultimately lead to an operating resonance frequency of desired deformation modes of Lamé mode, extensional mode, and shear mode lower than 10 MHz for bulk-mode MEMS devices. This operation frequency inhibits detachment and provides a relevant mass measurement of Aspergillus niger spores as theoretically predicted, and it has been suggested that highly sensitive and relatively uniform mass measurements may be carried out using square resonators operating in Lamé and extensional modes (Berthelot, Algré, Moularat, Robine, & Gehin, 2015). It has also been documented extensively that in-plane bulk-mode MEMS demonstrate deformation modes which result in high-Q factor in the air. Moreover, thickness independent frequency tuning enables one to optimize the resonator thickness as respect to the resistance against 1 LPM.

The resonator (see **Table 8** and **Figure 37**) is designed to detect sub-µm to a few micron size biological and non-biological airborne particles and to resist airflow during sampling as emphasized in **Chapter 2**. The deformation modes have been simulated in COMSOL. The t-shaped anchors which consist of tethers and anchor beams have been optimized and placed at the edge of the resonator in order to minimize the energy loss in Lamé mode, thereby attaining a high-quality factor. As it is known that the anchor loss is the dominant loss mechanism (Khine et al. 2007), anchors of the resonator have been designed to be feasible for highly sensitive and low power consumption mass sensors (see **Figure 35**). Ultimately, dimensions of the tether and width of the anchor beams were kept constant assuming that the large widths and short beam lengths result in higher air flow resistance in according to the classical bending stress approximation of a one end free silicon beam which can be as shown in **Figure 35-36** and described as:

$$\sigma_{max \ stress} = \frac{M_y \times \frac{L}{2}}{l} \tag{40}$$

Where M_y the bending moment of neutral axis, $\frac{L}{2}$ is the distance from the neutral axis (length), and *I* is a moment of inertia equal to $\frac{bh^3}{2}$, where *b* is the width and *h* is the thickness of the silicon beam. Then, the following equation in which resistance to flow rate (R_Q) is estimated and derived based on **Eq. 40**.

$$R_Q = \sqrt{\frac{Sb \times b \times h^2 \times \sigma_{max \ stress}}{3 \times L^2 \times \rho_o}} \tag{41}$$

Where we have used $P_{pressure} = \frac{\rho_o}{2} \times \left(\frac{R_Q}{S}\right)^2$ is the air-flow rate, *Sb* is the surface area of the beam, and ρ_o the density of air-resistance. The tensile yield stress of single crystal silicon has been taken as 6900 MPa (Petersen, 1982). Accordingly, a rough estimation has been done considering that each MEMS device will be subjected to 1 LPM air-flow at one of its anchors, which reflects the worst case



Figure 35 – SEM image of the MEMS indicates the tethers and the anchor beam (Left). Schematic of a one-end rigidly fixed and the other end suspended and bendable cantilever which is subjected to air flow.

scenario (see Figure 36). Because the t-shaped beams have been used as anchors that ideally increases the resistivity due to increased moment of inertia, and each resonator is delivered 1 LPM and is clamped from its 4 corners which should alleviate the flow resistance on each anchor. On the other



Figure 36 - Graph shows the estimation of the anchor length as a function of the maximum flow rate.

hand, the pressure induced by the impactor on each chip is to be experimentally determined and will contribute to the total pressure on the anchors. Besides, the microbalance thickness, and therefore the anchor thickness is 40 μ m while the anchor width is fixed as 56 μ m. As shown in Figure 36, the minimum resistible flow-rate has been estimated as 2.86 LPM for the design of the longest anchor length (169 μ m), which enables the sensor to be used as an impaction plate in the developed impactor.

Further to that the length of anchor beams were varied from 28 µm to 169 µm, and referred as short and long beams within the manuscript. The aim is to compensate the desired air flow resistance of the resonator and low energy losses at the nodes to obtain high signal-to-noise ratio at low operating voltages (Khine & Palaniapan, 2009). By contrast to Lamé mode, the tether design alters the quality factor and resonance frequency significantly in extensional mode. The stress imposed in tethers is not pronounced for Lamé mode as the resonator is clamped at the nodes (Xu & Lee, 2012). As shown in **Figure 37** in Lamé mode, shear waves are predominate over longitudinal waves and direction of motion as expansion and contraction are equal in one axis and the orthogonal axis, therefore the volume of the structure is preserved. The extensional mode can also be defined by longitudinal waves that are symmetrically contracting and extending the resonator in four directions. The resonance frequency of Lamé mode and the extensional mode can be estimated as follows (Khine et al., 2007), (Reza Abdolvand, Bahreyni, Lee, & Nabki, 2016):

$$f = \frac{1}{\sqrt{2L}} \sqrt{\frac{G}{\rho}} \quad and \quad f = \frac{1}{2L} \sqrt{\frac{E}{\rho}}$$
(42)

$$G = \frac{E}{2(1+\nu)} \tag{43}$$



Figure 37 – COMSOL simulation results of designed square resonators. (Left) The simulated resonance frequencies of 1st and 2nd Lamé mode are 4.1289 MHz and 8.2624 MHz, respectively. The 1st and 2nd extensional modes are 4.5880 MHz and 12.835 MHz, respectively. (Right) One of the flexural modes of the resonator (top and side-view) is at 0.1394 MHz. The red arrows indicate the direction of the movement.

Where f is the resonance frequency, L is the length of the resonator, G is the shear modulus, E is the Young's modulus, ρ is the density, and ν is the Poisson's ratio. As shear waves are predominant over longitudinal waves in Lamé mode and longitudinal waves are predominant over shear waves in extensional mode, the stiffness is defined by shear modulus in Lamé mode and Young's modulus of the structural material is defined for the extensional mode. Since the resonators are aligned along the [110] direction on the (100) anisotropic SCS SOI wafer, G, E, ν and are defined as 79.4 GPa, 169 GPa, and 0.064, respectively in the [100] direction while the density of silicon is 2330 kg/m³ (Xu & Lee, 2012). Then, the resonance frequency has been analytically estimated as 4.128 MHz and 4.258 MHz for Lamé and extensional mode, respectively. On the other hand, motional resistance (ohm) can be defined as follows:

$$R_{\rm m} = \frac{d^4 \sqrt{k_{\rm eff} m_{\rm eff}}}{Q \, \varepsilon_0^2 \, \varepsilon_r^2 \, V_{\rm p}^2 \, A^2_{\rm e}} \tag{44}$$

Table 8 –	The	design	narameters	of bulk-mode	square	resonators.
I able 0	Inc	acoign	parameters	or built mout	Square	resonators.

Lamé and Extensional mode square resonator design					
Parameter	Unit	Value	Parameter	Unit	Value
Resonance frequency (1 st mode Lame)	MHz	4.1289	Electrodes and resonator thickness	μm	40
Resonance frequency (1 st mode Extensional)	MHz	4.5880	Tether length	μm	56
Effective mass (Lame mode)	μg	46.6	Tether width	μm	56
Effective mass (Extensional mode)	μg	93.2	Anchor width	μm	56
Effective spring constant (Lame mode)	N/m	3.14e+7	Length of electrodes	μm	760
Effective spring constant (Extensional mode)	N/m	7.75e+7	Resonator length	μm	1000

As it can be seen from Eq. 42-44, the resonance frequency is thickness independent in such bulk-mode resonators, and the motional resistance is inversely proportional to the effective area of the resonator (A_e) , while the air-gap is proportional to the motional resistance. Therefore, thick and large surface area of bulk-mode MEMS resonators with small air-gap ultimately results in low motional resistance.

The simulation results of the designed 1 mm² resonators operating 1st and 2nd modes of Lamé and extensional and one of the out-of-plane flexural modes are shown in Figure 37. Different orders of bulk-mode enable to optimize the point and distributed mass sensitivity of the sensors. The latter, flexural out-of-plane modes may be benefitted to detach the particles. The resonance frequency of the anchors and tethers has been set to be far from the fundamental resonance frequency of any desired operating mode of the resonator. The one end-fixed and one end-hinged (movable) mode have been used for the prediction of the natural frequency of the anchors while the fixed-fixed beam mode is used for estimation of the natural frequency of the tethers. Furthermore, the designed beams have been analytically evaluated to be resistant to the 1 LPM flow rate by using a classical max value of bending stress approximation.

3.3.2 Microfabrication of MEMS resonators

The optimized fabrication flow has been shown in **Figure 38**. Since the air-gap reduction method parameters such as the smallest achievable and uniform patterning, required oxide thickness, and the DRIE recipe is well characterized, the initial electrode-to-resonator sizes are determined as 2 μ m and 1.8 μ m. The latter, a thick oxide ~1.6 μ m has been grown (see **Figure 39**). As a result, we have obtained 300 nm to 500 nm air-gaps from the 1.8 μ m patterns, and 600 nm to 700 nm air-gaps from the 2 μ m patterns (see **Figure 39**). The latter, high-aspect-ratio DRIE recipe is applied and SOI-based SCS resonators have been fabricated. Although the trench width is reduced down to 408 nm at the bottom which is coherent with the opening after the oxidation, it remains difficult to assess the aspect ratio due to non-uniform trench width along the trench depth. As it can be seen from **Figure 40**, the trench width as large as ~ 1.3 μ m begins at the top and it gets narrower at the bottom of the trench. Herein, the mean gap has been estimated as narrow as 868 nm. This results in an aspect ratio of as high as 53:1 for the case of silicon wafers which have been treated with the SOI wafers under the same conditions and each of them have been used for inspections after each fabrication steps. In



Figure 38 – A Schematic of the 4-masks fabrication flow of the air-gap MEMS inertial mass sensor.



Figure 39 – Cross-section SEM images show reduced air-gaps after \sim 1.6 μm oxidation of 1.8 μm patterning to 332 nm (A) and 2 μm patterning to 614 nm (B).





EHT = 1.50 kV

WD = 1.2 mm

10 µm

Mag = 1.40 K X

V 1 = 408.4 nm

Signal A = InLens

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Figure 41, a cross-section of the SOI-based MEMS device, which has been obtained from the initially 1.8 μ m spaced electrode-to-resonator is shown. The cross-section image reveals that the thickness of the resonator is reduced down to ~ 38 μ m. This could be due to the last step of the fabrication process which may cause excessive reactive-ion-etching (RIE) of silicon after the removal of the remaining polysilicon and silicon nitride. As the device has been cut by laser, the destruction of the structure is evident. Nevertheless, the profile of the gap looks very similar to that of the silicon test structures which have been processed under the same conditions. For the sake of simplicity, the gap profile of the device has been estimated as ~ 38 μ m depth to ~ 400 nm width, which results in ~ 95:1 aspect ratio. Although this result is expected to be the same for the same initially electrode-to-device spaced devices which should result in slightly different aspect ratio. As seen in **Figure 41-42**, the air-gap reveals a tapered shaped-gap that hinders the feasibility of this method. The variation of the width at the top and the bottom is demanding an improved DRIE recipe in order to form relatively more vertical trenches.

As it has been suggested that the DRIE etching profile can be improved by adjusting the following parameters (R. Abdolvand & Ayazi, 2005): *(i)* Increasing the switching frequency of the plasma gases while keeping the cycle time ratio time constant leads to a reduction in the roughness of the sidewalls by decreasing the isotropic etch time at the bottom of the trench before the next passivation step protects the sidewall. *(ii)* Increasing the platen power elevates the plasma ions flux and energy that improves the directionality of the reactive particles which increases the availability of plasma species at the bottom of a trench with a narrow opening. *(iii)* Reducing the chamber pressure increases the mean free path of the plasma particles and improves the directionality of the mixed



Figure 41 – The laser-cut cross-section image of the SOI-MEMS resonator reveals the air-gap profile and the thickness of the resonator/electrodes.

argon and oxygen plasma depassivation steps in between the passivation and etching steps with a short oxygen clean step at the end of each cycle may lead to relatively more uniform trenches (Reza Abdolvand & Ayazi, 2008). In Figure 42, the fabricated MEMS resonator with the Aluminum contact pads, isolation layers, and the electrodes have been shown. The tilted SEM image shows the air-gap from the top view. As it can be seen, the stripes have been formed around the edge of the



Figure 42 – The top SEM image shows the top view of the SOI-based MEMS resonator that is indicating the Al contact pads, the electrode, and the air-gap whose profile has been shown in the tilted bottom SEM image.



Figure 43 – SEM image of the resonator showing the basic electrical working principle.

resonator and the electrodes. These stripes have been previously attributed as a disadvantage of this method and correlated to the mask-induced vertical sidewall stripes (N.-D. Ciressan, 2009). However, more experiments are needed to investigate the source and composition of this occurrence. Finally, the square-shaped bulk-mode resonator which is surrounded by four electrodes to enhance the transduction can be seen in **Figure 43**. One of the anchors of all devices can either be used as a sense electrode or polarize the resonator. In the present experiments, one of the anchors has been used as a sensing electrode.

3.3.3 Electrical characterization and results

All the fabricated resonators have been characterized by an HP4194A impedance/gain-phase analyzer in the air. The combined AC (V_{in} =1V) and the polarization DC voltage (V_p =40V) have been applied to two opposing electrodes in order to enhance the electrostatic transduction. This measurement configuration is classified by the one-port measurement mode as the electrodes have only been used for the actuation (see **Figure 44**). The application of positive Vp on the electrodes polarizes the electrodes, and thus statically polarizes the resonator through the anchor by attracting negative charges. Combination of these applied voltages with V_{in} across a capacitive gap ultimately



Figure 44 - One-port drive and sense configuration measurement set up.

induce an oscillating electrostatic force which in turn excites the resonator. When the resonator oscillates at its specific resonance frequency (i.e. Lamé mode) where the vibration amplitude reaches its maximum, the modulation in the capacitive gap alters the resonance frequency of the applied V_{in} . The latter leads to produce i_m whose resonance frequency is the same with that of the oscillating resonator. As shown in Figure 43-44, the output signal (current) is then detected through the anchor. The impedance analyzer provides phase (°) and impedance (Z = R + jX) of the detected signal which consists of a real part (R) that is composed of the motional resistivity $(R_m = V_m/i_m)$ of the resonator and parasitic resistance originating from silicon current path and contact resistance. The imaginary part (jX) identifies the reactance that occurs due to the damping. Each motional resistance (R_m) values have been associated with corresponding phase angles (°). Then, linear contribution of background noise at 0Vp has been mathematically subtracted from real part of Z ($\text{Re}(Z-Z_0)$) in order to be able to extract Q-factor and it is plotted as a function of the resonance frequency. Hence, the quality factor $(Q = f_0 / \Delta f_{-3dB})$ has been estimated from the frequency band-width with -3 dB attenuation from the maximum resistance (R_{max}) which corresponds to 0.707 of maximum current (i.e. $i_{max}/\sqrt{2}$) and 0.707 of maximum voltage (V_m) which essentially proportional to resistance, thus the real part of the impedance curve has been used to estimate the Q-factor from R_{max} of 0.707 as described in Section 3.1.2.

In this work, all the electrical characterization has been carried out by using Z-probes (Signal-Ground). As the resonators render different deformation modes such as Lamé and Extensional to alter the mass sensing properties, the experimental characterization of the devices has been focused on Lamé and extensional modes, and the resonance frequencies are measured as 4.099 MHz and 4.467 MHz, respectively as shown in **Figure 45**. Owing to the fact that the simulated and the experimentally measured fundamental resonance frequencies are very close to each other, the detected resonance frequencies explores Lamé and extensional modes. The estimated quality factor exceeds 20000 for Lamé mode, while it is around 13000 for the extensional mode for the device whose anchor length is 56 μ m and the air-gap is corresponding to the initially 1.8 μ m patterned electrode-to-resonator gaps. The same device has also been used for the determination of the noise floor experiment to evaluate the minimum detectable mass with our experimental set-up and the preliminary mass sensing experiment which will be shown hereinafter. Since the low-power consumption mass sensors are highly desirable for their feasible adaptation to integrated circuits (IC), low operating voltage (V_p) is required to excite the resonators. The results in **Figure 46** show that the resonator with the small air-gap and the short



Figure 45 – The resonance frequency responses for Lamé mode and Extensional mode as 4.099091 MHz and 4.467613 and quality factors are estimated as 20364 and 13818, respectively at 40 V_p .



Figure 46 – Graphs are showing the result of resonance frequencies as a function of the polarization voltage from 0 Vp to 40 Vp in both modes at V_{in} =1V.

anchor has been excited as low as at 10Vp in both Lamé and extensional modes. The latter, the effect of anchor length on the resonance frequency and quality factor have been investigated for both modes. Based on preliminary experimental results, the effect of anchor length on the resonance frequency for the extensional mode is more pronounced than that of Lamé mode (see **Figure 47**). The larger anchor length more likely perturbs the extensional mode and leads to a decrease in the frequency. Besides, the anchor effect is more pronounced for the quality factor in Lamé mode (see **Figure 47**). Once the desired mass sensitivity is optimized, the anchor effect could be turned into an advantage by increasing the length for a higher signal-to-noise output at lower operating voltages. However, more experiments and more devices from different dies are needed to confirm these anchor effect implications. Furthermore, the motional resistance of each device with different anchor lengths in Lamé mode at $40V_p$ from the same die has been measured for 1.8 µm and 2 µm initially patterned

devices (see Figure 48). The devices out of the small patterns have shown slightly lower motional resistance as the mean gap is smaller. Although the difference can be originated from the variation in the structures or quality factor, the largest portion of the motional resistance difference should be originated from the air-gap as it is 4th order proportional to the air-gap. The smallest motional resistance (Re(Z)) has been estimated as 27.28 ohm and the highest as 2067.12 ohm from the initially 1.8 patterning device while the smallest motional resistance has been obtained as 58.49 ohm and the highest as 8019.23 ohm from the 2 µm patterning. The significant source of this variation among the same patterned devices should be originating from the oxidation variance across the wafer, which leads to different gap sizes. Besides, Re(Z) also includes parasitic resistance for the both cases.



Figure 47 - The estimated quality factor and measured resonance frequency as a function of anchor length for the smallest air-gap (initial 1.8 µm) devices from the same die.



Figure 48 – The estimated motional resistance (Re(Z)) as a function of anchor length. Comparison of the devices operating in Lamé mode at 40Vp is shown from the initial 1.8 µm and 2 µm patterning.

3.3.4 Minimum detectable mass

The sensitivity of the resonance MEMS can be derived based on the Sauerbrey's principle as (Sauerbrey, 1959):

$$\frac{\Delta f}{\Delta m} = -\frac{f_0}{2m_{eff}} \tag{45}$$

Where Δf is the resonance shift upon an added mass (Δm), m_{eff} and f_0 are the effective mass and the initial resonance frequency of the resonator, respectively. To estimate the minimum detectable mass in our experimental set-up, the frequency variation (Δf_{noise}) which is originated from the phase variation ($d\mathcal{O}_{noise}$), has been determined for Lamé and extensional modes (Eq 46). The frequency error can be estimated as follows (Bouchaala, Nayfeh, Jaber, & Younis, 2016):

$$\Delta f_{noise} \approx \frac{|d\emptyset noise|}{|d\emptyset/df|}$$
(46)

Where $d\emptyset/df$ has been determined from the phase as a function of resonance frequency slopes for the both modes (see Figure 49). It has been found as 7.80376×10^{-4} °/Hz for Lamé mode and 1.77×10^{-3} °/Hz for the extensional mode. The latter, the phase variation has been calculated by measuring the phase angle corresponding to the resonance frequency successively 6 times between approximately 10 seconds intervals. The phase noise has been found as 0.017° for Lamé mode and 0.020° for the extensional mode. As a result, a minimum resonance shift has been deduced as 22.23 Hz for Lamé mode and 11.32 Hz for the extensional mode. The corresponding minimum detectable mass then



Figure 49 – The phase curves for both modes of the same device described earlier showing the determination of the slope $|d\emptyset| / |df|$ for the noise floor.

can be estimated as 0.51 ng and 0.47 ng for Lamé and extensional modes, respectively. The noise is usually originated either internally from the thermo-mechanical noise source due to the thermal fluctuations around the resonator or externally from the electric connections. In this case, the main source of the noise has been more likely originated from the electrical connections due to the poor Aluminum contacts quality in our experimental set-up.

It should be mentioned that the determination of the minimum detectable mass capability is not enough to calibrate the sensor. The maximum mass loading efficiency should be evaluated in order to clarify the longevity of the sampling which will enable one to collect a reliable mass concentration in a given time. Although the mass loading capacity has not been experimentally deduced yet, it is known that the effective mass of an added mass should be much smaller than the effective mass of the resonators in order to be able to carry out a sensitive added mass estimation upon the frequency shift in the Sauerbrey's equation (Prasad, Seshia, Zielinski, Kalberer, & Jones, 2014). Consequently, this mass sensor enables to measure down to sub-ng, which leads to determining very small airborne particles concentration.

3.3.5 **Proof of concept: Mass sensing**

To assess the mass sensing properties based on resonance frequency shift due to added mass, a proof of concept localized mass sensing experiment has been conducted. A small volume of 1 μ L syringe has been manually used to deposit a small deionized (DI) water droplet on a random location of the 1 mm² resonator surface. A suspended small water droplet can form at the tip of a needle due to surface tension that creates a force keeping the droplet attached at the tip. The latter, the needle has been slightly approached to the resonator surface in order to maintain a contact between the drop and the surface. Then, the needle has been slowly lifted up from the surface. When the binding forces between the droplet and the surface overcome the surface tension generated force, a part of the droplet or the entire droplet can be deposited on a random location of the surface (see Figure 50). Although the size of the deposited droplet, the position of the deposition, and therefore physical added mass



Figure 50 –Optical microscopy images are showing before DI water deposition and after the evaporation of the droplet. The inset magnifies the evaporated water droplet which reveals the residue. The dust particles are evident on the resonator (Scale bars show 100 µm, and diameter of the residue is 27.7 µm).

cannot be repeated and determined with this method, the resonance frequency shift can be observed due to an added mass. This experiment facilitates the utility of the MEMS devices as a mass sensor. The resonance frequencies of the device for both modes have been measured before the deposition and after the evaporation of the droplet which takes several seconds. The latter, remaining residue has been observed due to possible organic contaminants and inorganic salt as it has also been encountered previously (Prasad et al., 2014) (see **Figure 50-51**). The mass of the remaining residue has been estimated with the resonance frequency shift of both Lamé and extensional modes. Each resonance frequency response has been measured at least 6 times between approximately 10 seconds intervals to deduce the resonance frequency fluctuation. The variations have been calculated by multiplying standard deviations (σ =11.62 Hz for Lamé mode and σ =10.95 Hz for extensional mode) by 2. The equivalent quantities are higher than the previously measured noise levels for the both modes. Furthermore, the resonance fluctuations before and after the droplet deposition have shown to be much less than the frequency shifts upon the added mass that ensures the shift is the reason of the deposited droplet (see Table 9).



Figure 51 – Resonance frequency shifts upon the remaining residue from the water droplet evaporation in Lamé mode (left) and in the extensional mode (right).

	Resonance f₀ before (Mean average)	Resonance f ₀ after (Mean average)	Δf	Added mass
Lamé mode	(4099106 ± 23) Hz	(4099067 ± 24) Hz	(38± 13) Hz	(0.88 ± 0.30) ng
Extensional Mode	(4467618 ± 22) Hz	(4467506± 17) Hz	(111 ± 11) Hz	(4.64 ± 0.45) ng

Table 9 – A proof of concept for the added mass estimation in both modes.

Interestingly, the corresponding localized mass estimation for Lamé mode (0.88 ± 0.29) ng is more than fourfold smaller than that of extensional mode (4.64 ± 0.45) ng (see **Table 9**). As the effective mass of a resonator at a specific location is a function of the vibration amplitude of the structure at the same location, the residue is subjected to different vibration amplitude in both modes. Thus, the estimated effective mass of the residue is different for both cases, whereas the location of the residue is close to the maximum displacements antinodes for the extensional mode. Consequently, the residue has experienced larger displacements and therefore higher velocities that lead to a larger kinetic energy contribution to the system which results in larger frequency shift (Zielinski, Prasad, Seshia, Kalberer, & Jones, 2015). Thereby, the estimated effective mass of the residue is more likely to be overestimated in extensional mode. In contrast, Lamé mode demonstrates a more uniform sensitivity due to its relatively and homogeneously distributed vibration amplitude antinodes and resulted in a more reasonable mass estimation.

3.4 Conclusions and future perspective

This work has focused on the fabrication of sub-µm bulk mode MEMS resonators by the thick oxide as a mask layer technique for the realization of real-time bioaerosol and aerosols mass measurements. Since this fabrication method has not received a lot of attention in the literature, the optimization process and the major encountered issues have been reported herein. This fabrication method is cost effective and less complex than the widely used sacrificial layer removal-based methods. The main difficulty is to optimize the oxide thickness which determines the air-gap and the DRIE recipe which enables high-aspect-ratio suspended MEMS resonators.

In this work, the ~ 1.6 μ m oxide has growth on initially 1.8 μ m spaced electrode-to-resonator gap. The latter, the gap has been reduced to ~ 300 nm to ~ 500 nm. By the application of the DRIE, the conic shape air-gap has been formed. The mean air-gap can be estimated as ~ 868 nm, which result in 45:1 aspect ratio. Besides, the smallest opening of the trench, which is at the bottom, is ~ 400 nm. This results in a 95:1 aspect ratio in the SOI-based ~ 38 μ m devices. Therefore, high-aspect-ratio bulk-mode MEMS resonators have been successfully fabricated and operated in Lamé and extensional modes. The later, the minimum detectable mass has been estimated as 0.51 ng for Lamé mode, and 0.47 ng for extensional mode. As a result, the fabricated MEMS sensors showing sub-ng mass resolution. The proof of concept mass measurements has been also conducted and frequency shifts upon evaporated water residue have been observed. Although the physical and effective mass (i.e. before and after) quantification of the water residue is difficult in terms of the comparison, the frequency shift is evident.

This fabrication technique has enabled to fabricate high-performance inertial mass sensors with a promising mass resolution. However, more experiments are needed to improve the verticality of the trenches, investigate more in-depth the point mass sensitivity, and thus calibrate the sensor for both modes.

In the future work, the fabricated chips should be mounted and wire bonded on a printed circuit board which will enable miniaturization of the experimental set-up on a small chip, operating the sensors in superior modes due to the complexity of designed and fabricated electrodes and automatization of the measurements with reduced noise floor. Therefore, the mass resolution is expected to be further enhanced. As one of the main goals of this project is to miniaturize the whole airborne particles detection system, the size of the chips ($6.4 \text{ mm} \times 6.4 \text{ mm}$) will be further reduced and adapted to a fully microfabricated impactor. As depicted in **Chapter 2**, the black silicon surface has shown unprecedented success to confine the deposition pattern of the impacted airborne particles. Therefore, it is essential to functionalize the sensor surface with black silicon. The latter, it will pave the way for the fabrication of

embedded microchannels from anchors towards localized circular black silicon surface (diameter of 700 μ m) which will deliver water to clean the surface due to the Lotus effect. A similar approach has been recently performed to weigh fluids and characterize liquid samples without fully immersing the sensor in the liquid which avoid viscous damping related to performance deterioration (Enoksson, Stemme, & Stemme, 1995) (Burg et al., 2007) (Hadji, Virot, Picard, Baléras, & Agache, 2017).

All in all, the fabricated MEMS sensing and cleaning system can be integrated to a fully microfabricated impactor to realize a compact and ready to plug-in to a daily used electronic device for continuous and real-time bioaerosol and aerosols mass measurements system.

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Zielinski, A. T., Prasad, A., Seshia, A. A., Kalberer, M., & Jones, R. L. (2015). Effects of spatial sensitivity on mass sensing with bulk acoustic mode resonators. *Sensors and Actuators A: Physical*, 236, 369–379. https://doi.org/10.1016/j.sna.2015.11.003
The shift in the resonance frequency of an oscillating resonator in inertial mass sensors occurs upon an added mass and it can be evaluated based on Sauerbrey's principle as shown in **Chapter 1, Eq. 3**. Though this rule has been proven with the estimation of a homogeneously distributed added mass (e.g. thin film) on an oscillating resonator (e.g. QCM), it will not necessarily be applied in the case of homogeneously added distributed particles or a localized particle due to the non-homogenous vibration amplitude of inertial sensors. As these sensors are composed of nodes and antinodes on their active surface, the efforts to precisely determine the physical mass of a localized added mass have always been limited. So far, there is no documented study which has shown an accurate correlation between the physical mass of an added particle and the measured mass (i.e. effective mass) from the resonance frequency shift.

Firstly, the measured quantity represents the effective mass rather than the physical mass of the added mass which can be significantly different than the physical mass in some cases (Berthelot, Algré, Moularat, Robine, & Gehin, 2015).

Secondly, the non- homogeneous vibration amplitude distribution may lead to a wide variety of effective mass determination of a localized particle. Indeed, the studies in the literature have shown a proportional relation between the resonance frequency shifts and numbers of added mass (i.e. particles detection based on the resonance frequency shift). But, when it comes to accurately measure the physical mass of a particle, the frequency shift-derived mass estimation is either never presented or accurate. Therefore, bulk-mode (i.e. Lamé mode) MEMS sensors with relatively homogenous vibration amplitude should lead us to determine an accurate correction factor which will result in an estimation of the precise physical mass of several added particles.

In this chapter, VOAG generated monodisperse spherical fluorescent particles are detected with the MEMS mass sensors (see Chapter 3) integrated impactor (see Chapter 2). Upon consecutive impactions on MEMS, the resonance frequency shifts of different sensors have been characterized. The mass of impacted particles is compared with the mass deduced from the shifts. The latter, impacted monodisperse particles have been counted from the active surface area of the resonator, and thus the local

collection efficiency is presented.

In the following, the mass sensors will be presented and the monodisperse fluorescent particles used as test particles. Then, the integration and impaction procedures will be explained. Next, the mass sensing properties of the detection system will be studied. The latter, the calibration effort for one of the sensors will be presented.

4.1 Characterization of MEMS mass sensors

In this impaction study, four different MEMS devices have been tested as a mass sensitive impaction plate. Devices are referred to as device 1, device 2, device 3, and device 4 within the manuscript. As seen in Table 1, Devices are distinguished from each other with their air-gaps distance and the anchor lengths. The initial air-gap of device 1 and device 2 is 2 μ m while it is 1.8 μ m for device 3



Figure 52 – Resonance frequency measurements of devices used in the impaction study.

	Initial	Anchor	Resonance	Quality	Resonance	Quality
	Air-gap	length	Frequency (Lamé)	factor	Frequency	factor
	(µm)	(µm)	(Hz)	(Lamé)	(Extensional) (Hz)	(Extensional)
Device 1	2	56	(4100824±15)	~ 15000	(4460008±19)	~ 18000
Device 2	2	169	(4104655±7)	~ 18000	(4377444±11)	~ 18000
Device 3	1.8	28	(4100297±12)	~ 20000	(4477086±8)	~ 20000
Device 4	1.8	169	(4102512±10)	~ 19000	(4377022±7)	~ 18000

Table 10 - The properties of different MEMS mass sensors used in the impaction study

and device 4. The anchor lengths of device 1 and device 3 are $56\mu m$ and $28\mu m$ (the shortest), respectively. Device 2 and device 4 have the longest anchor lengths as $169\mu m$. The devices have been chosen due to their low noise electrical characteristics as shown in **Figure 52**. Although the variation in the resonance frequency among the devices is not expected to influence the mass sensing properties, the air-gap may alter the sensing properties due to its effect on the signal-to-noise ratio. Furthermore, quality factor variation among the devices would influence the minimum mass sensing capability of the sensors (see **Table 10**).

4.1.1 Frequency stability of MEMS

To ensure a reliable mass measurement, it is essential to assess external sources which may contribute to the resonance frequency shifts, and thus mass measurements. Although the temperature and humidity fluctuations can be considered as external sources (i.e. ambient effects) during the experiments, the probe up-down error has also been observed. All the electrical characterization tests have been carried out in the air. The effects of abrupt temperature and humidity changes on the resonance frequency cannot be avoided when the sensors are characterized in the air. Moreover, the contamination of the sensors is inevitable unless they are kept in a sealed vacuum box. On the other hand, as long as the probes have been lifted up in order to take the device out of the probe station and lifted down to initiate a new measurement, unanticipated frequency shifts occur. To evaluate the effect of the ambient, the device should be tested in an environment where the temperature and humidity can be controlled.

The unwanted shifts originated from the adsorption of water molecules, contaminants, and probe up-down error can be quantified and the corresponding deposited mass can be evaluated based on the Sauerbrey's relation. To estimate the unwanted resonance frequency shift induced by the probes, one of the devices (device 3) used in the impaction study has been repeatedly characterized for 10 times with several seconds intervals (after the impactions). After each measurement, all the Z probes (Ground-Signal) used in the characterization are rapidly lifted up and lifted down onto the contact pads. As shown



Figure 53 - The determination of error induced by the probes for both modes. Lamé mode (left) and Extensional mode (right) are shown.

in Figure 53, the measured resonance frequencies and Q-factors have been recorded for both modes. The fluctuation in resonance frequency and Q-factor can be clearly seen in Figure 53. Indeed, the amplitude of the resonance peaks significantly decreases over the tests as well. This should be due to the damages on contact pads as the probes are contacted Aluminum pads which are easily deformable by the contact of the probes. The electrostatic force then can be weakening by the poor interface between the probes and pads, which may lead to a reduction in the amplitude of the signals. The probe up-down induced variability ($2\times\sigma$) has been found to be 35.2 Hz for Lamé mode and 68.5 Hz for extensional mode. The uncertainty of the probe up-down has been added to the uncertainty of the mean resonance frequencies (before and after). The latter, the uncertainty for each shift and corresponding mass uncertainty have been calculated (see Table 11). In extensional mode, the mass uncertainty (measurements + probe up-down) is quite close to the generated quantities (see next section), therefore Lamé mode has been used to analyze the mass of deposited particles in all impaction experiments.

The resonance frequency (Lamé mode) of each device has been measured at least 6 times with 10 seconds intervals prior and following to each impaction and the uncertainty in the mean resonance frequencies (excluding the probe up-down uncertainty) has been shown (see Table 1). This means that once the contact between the pads and probes are well-maintained, the resonance frequency measurement uncertainty is insignificant (considering no contamination and no abrupt changes in the ambient) in comparison to the probe up-down added total uncertainty.

4.2 Generation of monodisperse fluorescent particles

The VOAG enables to generate monodisperse and various concentrations of aerosols. Successive impactions of a different number of generated particles would enable one to calibrate the sensors. Therefore, monodisperse fluorescent test particles with mean median aerodynamic diameter of (\overline{MAD}) of 1 µm are generated by the VOAG (see Figure 3 and Chapter 2). The number of total generated



Figure 54 - The APS data of the successive impactions. The left-hand side shows the first impaction data, the middle shows the second impaction data, and the right-hand side shows the third impaction data.

particles for each impaction have been estimated as described in Eq. 15 in Chapter 2. Mass of the fluorescent particles (M_m) is calculated for each device $(\#_p/10 \text{ nozzles})$ as follows:

$$M_m = \#_p / 10 \times \rho_r \times \frac{4}{3} \times \pi \times (\frac{d_{me}}{2})^3 \tag{47}$$

Where $\#_p$ is the number of generated particles, ρ_r is the density of fluorescent particles which is equal to 1530 $\frac{kg}{m^3}$, and d_{me} is the mass equivalent diameter of the particles which is equal to 0.8 (see Chapter 2 section 2.3.1). When a stable monodisperse particles generation has been maintained for each impaction, three consecutive impactions for four different MEMS devices have been performed. The impactions times such as 150sec, 160sec, and 280sec in the first, second, and last impactions, respectively have been chosen in order to obtain the desired amount of generated mass for each impaction. These three generations result in (8567±463) fluorescent particles per device with the corresponding mass of (3.52±0.08)ng, (21145±289) particles per device with the corresponding mass of (8.67±0.12)ng, and (41777±638) particles per device with the corresponding mass of (17.14±0.26)ng, respectively (see Figure 54). Subsequent to each generation, three consecutive impactions have been carried out.

4.3 Experimental procedure of impaction

As shown in Figure 55, four different MEMS mass sensors (each chip size: 6.4 mm× 6.4 mm) have been used for individual impaction plates. In addition to the previously described alignment procedure, it has to be noted that the thickness of silicon/BSi impaction plates, which have been used for the deposition characteristic study is $(500 \pm 25)\mu m$ (see Chapter 2).

However, the thickness of SOI wafers used to fabricate the sensors is $(300 \pm 25)\mu m$. Thus, a piece of double-sided scotch tape with a thickness of ~ 200 µm has also been added to maintain the same distance between the chips and nozzles as that of the deposition characteristic study in Chapter 2. However, the flexibility and deformability of the tapes can easily induce errors which ultimately result in a variation in the distance between the chips and nozzles. It is known that the bounce effect may be more pronounced at S/W < 1 (Grinshpun et al., 2005). Hence, the opposite situation where S/W > 1 may also alter the bounce effect (see Chapter 2). Ultimately, the deposition pattern can be slightly different than the previously shown results.

Besides, \overline{MAD} of monodisperse fluorescent particles used in this experiment is rather 1 µm in order to be able to deposit the sufficient amount of particles by reducing the bounce effect on the primary impaction zone and ease the counting after the impaction. Furthermore, this study also aims to explore the mass resolution of the sensors, and therefore the mass of generated particles (per device) has been approximately chosen to be around 3.52 ng in the first, 8.67 ng in the second, and 17.14 ng in the last impaction. The deposition characteristic study (see **Chapter 2**) has suggested that the local collection efficiency of particles with d_{ae} of 0.92 µm at the primary impaction zone (0.75 mm²) is (17.9 ± 1.8)%. Hence, the first, second, and third impactions are ideally expected to result in minimum (0.7, 1.7, 3.4)ng



Figure 55– The image shows 4 MEMS mass sensors placed and aligned on the impaction plate (Outer diameter of the plate is 8 cm).

of successively deposited particles on the resonator surface (1 mm^2) , respectively. It has to be noted that there is no cleaning that has been performed between each impaction.

Table 11 presents the experimental procedure with a schematic by which shows the parameters. Before and after each impaction, MEMS sensors have been electrically characterized with the same procedure described in **Chapter 3**. Each MEMS device has been measured at least 6 times with 10 seconds intervals to deduce the mean resonance frequency before (f_{nb_d}) and after (f_{na_d}) each impaction. Following an impaction, the resonance frequency shift (Δf_{n_d}) and the corresponding mass (Δm_{n_d}) are calculated. As the impactions have not been carried out in real-time and the sensors are demounted from the impactor between each impaction, f_{na_d} is not the same to $f_{(n+1)a_d}$. Thus, resonance frequencies are measured before each impaction (f_{nb_d}) and the frequency shift between the next and previous impactions are calculated (Δf_{nbna_d}) (see **Table 12**). Besides, the VOAG generated monodisperse particles can be characterized with the following parameters: mean concentration (C_n) , number of generated particles $(\#_{p_n})$, mean median mass of generated particles (M_{m_n}) , and aerodynamic diameter of generated particles (d_{ae_n}) . Lastly, SEM images are taken between each impaction for inspections. The abovementioned procedure has been repeated three times to perform three consecutive impactions.

	Device	1	Device 2	Device 3	Device 4		
Before	»	f_{b_1}	f_{b_2}	f_{b_3}	\checkmark	f_{b_4}	
Impaction 1	C_l , # p_1 , M	m_1 , d_{ae_1}	C_l , $\#_{p_1}$, M_{m_l} , d_{ae_l}	C_l , $\#_{p_1}$, M_{m_l} , d_{ae_l}	C_l , # p_1 , M_{m_l}	,d _{ae_1}	
1011	>	f_{1a_1}	f_{1a_2}	f_{1a_3}		f_{1a_4}	
		Δf_{1_1}	Δf_{1_2}	Δf_{1_3}	Z	$4f_{1_4}$	
		Δm_{1_1}	Δm_{1_2}	Δm_{1_3}		$1m_{1_{4}}$	SEM
	V	Δf_{2b1a_1}	$\checkmark \Delta f_{2b1a}$	$_2 \qquad \checkmark \Delta f_{2b1a}$	<u>_</u> 3 ↓ △	f_{2b1a_4}	measurement 1
Before	>	$f_{2b_{1}}$	f_{2b_2}	f_{2b_3}	j	f_{2b_4}	
Impaction 2	C_2 , $\#_{p_2}$, M	m_2 , d_{ae_2}	C_2 , $\#_{p_2}$, M_{m_2} , d_{ae_2}	C_2 , $\#_{p_2}$, M_{m_2} , d_{ae_2}	C_2 , # p_2 , M_{m_2}	,d _{ae_2}	
15UL	>	f_{2a_1}	f_{2a_2}	$f_{2a_{3}}$	j	f_{2a_4}	
		Δf_{2_1}	Δf_{2_2}	Δf_{2_3}		$4f_{2_4}$	SFM
		Δm_{2_1}	Δm_{2_2}	Δm_{2}	3 2	$4m_{2_4}$	measurement 2
core	×	Δf_{3b2a_1}	$\checkmark \Delta f_{3b2a}$	$_2 \qquad \qquad \Delta f_{3b2a}$	<u>_</u> 3 [♥] Δ	f_{3b2a_4}	
Bere	~	J3b_1	J3b_2	J3b_3	J	3b_4	
Impaction 3	C_3 , $\#_{p_3}$, M	m_3 , d_{ae_3}	$C_3, \#_{p_3}, M_{m_3}, d_{ae_3}$	C_3 , # _{p_3} , M_{m_3} , d_{ae_3}	C_3 , $\#_{p_3}$, M_{m_3}	,d _{ae_3}	
tally	>	$f_{3a_{1}}$	f_{3a_2}	f_{3a_3}		f_{3a_4}	SEM
	\downarrow	Δf_{3_1}	Δf_{3_2}	$\int \Delta f_{3_3}$		Δf_{3_4}	measurement 3
		Δm_{3_1}	Δm_{3_2}	$_2 \qquad \Delta m_{3_3}$	3 4	Δm_{3_4}	

Table 11 – Parameters used in the impaction study.

 Table 12 – Description of the symbols used in Table 11.

п	Number of the impaction
b	Before impaction
a	After impaction
ba	Frequency shift (before – after)
d	Number of the device

4.4 Study of particle detection and mass sensing

Figures 56 and 57 present SEM images that have been taken after impactions and electrical characterizations. As previously described in Chapter 2, the bounce effect is a mechanism that enlarges

the deposition pattern. The large pattern leads to the deposition of particles outside of the active area. As seen, the particles have also been deposited on the electrodes and isolation plates. But, none of the deposited particles have been found in the air-gap. As the images have been taken after the electrical characterizations, the movement of the resonator may provoke de-attachment of the particles which are deposited between the gap and resonator. To prove this hypothesis, the sensor should be inspected with SEM before the electrical characterization.

The detected particles are not homogenously distributed on the sensor surface. One of the reasons could be the misalignment. Besides, as it has been mentioned in **Chapter 3**, the last MEMS fabrication step is the removal of remaining polysilicon and nitride layer by reactive-ion-etching (RIE). Apparently, this step should be well-controlled in terms of its etching homogeneity in order to avoid over-etching of the sensor surface or avoid remaining residues. Some of the surfaces of the sensors show a porous characteristic either due to over-etching or the effect of the polysilicon or nitride film roughness that can be patterned to the silicon surface. This leads to a difficulty to observe particles in SEM investigation due to poor contrast between the porosity and deposited particles on the surface. For this reason, only one of the devices used in all impactions has been investigated for further analysis. Because, this sensor (device 3) shows the most uniform surface that leads to good SEM images in which deposited particles are relatively more distinguishable from the surface during a large inspection area.

The devices have shown different resonance frequency shifts upon the same amount of generated particles in the successive impactions. As mentioned, four different sensors have been used in the successive impactions. Among them, device 4 has exhibited a shift $(\Delta f_{l_{-}4} = (13\pm50)\text{Hz})$ within the uncertainty in the first impaction and has shown a positive shift in the second impaction (see Table 12). As the positive shift occurred, the Sauerbrey relation does not apply to this case. The positive shift upon an added mass is a commonly observed unwanted result (Tamayo, Ramos, Mertens, & Calleja, 2006) (Pomorska et al., 2010) (Olsson, van der Mei, Johannsmann, Busscher, & Sharma, 2012). It has been attributed to a coupled resonators model in which the particle behaves like a resonating body, and the resonance shift is a competition between the mass loading effect and the stiffness effect. As the same particles of origin used in all experiments and only device 4 shows a positive frequency shift, the elasticity of the particle is not the reason of dominant stiffness effect. But, (Labędź, Wańczyk, & Rajfur, 2017) have suggested that the stiffness effect can be dominant when the deposited mass is located at the nodes of the sensor. Presumably, device 4 has experienced a misalignment that causes non-homogeneous particles deposition where the particles are mainly deposited on the nodes of the resonator. Therefore, it is



Figure 56 - SEM of the impacted particles: The particles are deposited on the anchor and electrodes (top-left). The particles are around the air-gap of different devices.



Figure 57– Dispersion of the particles towards the ground plate on the chip (left), the porous sensor surface of one of the devices (right). Red circles indicate some of the particles.

crucial to achieving a homogeneous deposition and a good alignment between the deposition pattern and the resonator.

Table 13 presents the results of three consecutive impactions and related parameters. The resonance frequency shifts occur for all the devices $(\Delta f_{n_{-}l}, \Delta f_{n_{-}2}, \Delta f_{n_{-}3}, \Delta f_{n_{-}4})$ after each impaction of generated particles $(\#_{p_{-}l}, \#_{p_{-}2}, \#_{p_{-}3})$. All the shifts (except $\Delta f_{l_{-}4}$) exceed the uncertainty limit that has been identified previously.

On the other hand, in all impactions, the mass of generated particles $(M_{m_{-}l}, M_{m_{-}2}, M_{m_{-}3})$ is greater than the measured mass from the resonance frequency shifts of all the devices $(\Delta m_{n_{-}l}, \Delta m_{n_{-}2}, \Delta m_{n_{-}3}, \Delta m_{n_{-}4})$. In fact, a number of generated particles represent a maximum number of particles which are present in the experimental set-up. But, all the generated particles may have never been able to reach to the inlet of the impactor due to losses during the transportation. Besides, the uncertainty of the number of generated particles is underestimated due to the fact that the uncertainties in the impaction time and the flow rate have not been taken into account (see **Chapter 2, Eq. 15**). Although the particles reach to the inlet of the impactor, they may experience impactor related losses as well. Furthermore, all the impacted particles should be able to deposit on the active surface area of the resonator. As shown in SEM images, this is not the case as the particles are also dispersed outside of the resonator. Therefore, it is expected to find a discrepancy between the measured and the generated mass.

As mentioned previously, the sensors have been demounted from the impactor after each impaction. As a result, the sensors are exposed to the air. Therefore, the unexpected resonance frequency shifts between each impaction have been identified for all the devices (Δf_{nbna_1} , Δf_{nbna_2} , Δf_{nbna_3} , Δf_{nbna_4}). As seen in **Table 13**, the shift for device 3, before the second impaction and after first impaction (Δf_{2b1a_3}) equals to (27±51)Hz which is lower than the identified uncertainty. This points out that the first and second impactions for device 3 lead to a more reliable mass measurement in comparison to the others. However, the reason for these dramatic shifts between each impaction (Δf_{nbna} d) is still unknown.

Figure 58 presents the resonance frequency shifts of all the devices versus the generated number of particles. Device 1 and device 3 exhibit coherent relations between the number of generated particles and the shifts. Device 1 results $\Delta f_{1_1} = (71\pm53)$ Hz against to (8576±202) of generated particles in the first impaction while results $\Delta f_{2_1} = (200$ Hz±56)Hz against to $\#_{p,2} = (21145\pm289)$ of particles in the second impaction, which leads to a plausible relation. Device 3 results in $\Delta f_{1_3} = (75\pm52)$ Hz against to (8576±202) of generated particles in the first and results in $\Delta f_{2_3} = (145\pm51)$ Hz against to $\#_{p,2} = (21145\pm289)$ # of particles in the second impaction, which also leads to a reasonable relation. The linearity is not expected due to the fact that a number of generated particles is less than the number of impacted particles due to losses, large deposited area, and the misalignment. The reason for the poor performance of all the devices

	Device 1	Device 2	Device 3	Device 4	
	Ļ				Ļ
$C_{l} (\#/cm^{3})$	(3.44±0.08)	(3.44±0.08)	(3.44±0.08)		(3.44±0.08)
$\#_{p_l}(\#)$	(8576±202)	(8576±202)	(8576±202)		(8576±202)
$d_{ae_l}(\mu m)$	(1.006±0.003)	(1.006±0.003)	(1.006±0.003		(1.006±0.003)
M_{m_l} (ng)	(3.52 ± 0.08)	(3.52±0.08)	(3.52±0.08)		(3.52±0.08)
	\checkmark	Ļ	\downarrow		↓
$f_{b_l} = (410082)$	4±38)Hz	$f_{b_2} = (4104655 \pm 36)$ Hz	$f_{b_{3}} = (4100298 \pm 36)$ Hz	$f_{b_4} = (4102512 \pm 36)$ Hz	
$f_{Ia_{l}=}(410075)$	4±38)Hz	f_{la_2} =(4104536±36)Hz	$f_{Ia_3}=(4100223\pm 36)$ Hz $f_{Ia_4}=(410249)$		(4102499±36)Hz
$\Delta f_{l_l} = (71 \pm 53) \text{Hz}$		$\Delta f_{1_2} = (119 \pm 51) \text{Hz}$	$\Delta f_{I_{3}=}$ (75±52) Hz $\Delta f_{I_{4}}$		(13±50)Hz
$\Delta m_{I_{-}I} = (1.6 \pm 1.2)$ ng		$\Delta m_{1_2} = (2.71 \pm 1.15)$ ng	$\Delta m_{I_{3}} = (1.71 \pm 1.18)$ ng Δm		=(0.29±1.14)ng
$\Delta f_{2b1a_1} = (78\pm52) \text{Hz}$		$\Delta f_{2b1a_2=}$ (84.08±62)Hz	$\Delta f_{2bla_{3}=}$ (27±51)Hz $\Delta f_{2bla_{4}=}$ (43=		₄₌ (43±51)Hz
$f_{2b_l=1}$ (4100832±36)Hz		$f_{2b_2}=(4104620\pm 50)$ Hz	$f_{2b_{3}=}$ (4100250±36)Hz $f_{2b_{4}=}$ (4102456±		102456±36)Hz

Table 13 - The results of three successive impactions with four different MEMS mass sensors.

$C_2 (\#/\text{cm}^3)$	(7.93 ± 0.11)	(7.93 ± 0.11)	(7.93 ± 0.11)	(7.93±0.11)
$\#_{p_2}(\#)$	(21145±289)	(21145±289)	(21145±289)	(21145±289)
$d_{ae_2}(\mu m)$	(0.994±0.002)	(0.994±0.002)	(0.994±0.002)	(0.994±0.002)
M_{m_2} (ng)	(8.67±0.12)	(8.67±0.12)	(8.67±0.12)	(8.67± 0.12)
	\downarrow	Ļ	Ļ	↓
f_{2a} ₁₌ (4100631±42)Hz		$f_{2a_2=}(4104485\pm36)$ Hz	$f_{2a_3=}(4100104\pm36)$ Hz	$f_{2a_4}=(4103684\pm36)$ Hz
$\Delta f_{2_{-}l} = (200 \pm 56) \text{Hz}$		$\Delta f_{2_2}=(135\pm62)$ Hz	$\Delta f_{2_3}=(145\pm51)$ Hz	$\Delta f_{2_4} = (+ \text{ shift})$
$\Delta m_{2_l} = (4.55 \pm 1.26)$ ng		$\Delta m_{2_2} = (3.07 \pm 1.4)$ ng	$\Delta m_{2_3} = (3.31 \pm 1.16)$ ng	$\Delta m_{2_4} = (+ \text{ shift})$
$\Delta f_{3b2a_l} = (193 \pm 56) \text{Hz}$		$\Delta f_{3b2a_2=}(195\pm51)$ Hz	$\Delta f_{3b2a_3}=(221\pm52)$ Hz	$\Delta f_{3b2a_4}=(595\pm50)$ Hz
f_{3b} = (4100824±36)Hz		$f = (4104690 \pm 26) II_{-}$	$f = (4100225 \pm 28) II_{\pi}$	$f = (4102080 \pm 26) II_{\pi}$

$C_3 (\#/{\rm cm}^3)$	(9.0±0.1)	(9.0±0.1)	(9.0±0.1)	(9.0±0.1)
$\#_{p_3}(\#)$	(41777±638)	(41777±638)	(41777±638)	(41777±638)
$d_{ae_3}(\mu m)$	(1.026±0.001)	(1.026±0.001)	(1.026±0.001)	(1.026±0.001)
$M_{m_{3}}$ (ng)	(17.14±0.26)	(17.14±0.26)	(17.14 ± 0.26)	(17.14±0.26)
	1	1	1	
	¥	\downarrow	\checkmark	\checkmark
$f_{3a_l} = (410074)$	0.5±36)Hz	<i>f_{3a_2=}</i> (4104564±48)Hz	∫ <i>f_{3a_3=}</i> (4100161±36)Hz	<i>f_{3a_4=}</i> (4102459±36)Hz
$\frac{f_{3a_{1}}}{\Delta f_{3_{1}}} = (410074)$	0.5±36)Hz	$f_{3a_2=}(4104564\pm48)\text{Hz}$ $df_{3_2=}(116\pm59)\text{Hz}$	$f_{3a_3=}(4100161\pm36)\text{Hz}$ $\Delta f_{3_3=}(165\pm51)\text{Hz}$	$f_{3a_{4}=}(4102459\pm36)\text{Hz}$ $\Delta f_{3_{4}=}(630\pm51)\text{Hz}$



Figure 58- The resonance frequency shifts versus the number of generated particles

in the third impaction is still to be understood.

Finally, **Figure 59** presents the relation of measured mass from the resonance frequency shift and the mass of generated particles for device (1, 2, and 3). As seen, Δm_{n_d} is lower than M_m in all the cases. In addition to the abovementioned explanation, the added mass estimation based on the Sauerbrey's equation may not be accurate due to the non-homogeneity of the deposition and the vibration amplitude of the sensors. Therefore, it is crucial to achieving a reliable quantification of the collected particles in order to calibrate the sensors by defining a correction factor.





Figure 59– The graphs show the mass estimation from the resonance frequency shift versus generated particles mass for 3 different MEMS devices.

4.5 Calibration of selected MEMS mass sensor

4.5.1 Resonance frequency analysis

Figure 60 presents treated SEM images which show the results of the successive impactions of



Figure 60– The treated and scaled SEM images show the deposition pattern of impacted particles on device 3 after each consecutive impaction. The evident scratch on the resonator is due to the device manipulation for SEM in the impaction 3 image.

device 3. The images reveal that the first impaction has resulted in a slight misalignment which causes the deposition of the particles towards one of the electrodes (left-side electrode). As it can be clearly seen, the second impaction has increased the number of particles on the sensor surface. But, at first glance, the last impaction has not concluded a significant increase in the density of the particles, unlike the second impaction. Therefore, the collection efficiency would be expected low in the last impaction.

Figure 61 shows the mean resonance frequency measurements of device 3 before and after each impaction. As the measurements have not been carried out in real-time, it is difficult to predict the reason for signal level improvements in the second and the last impactions. The quality factor degradation upon the impacted particles ultimately reduces the sensitivity of the sensor. Hajjam, Wilson, & Pourkamali, 2011 have documented that Q-factor of their mass sensor has not been notably affected by the deposition of particles of different size. Zielinski, Kalberer, Jones, Prasad, & Seshia, 2016 have not highlighted Q-factor information during particles exposure due to non-linear effects that have been observed in most of their experiments. Moreover, severe fluctuations in Q-factor during the exposure have been observed and attributed to the possible influence of flow rate, relative humidity, and particle adsorption. To better understand the underlying mechanisms that are responsible for Q-factor response against to particles deposition, more robust and real-time experiments are needed. Instinctively, Q-factor response as a function of time would not be stable during the exposures, and therefore it cannot provide useful data.

As it can be seen in Figure 61 and Table 12, f_{2b_3} and f_{la_3} are not the same and resulted in $\Delta f_{2b_{1a_3}} = (27.21 \pm 51)$ Hz, which does not exceed the total measurement uncertainty (measurements + probe up-down). But, $\Delta f_{3b_{2a_3}}$ is identified as (220.96±52)Hz between the second and third impactions. This



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Figure 61 – Graphs show the resonance frequency shift after each impaction for device 3.

massive frequency shift could be originated from a combination of the errors induced by the electrical characterization and ambient effects (humidity, temperature, dust etc.). Because, the sensors have been demounted from the impactor before each impaction, transported from one laboratory to another in the impactor, and analyzed with SEM in the following day. As Δf_{2bla_3} is within the limit, Δf_{1_3} and Δf_{2_3} have been demonstrated by considering the resonance frequency after the first impaction is equal to the resonance frequency before the second impaction ($f_{1a_3} = f_{2b_3}$) in order to exhibit the successive shifts in **Figure 62**. To prove this finding, SEM images of the impactions have been investigated in order to count the particles. The mass of the collected particles have been calculated from the countings and compared with the estimated mass which is deduced from the resonance frequency shift of device 3.





4.5.2 Particle counting procedure

The counting of the particles has been carried out manually because of the high mistake rate of available particle counting software. Furthermore, SEM images have failed to show a high contrast and sufficient resolution of 1 mm2 desired investigation area on which the collected particles should be distinguishable at a given magnification. The particle counting protocol is defined in this section. **Figure 63** presents the protocol for the first impaction and for device 3. To ease the counting, five identical rectangular surfaces, namely A, B, C, D, and E with (0.25 mm \times 0.4 mm = 0.1 mm2) surface areas have



Figure 63 – The particle counting estimation from 5 different locations of device 3 after the first impaction.

been extracted out of the resonator surface. The location of the areas has been solely extracted from near the corners (anchors) and centers of the active surface (1 mm^2) . The latter, the particles have been counted on each identical rectangular surface. Although the deposition is not ideally uniform across the resonator, the average value of the number of counted particles from each rectangular surfaces has been taken, which represents the total number of particles on 0.1 mm^2 . The latter quantity has been multiplied with 10-factor to obtain a representative estimation of the total number of counted particles on the resonator surface of 1 mm^2 . As a result, the total number of (1096 ± 463) particles with \overline{MAD} of $(1.006\pm 0.003)\mu\text{m}$ size has been estimated as the number of collected particles on the resonator. This number of fluorescent particles corresponds to $(0.45 \pm 0.19)\text{ng}$.



Figure 64- The particle counting estimation from 5 different locations of device 3 after the second impaction.

Following that the total number of collected particles has been counted with the same procedure for the second and third impactions (see **Figure 64** and **65**). However, it should be mentioned that the total number of counted particles from the second impaction and the third impaction have been subtracted from the first impaction and the second impaction, respectively (e.g. (5496-1096) for impaction 2, (7366-5496 for impaction 2). As a result of these counting, (4400 \pm 1400) fluorescent particles with \overline{MAD} of (0.994 \pm 0.002)µm size have been found on the resonator, which corresponds to the mass of (1.8 \pm 0.6)ng total deposited particles in the second impaction. The latter impaction results in a number of (1870 \pm 1794) fluorescent particles with \overline{MAD} of (1.026 \pm 0.001)µm µm size that equals the mass of (0.77 \pm 0.73)ng particles on the resonator surface. As it has been predicted previously, the impaction 3 might have been subjected to a significant misalignment and lead to a reduced number of particles deposition.



Figure 65 - The particle counting estimation from 5 different locations of device 3 after the third impaction.

4.5.3 Local collection efficiency estimation

Figure 66 presents the particle collection efficiency by means of the number of counted particles on the active surface area of the resonator and the number of VOAG generated particles. The latter implies the maximum number of particles has been presented in the experiments which include the particle losses during the transportation from the VOAG to the sampler inlet, the losses in the impactor, and misalignment. In **Chapter 2**, the local collection efficiency of the particles with \overline{MAD} of 0.92 µm size at the primary impaction zone has been estimated as (17.9 ± 1.8) %. As seen in **Figure 66**, when the uncertainties are taken into the account, the collection efficiency in the first and second impactions is



Figure 66 - The estimated local collection efficiency by means of counted particles on the device 3 versus the number of generated particles for three consecutive impactions.

coherent with the estimated local collection efficiency in Chapter 2.

In order to investigate the impaction characteristics, a new nozzle plate (800 μ m height) should be fabricated to maintain the desired distance between the SOI-based chips (300 ± 25) μ m height and the nozzles (500 μ m diameter). Besides, more experiments with better alignments are also needed to confirm the local collection efficiency.

4.5.4 Mass calibration of the sensor

Figure 67 presents relations between the mass and number of counted particles and the mass from the resonance frequency shifts. Detailed results are summarized in **Table 14**. The mass estimation from the resonance frequency shift overestimates the physical mass of the counted particles in the first





Figure 67 – Analysis of device 3: The mass estimation from the shifts as a function of total counted particle mass (top left). Frequency shifts are versus the counted mass of particles (top right). Frequency shifts versus numbers of counted particles in three consecutive impactions (bottom).

and second impactions. Although the fabrication tolerance slightly alters the designed and expected dimensions (and thus the effective mass) of the resonator such as the thickness of the resonator which is expected to be 40 μ m instead of ~ 38 μ m (see **Chapter 3**), it has an insignificant effect on the added mass estimation. In **Figure 67**, the correlations demonstrate a promising result in which the measured frequency shifts are coherent with the mass and number of counted particles in the first and second impactions. Therefore, the experiments ensure a reliable detection of collected monodisperse fluorescent particles by considering the fact that impaction 3 has suffered from severe misalignment.

As a result, Sauerbrey's equation does not apply for a precise mass determination of homogenously distributed particles, and therefore, a correction factor is required. The inadequate result of

Device 3	$\Delta f_{n_{-3}}$ (Hz)	Δm_{n_3} (ng)	Number of counted particles (#)	Counted particles mass (ng)
Impaction 1	(75±52)	(1.71±1.18)	(1096 ± 463)	0.45 ± 0.19
Impaction 2	(145±51)	(3.31±1.16)	(4400 ± 1400)	1.8 ± 0.6
Impaction 3	(165±51)	(3.74±1.17)	(1870 ±1794)	0.77 ± 0.73

Table 14– Detailed results of consecutive impactions for device 3.

impaction 3 has made the adjustment of a correction factor impossible. Nevertheless, the mass sensitivity can be calculated from the result of the first and second impactions as they exhibit the most relevant results. The mass sensitivity of the sensor is found to be (167 ± 135) Hz/ng in the first impaction and (81 ± 39) Hz/ng in the second impaction. Although the effective mass of the resonator is increased after the first impaction, the sensitivity calculation of the impaction 2 is still relevant due to the negligible effect of the added mass in comparison to the effective mass of the resonator. The theoretical localized mass sensitivity can be described as follows (Cagliani & Davis, 2011):

$$s = \frac{f}{2m_{eff}} \tag{48}$$

As shown in Chapter 3, Table 2, the effective mass of the resonator (m_{eff}) operating in Lamé mode is 46.6µg and the theoretical resonance frequency (f_o) is equal to 4.13 MHz. Therefore, the theoretical sensitivity of the sensor can be calculated as 44.3 Hz/ng, which matches the sensitivity obtained from the first and second impactions of device 3.

Although the mass of counted particles has been found from device 3, it has been also correlated with the measured mass from device 1 and 2 in impaction 1 and 2. Figure 68 presents the calculated mass from frequency shifts of device (1, 2, and 3) and the collected particles mass. The correlation proves that the mass of collected particles (from device 3) is consisted with the mass of measured particles for also device 1 and 2. Finally, Figure 69 presents the slope of the best-fit line which defines the experimental sensitivity of the sensors as (53 ± 33) Hz/ng.



Figure 68 – Counted particles mass as a function of the measured mass for device 1,2, and 3 in impaction 1 and 2.



Figure 69 - Counted particles mass as a function of resonance frequency shift for device 1, 2, and 3 in impaction 1 and 2. The slope indicates the experimental sensitivity.

4.6 Conclusion and future perspective

In the context of this study, the impacted monodisperse fluorescent particles on the resonator surface have been manually counted and the mass of collected particles is calculated. The resonance frequency shifts upon the collection of particles have resulted in a reliable estimation of the mass of particles. Although the present electrical measurement set-up generates a considerable uncertainty which ultimately decreases the mass sensitivity, the sources of the uncertainty have been identified and added to the measurements.

Sauerbrey's added mass-resonance frequency shift relation does not apply to the case of homogenously distributed particles. Therefore, a reasonable correction factor is needed to ensure a good calibration of the sensors. However, the calibration factor has not been determined in this study due to impaction 3 which has subjected to a severe misalignment and other unknown factors. For device 3 which is operating in Lamé mode, the experimental mass sensitivity shows a coherent result with the theoretical mass sensitivity. Furthermore, the collection efficiency by means of the number of generated particles and the number of counted particles on the active area of the resonator (i.e. local collection efficiency) is found to be also coherent with the estimated local collection efficiency at the primary impaction zone in **Chapter 2**.

As a result, the fabricated MEMS mass sensors are successfully integrated into the developed impactor. MEMS mass sensors have achieved to detect and perform mass measurements of the impacted fluorescent particles with a promising precision. While more impactions are needed to calibrate the detection system which will deliver the mass of homogeneously distributed particles on the resonator, real-time measurements with better alignment are needed to obtain more accurate results.

In the context of future perspectives, a functionalized and nanostructured (e.g. black silicon) MEMS sensor array can be used to minimize the bounce effect, localize the primary impaction zone, increase the collection efficiency, and may provide a specific detection of different origin of airborne particles.

The goal of the developed system is the entire integration of the sensor array, which consists of ten MEMS mass sensors to the developed impactor. The sensors and slits where the air-flow exists can be microfabricated on an SOI wafer (see Figure 70). Then it should be placed on a printed circuit board (PCB) and wire bonded. While this chip-scale impactor system enables the alignment of the sensors with the nozzles, it facilitates reliable, sensitive, and real-time mass concentration measurements.

The detection system is not only expected to be sensitive, showing fast, linear, and reproducible responses, but also be selective to a different group of bioaerosols. As the sensor array consists of ten



Figure 70 – The design of fully-microfabricated arch-shaped slits surrounding a MEMS mass sensor array which is well-aligned with nozzles (interconnections are excluded for the sake of simplicity) (Designed in Coventor software).

sensors, each sensor can be specifically addressed to a different group of bioaerosols by establishing a data acquisition system which can simultaneously acquire, filter, and correct data from all the sensors. This system would minimize the potential risk to release inaccurate and unconfirmed data to the public.

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Outcome of this thesis:

Journal publications

1. U. Soysal, E Géhin, E Algré, B Berthelot, G Da, E Robine, Aerosol mass concentration measurements: Recent advancements of real-time nano/micro systems, Journal of Aerosol Science 114, December, 42-54 (2017)

2. Ugur Soysal, Frédéric Marty, Evelyne Géhin, Charles Motzkus, Emmanuelle Algré, Fabrication, electrical characterization and sub-ng mass resolution of sub-µm air-gap bulk-mode MEMS mass sensors for the detection of airborne particles (Under review, Journal of Microelectronic engineering)

3. Ugur Soysal, Evelyne Géhin, Frédéric Marty, Emmanuelle Algré, Charles Motzkus, Exploring deposition characteristics of aerosol and bioaerosols on silicon and black silicon by impaction for the development of MEMS mass sensors (To be submitted in Journal of Aerosol Science)

4. Ugur Soysal, Evelyne Géhin, Frédéric Marty, Emmanuelle Algré, Charles Motzkus, The road to a highly sensitive bulk-mode MEMS mass sensor array-integrated impactor for the real-time mass measurement of aerosol and bioaerosols (**To be submitted** in Sensors and Actuators: Physical A)

<u>Patent</u>

1. Capteur de particules fines avec microbalances en cascade (**Pending, 2018**)

Proceedings

 U. Soysal, F. Marty, E. Algré, E. Géhin, C. Motzkus, Sub-µm air-gap resonant MEMS mass sensors fabrication and electrical characterization for the detection of airborne particles, in: 2018 Symp. Des. Test Integr. Packag. MEMS MOEMS DTIP, 2018: pp. 1–5. doi:10.1109/DTIP.2018.8394231.

International and national conference presentations

- Deposition characteristics of aerosol and bioaerosols by inertial impaction, Ugur Soysal, Evelyne Géhin, Frédéric Marty, Emmanuelle Algré, Charles Motzkus, CFA/ASFERA Paris, France, 22nd-23th January (2019) (Oral presentation) (National)
- Deposition characteristics of bioaerosols: Towards black silicon-based MEMS bioaerosol detection, Ugur Soysal, Evelyne Géhin, Frédéric Marty, Emmanuelle Algré, Charles Motzkus, IAC St. Louis, USA, 2nd – 7th September (2018) (Poster) (International)
- Sub-µm air-gap resonant MEMS mass sensors fabrication and electrical characterization for the detection of airborne particles, Ugur Soysal, Frédéric Marty, Emmanuelle Algré, Evelyne Géhin, Charles Motzkus, DTIP Rome, Italy 22nd May – 25th May (2018) (Poster) (International)

RÈSUMÈ

Grâce au développement des techniques de micro-fabrication, il devient désormais possible de réaliser des systèmes miniatures de mesure de la concentration en particules polluantes dans l'air. Ainsi, l'utilisation conjointe d'un système d'échantillonnage adéquat et d'un microsystème électromécanique (MEMS), comme capteur inertiel de masse, permet de former un dispositif individuel de contrôle de pollution particulaire. La méthode d'échantillonnage permet de prélever puis d'emmener les aérosols de l'air ambiant au capteur, alors que le MEMS permet de détecter puis d'estimer la masse déposée à partir d'un décalage de sa fréquence de résonance.

Dans ce contexte, une revue bibliographique approfondie a été menée sur les méthodes de mesure de masse traditionnelles et actuelles. Notamment, les avancées concernant les différentes méthodes émergeantes permettant une analyse en temps réel ont été examinées. Les MEMS en silicium à déformation de volume ont alors été choisi comme capteur de masse, couplé à système d'échantillonnage approprié.

La possibilité de miniaturiser les méthodes d'échantillonnage a ensuite été étudiée et l'impacteur inertiel a été choisi comme la plus appropriée des méthodes. En accord avec la théorie classique d'impaction, l'impacteur a été dimensionné et conçu puis fabriqué et caractérisé. Des dépôts d'aérosols monodispersés (fluorescéine) et de bioaérosols (Aspergillus niger, Staphylococcus epidermidis, Pseudomonas fluorescens) ont été réalisés, à l'aide du micro-impacteur, sur des surfaces de silicium poli et sur des surfaces de silicium nanostructuré (Silicium noir) et leurs propriétés ont été étudiées. Les résultats expérimentaux ont mis en évidence que la taille des particules joue un rôle déterminant dans les caractéristiques de dépôt, du fait des mécanismes de rebond et de réentrainement.

Afin de développer un détecteur inertiel de masse, des capteurs MEMS, ont été fabriqués avec succès, par microfabrication en utilisant un oxyde épais pour réduire la taille des gaps électrostatique à des dimensions sub-microniques. Cette méthode permet alors de réaliser des résonateurs MEMS à gap d'air avec de très fort rapport d'aspect. Les dispositifs réalisés ont ensuite été caractérisés électriquement et la résolution en mesure de masse a été étudiée. Ces capteurs MEMS à fort rapport d'aspect ont été actionnés suivant deux modes de déformation de volume (Lamé et mode extensionnel), et une résolution en masse inférieure au nanogramme a pu être démontrée.

Finalement, les capteurs MEMS ont été intégrés au microimpacteur et des particules mondispersées de fluorescéine ont été successivement impactées sur les capteurs. Le décalage de la fréquence de résonance des capteurs MEMS a été mesurée et la masse déposée a été évaluée à l'aide du principe de Sauerbrey. Les capteurs MEMS ont permis de détecter et de mesurer la masse de particules de fluorescéine avec une précision très prometteuse. Bien que de nouvelles impactions soient nécessaires pour calibrer les capteurs, la sensibilité en masse théorique est en accord avec celle mesurée pour les différentes impactions. Le système de détection de particules, développé dans le cadre de cette thèse, ouvre donc la voie à la détection et la mesure de masse d'aérosols et de bioaérosols en temps réel.

ABSTRACT

Microfabrication methods are an emerging technology which enables to build micro scale airborne particle mass concentration measurement systems. A personal airborne particle monitoring system can be achieved by combining an appropriate sampling method with inertial microelectromechanical systems (MEMS) mass sensors. While aerosol sampling methods can take airborne particles from ambient air and transport to a detector in the most efficient way, MEMS provide the detection and estimation of the mass based on a shift in the resonance frequency of oscillating sensors.

In this context, an extensive literature review is proposed in order to examine the mass concentration measurement methods from past to present. The methodological tendencies for advanced real-time aerosol mass concentration measurement are evaluated. Finally, bulk-mode silicon-based MEMS mass sensor is chosen to be coupled with an appropriate aerosol sampler.

Following that the miniaturization possibilities of aerosol sampling methods are discussed and inertial impactor is chosen as a suitable aerosol sampling method. Then, the impactor is designed, fabricated, and characterized based on the classical impaction theory. The latter, the deposition characteristics of monodisperse aerosol (fluorescent) and bioaerosols (Aspergillus niger, Staphylococcus epidermidis, Pseudomonas fluorescens) are explored by inertial impaction on silicon and nanostructured silicon (i.e. black silicon). The empirical results show that the size of airborne particles plays a key role to determine the deposition characteristics of the impaction by the mechanism of rebound and reentrainment (i.e. bounce effect) of the particles.

In the context of developing an inertial mass sensor, sub-µm air gap MEMS mass sensors have been successfully fabricated based on the thick oxide as a mask layer method. This method enables to fabricate high-aspect-ratio air-gap MEMS resonators. Then, the devices are electrically characterized and the mass resolution is investigated. As a result, high-aspect-ratio MEMS sensors are operated in two different bulk modes (Lamé and extensional modes) and the mass resolution of the sensors is found to be as sub-ng.

Finally, the fabricated MEMS mass sensors are integrated into the developed impactor and monodisperse fluorescent particles are successively impacted on the sensors. The shift in the resonance frequency of MEMS mass sensors are evaluated based on Sauerbrey's principle. Ultimately, MEMS mass sensors have achieved to detect and perform mass measurements of the impacted fluorescent particles with a promising precision. Although more impactions are needed to calibrate the sensors, the theoretical mass sensitivity of the device is matched with the experimental mass sensitivity obtained from successive impactions. Therefore, the developed airborne particle detection system paves the way for real-time detection and mass measurements of aerosol and bioaerosols.