

Etude de composants piézoélectriques à base de couches épaisses imprimées et libérées : application à la détection de COVs à l'aide de micropoutres avec couche sesnible de silice mésoporeuse

Onuma Santawitee

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Study of piezoelectric devices based on free-standing printed thick-films: Application to VOCs detection using micro-cantilevers with mesoporous silica sensitive coating

Sous la direction de Mme Hélène DEBEDA et Mme Chanchana THANACHAYANONT

Soutenance le 24 Septembre 2020

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Titre : Etude de composants piézoélectriques à base de couches épaisses imprimées et libérées : Application à la détection de COVs à l'aide de micropoutres avec couche sesnible de silice mésoporeuse

Résumé :

Ces dernières années, des procédés de sérigraphie associés à la technique de la couche sacrificielle ont été développés pour préparer des microsystèmes piézoélectriques à base de couches épaisses de titanate de zirconate de plomb (PZT ou Pb(Zr,Ti)O₃). Cependant, les choix des matériaux et les conditions de traitement (telles que la composition des encres de sérigraphie, les conditions d'impression et le traitement thermique) pourraient affecter la microstructure et par conséquent les propriétés électromécaniques des transducteurs à couches épaisses imprimés. Avec des films épais de PZT déposés sur une couche sacrificielle composite à base d'époxy et de SrCO₃, une porosité résiduelle est observée au sein des films de PZT. Ainsi, les films de PZT obtenus ont des propriétés piézoélectriques inférieures à celles d'un PZT massif commercial. Ce travail met en évidence l'amélioration possible des propriétés des films piézoélectriques imprimés par une préparation appropriée de l'encre de PZT et le choix des matériaux des électrodes et de la couche sacrificielle. Avec le dépôt sur une couche sacrificielle de polyester et en utilisant une encre de PZT à base de nanoparticules de PZT et avec 3 % en poids d'aide de frittage LBCu (Li2CO₃, Bi2O₃ et CuO), les microdisques de PZT libérés ont montré une meilleure densification après une cuisson à 900°C $(\approx 7,4 \text{ g/cm}^3)$. En outre, les électrodes en Ag/Pd ont permis d'obtenir une meilleure interface PZT/électrodes par rapport aux électrodes en Au. En conséquence, des valeurs plus élevées du coefficient de couplage électromécanique effectif (\approx 45%) et de permittivité relative (\approx 1200) ont été obtenues. Dans la deuxième partie de ce travail, l'encre optimisée a été utilisée pour la fabrication d'une micro-poutre dédiée à la détection des composés organiques volatils (COVs). Le principe de ce capteur est basé sur la mesure des décalages de fréquence de résonance de la micropoutre en vibration lorsqu'elle est exposée à des espèces cibles. Avec la micropoutre recouverte d'une couche sensible présentant une capacité de sorption élevée, ces décalages peuvent être négatifs en raison d'une augmentation de la masse. Pour cette application, différentes géométries de micro-poutres en PZT ont été fabriquées (de $3 \times 1 \times 0.1$ mm³ à $6 \times 2 \times 0.1$ mm³). Ensuite, la micro-poutre de taille $3 \times 2 \times 0.1$ mm³ a été choisie pour l'application de détection parce qu'elle donnait des valeurs acceptables de sensibilité massique ($\approx 27 \text{ Hz/}\mu\text{g}$) et qu'elle présentait une surface suffisante pour le dépôt de la couche sensible. La silice mésoporeuse (MCF-Si) est un type de matériau qui est intéressant pour être utilisé comme récepteur en raison de la grande taille de ses pores et de leur volume. Ici, elle a été synthétisée par la méthode sol-gel avant d'être fonctionnalisée par l'hexaméthyldisilazane (HMDS) pour être plus hydrophobe. Les MCF-Si fonctionnalisés ont une surface, une taille de pores et un volume de pores de \approx 484 m²/g, 6,59 nm et 0,906 cc/g, respectivement. Enfin, ce matériau poreux (≈50 µg) a été déposé sur l'extrémité libre d'une micropoutre de PZT avant la détection des COVs à température ambiante. De faibles réponses sous des vapeurs d'eau, d'éthanol et de benzène ont été constatées alors que le capteur a montré une très bonne sensibilité à la vapeur de toluène. De plus, les décalages de fréquence se sont avérés positifs ou négatifs en raison d'une compétition entre les effets de masse et de rigidité. Une dépendance avec la nature de la surface de la micropoutre (avec ou sans couche sensible) et avec la composition et concentration du gaz a été notée. Avec les valeurs de sensibilité au toluène (≈ 0.24 Hz/ppmv) et la limite de détection (25 ppmv), le capteur serait bénéfique pour la surveillance de l'environnement.

Mots clés : [composés organiques volatile, sérigraphie, silice mésoporeuse, matériaux piézoélectriques, micro-poutre, couche sacrificielle]

Title : Study of piezoelectric devices based on free-standing printed thick-films: Application to VOCs detection using micro-cantilevers with mesoporous silica sensitive coating

Abstract :

In recent years, screen-printing process associated with sacrificial layer technique have been developed to prepare piezoelectric MEMS (MicroelectroMechanical Systems) based on lead zirconate titanate (PZT or $Pb(Zr,Ti)O_3$) thick films. However, material choices and process conditions (such as pastes compositions, printing conditions and thermal treatment) could affect microstructure and consequently electromechanical properties of printed thick films transducers. With PZT thick films deposited on a composite sacrificial layer based on epoxy and SrCO₃, a residual porosity within PZT films is observed. Thus, the obtained PZT films have lower piezoelectric properties compared to a bulk commercial PZT. This work points out improvements of the properties of the printed piezoelectric films by appropriate PZT paste preparation and differences in choices of electrode and sacrificial layer materials. With deposition on a polyester sacrificial layer and using PZT paste containing nano-PZT particles and 3 wt% LBCu sintering aid (Li₂CO₃, Bi₂O₃, and CuO), free-standing PZT micro-disks showed improved densification after firing at 900°C (≈7.4 g/cm³). Furthermore, Ag/Pd electrodes led to better PZT/electrode interface compared to Au electrodes. As a result, higher values of effective electromechanical coupling coefficient (\approx 45%) and relative permittivity (\approx 1200) were obtained. In the second part of this work, the optimized paste was used for processing of a micro-cantilever dedicated to Volatile Organic Compounds (VOCs) detection. The principle of this sensor is based on the measurement of resonant frequency shifts of the vibrating cantilever when exposed to target species. When the cantilever coated with a sensitive coating presenting high sorption capacity, these shifts could be negative due to a mass increase. For this application, various geometries of PZT cantilevers were fabricated (from $3 \times 1 \times 0.1$ mm³ to $6 \times 2 \times 0.1$ mm³). Then, the cantilever in size of $3 \times 2 \times 0.1$ mm³ was chosen for sensing application because it gave acceptable values of mass sensitivity ($\approx 27 \text{ Hz/}\mu\text{g}$) and had enough surface area for receptor depositing. Meso-cellular foam silica (MCF-Si) is one type of mesoporous materials which is attractive to be used as receptor (sensitive layer) due to its large pore size and pore volume. Here, it was synthesized by sol-gel method before functionalization by hexamethyldisilazane (HMDS) to be more hydrophobic. HMDS functionalized MCF-Si's surface area, pore size and pore volume were $\approx 484 \text{ m}^2/\text{g}$, 6.59 nm and 0.906 cc/g, respectively. Finally, this porous material ($\approx 50 \ \mu g$) was dropped onto the free-end of the PZT cantilever before detection of VOCs at room temperature. Low responses under vapors of water, ethanol and benzene were noticed whereas the sensor showed a very good sensitivity to toluene vapor. Also, frequency shifts could be positive or negative because of a competition between mass and stiffness effects. These effects depended on cantilever surface (uncoated or coated with sensitive layer) and on the target vapor nature and concentration. With the acceptable values of sensitivity to toluene (≈ 0.24 Hz/ppmv) and the limit of detection (≈ 25 ppmv), the sensor would be benefit to environmental monitoring field.

Keywords: [volatile organic compounds, screen-printing, mesoporous silica, piezoelectric materials, microcantilever, sacrificial layer]

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Preface

Detection of Volatile Organic Compounds (VOCs) with miniaturized chemical gas sensors is at the heart of the concerns. VOCs are indeed harmful organic chemicals that promptly generate vapors at ambient temperatures. Their sources are in the air today. They are not only originated from nature sources, but also from human activities. Consequently, monitoring their values with gas sensors is necessary for safety conditions in several fields such as chemical industries and environmental organizations.

Chemical gas sensors contain two important parts: a receptor and a transducer. The receptor detects and transforms chemical information into a form of energy which is measured and transformed into useful analytical signals by the transducer. Sensors performances are strongly influenced by the transducer types and receptor choices. Among VOCs gas sensors, MicroElectroMechanicalSystems (MEMS) resonant cantilevers have proven their high sensitivity. These types of sensors are gravimetric sensors, covered with a sensitive coating having the role of trapping the gas molecules. Consequently, in presence of the gas, due to gas sorption in the sensitive coating, a negative resonant frequency shift is usually measured. The nature of the sensitive coating will determine the selectivity. For the cantilever operating, piezoelectric effect can be particularly useful, with actuation and read-out due to the direct piezoelectric effect, and inverse piezoelectric effect respectively. This thesis work focuses on optimization and characterization of the two parts constituting the cantilever based sensor: the piezoelectric transducer and the sensitive coating. This interdisciplinary work has been conducted during the two first years within the PHC Siam project which started in 2017 among two French laboratories: IMS Bordeaux and LUSAC Cherbourg and, on the Thai side with collaboration of the Chemical Engineering department of the Chulalongkorn University (CU) and the National Metal and Materials Technology Center (MTEC). The major purpose of this PHC Siam project entitled "Detection of benzene and formaldehyde vapors using mesoporous silica-coated piezoelectric cantilevers" was VOCs detection with sensors based on micro-cantilevers coated with mesoporous silica. For this PhD, the target gases were mainly toluene and benzene, which activate smog pollution in Thailand (especially Bangkok) at high level mainly because of vehicle emission. The role of each partner in this PhD work will be further detailed.

Piezoelectric ceramics based on lead zirconate titanate, $Pb(Zr,Ti)O_3$ or PZT are, despite their lead content, still favourable materials for production of various transducers applications such as MEMS due to their notable piezoelectric properties. However, the PZT bulk ceramics are fragile. This disadvantage makes them inconvenient to adjust their size and shape for integration in the microelectronic systems or for shaping of MEMS. Thick film technology developed for manufacturing hybrid micro-electronic circuit is an interesting option for fabrication of printed sensors or more recently flexible electronics. In classical thick film technology process, after preparation of a paste with adapted rheology, a thick film layer is screen-printed on a substrate. This step consists in deposition of the paste onto a substrate through a finely-woven screen with etched patterns. This technique gives film thickness in the range of 10-100 μ m with a variety of geometries designed. It is very attractive because of flexibility, low cost and high volume production. With this technique, piezoceramics based on screen-printed thick films can allow sensor or actuator applications. A sintering step followed by poling will achieve piezoelectric properties. If the application requires resonance use of the piezoelectric layer, thick films which are usually bound to the substrates should be free-standing film.

All printed piezoelectric MEMS based on PZT material have been developed for more than 10 years at IMS Laboratory for various applications such as gravimetric sensors (particle or gas sensing), structural health monitoring or energy harvesting. PZT bridges, cantilevers or disks with electrodes could be obtained by combining thick film technology with sacrificial layer process to achieve freestanding piezoelectric layers. In particular, self-actuated and readout cantilevers based on a PZT layer sandwiched between electrodes layer were successfully applied to VOCs detection. Because of their symmetric structure, longitudinal vibration mode was promoted. This mode was interestingly giving higher sensitivity than bending mode classically used, due to its higher resonant frequency. Various kinds of sensitive coatings were used such as polymer, microporous zeolite or carbon nanotubes. The process for the fabrication of the cantilever is straightforward with successive layer printing followed by the thermal treatment. Then, depending on the sacrificial layer nature, mineral or organic, either a soft etching is led at the end of the process or the layer is burnt out during the thermal treatment. The sensitive coating is finally deposited on the cantilever. Nevertheless, piezoelectric thick films can present residual porosity which can be critical for piezoelectric effect and gas detection. Also, the high thermal treatment (900°C) of the piezoelectric layer with electrodes possibly lead to interface issues, warpage, delamination, and so on. As a result, the main purposes of this PhD work are:

- (1) Optimization of the PZT cantilever transducer performances through the material choices, geometries, and adaptation of the processing conditions to reach the best densification: In this part, LUSAC Laboratory will bring its expertise in ceramic sintering to improve PZT densification.
- (2) Synthesis of a high surface area materials for sensitive coating: In this work, a mesoporous material has been chosen because it presents a high surface area and regularly well defined pore system (diameter 2-50 nm) whose morphologies can fit to VOCs molecules and can be controlled through *ad-hoc* synthesis. The synthesis of mesocellular foam silica (MCF-Si) and its functionalization for improving its performances under VOCs will be conducted by CU.
- (3) *Microstructure and interface characterizations of the mesoporous and the cantilevers*, with a contribution of MTEC
- (4) Finally, deposition of the functionalized MCF-Si sensitive coating and VOCs detection

This thesis manuscript is divided into four chapters which are the following:

Chapter one presents various VOCs definitions from different organizations, fundamental gas/vapor sensors, concerned knowledges of mass sensing based on piezoelectric transducers and sensitive (sensing) layer, and literature reviews of developed cantilever transducer for VOCs detection.

Chapter two details fabrication of thick film transducer with material selection, paste preparation, transducer design, and used equipment. The multilayer printing and thermal treatment are also explained in this chapter.

Chapter three contains four parts of optimization of screen-printed PZT transducers fabrication and microstructural and electromechanical characterization. Part one is study on effects of PZT compositions in terms of the ratios of sintering aid's formulas and PZT particle sizes on densification of free-standing-disks printed onto polyester sacrificial layer. Part two is study on the tendency of using sacrificial layer based corn starch. Then, the PZT disk characteristics are illustrated in Part three. Final part reveals utilization of optimized PZT paste in fabrication of cantilever transducers. The four cantilever sizes are fabricated and characterized. The appropriate cantilever is selected for using as transducer in VOCs sensors for Chapter four.

Chapter four focuses on syntheses of the functionalized MCF-Si and the construction of VOCs sensors with PZT cantilever transducers and functionalized MCF-Si sensitive layer (the receptor). The sensing systems are explained. Effect of environment (temperature and relative humidity) on the sensors is studied. The responses of this sensors under three kinds of VOCs (benzene, toluene, and ethanol) are noticed and analyzed.

Finally, this manuscript ends with the general conclusions and some perspectives for future work and experiments.

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This chapter will provide definitions of volatile organic compounds (VOCs). Their sources and effects on the environment and human's health will be explained; particularly, the information of toluene and benzene vapors will be given. Moreover, fundamental components of gas sensors will be presented. The development of gas sensors based on resonant cantilever transducers coated with sensing layer based on mesoporous materials will be detailed before presenting the objectives of this thesis.

1.1 Volatile organic compounds (VOCs)

1.1.1 Definition

VOCs are a group of organic substances having high rate of volatility at ambient temperature [1]. Although many organizations offer different VOCs definitions, they are ordinarily classified by physico-chemical properties such as boiling point and vapor pressure [2]. The examples of various VOCs definitions from different organizations are as the following:

• The European Union (EU)

According to the Industrial Emissions Directive 2010/75/EU, "Organic compound" means any compound containing at least the elemental carbon, hydrogen, halogens, oxygen, sulphur, phosphorus, silicon or nitrogen, with the exception of carbon oxides and inorganic carbonates and bicarbonates. "Volatile organic compounds (VOCs)" mean any organic compounds having at 293.15 K a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use.

• The U.S. Environmental Protection Agency (EPA)

According to 40 CFR 51.100(s) when CFR is an abbreviation of code of federal regulations, "Volatile organic compounds (VOCs)" mean any compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

• The World Health Organization (WHO)

According to a WHO meeting report in 1987, VOCs are a class of organic indoor pollutants classified by the ease of emission into four groups [3] as shown in Table 1.1.

Order	Description	Abbreviation	Boiling Point Range	Example Compounds
1	Very Volatile Organic	VVOC	0°C to 50-100°C	Propane, Butane
	Compounds			
2	Volatile Organic Compounds	VOC	50-100°C to 240-260°C	Benzene, Toluene,
				Ethanol
3	Semi Volatile Organic	SVOC	240-260°C to 380-400°C	Di-n-butylphthalate,
	Compounds			Organochlorine pesticides
4	Particulate Organic Matter	РОМ	>380°C	Hexadecanoic acid,
				Azelaic acid

Table 1.1 Classification of volatile organic compounds (Adapted from [3])

1.1.2 VOCs sources and their effects on the environment and human's health

Several VOCs sources are classified into 3 categories: stationary, nature, and mobile as shown in Table 1.2 [4]. According to the U.S. Environmental Protection Agency (EPA), VOCs are one of many primary air pollutants causing the air pollution such as ground-level ozone and smog (Figure 1.1). Although, there is presence of VOCs both indoor and outdoor air, the indoor concentrations of some VOCs are higher than those in outdoor air. Gaining excessive VOCs probably affect human health such as headaches, food bore mycotoxin, skin, eye, nose and throat irritation, and cancer risk, etc. [5]. Many organizations gave limitation of VOCs values in the indoor air as shown in Table 1.3. As reasons mentioned earlier, monitoring VOCs has become a serious requirement due to stringent regulations applied in many countries in the world.

Source	Detail
Stationary	Mostly related to energy generation and usage, including plants emissions, municipal
	emissions, chemical product emissions, etc.
Mobile	Mainly energy-related, including cars, trains, lorries, ships, motorbikes, etc.
Nature	Wildfire, sea spray, volcano, geothermal sources, etc.

Table 1.2 Air pollutants' sources	[4]
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Remarks:

 O_3 is ground-level ozone ($O_3 = NO_x + VOCs + Heat \& Sunlight$). 1.

2. PM is Particulate Matters.

Figure 1.1 Formation of smog (Developed from Wang [4] and free images from vectorstok.com).

VOCs name and formula		Properties	IDLH ¹	TLV ²	
Acetone (C ₃ H ₆ O)	н₃с↓сн₃	Colorless, pungent odor, sweetish taste, flammable	20,000 ppmv NIOSH	750 ppmv ACGIH	
Acetylene (C ₂ H ₂)	НС≡СН	Colorless, distinctive odor, low toxicity	N/A	N/A	
Benzene (C ₆ H ₆)	$\langle \rangle$	Colorless, strong aroma, highly flammable, Chronic toxicity	500 ppmv NIOSH	1 ppmv OSHA	
Cyclohexene (C ₆ H ₁₀)	\bigcirc	Colorless, mild solvent odor, flammable, low acute toxicity	10,000 ppmv NIOSH	300 ppmv ACGIH, OSHA, NIOSH	
Ethanol (C ₂ H ₅ OH)	н₃с∕∕он	Colorless, alcoholic smell and taste, flammable, low toxicity	3,300 ppmv NIOSH	1,000 ppmv OSHA	
Formaldehyde (CH ₂ O)	O=CH ₂	Colorless, pungent odor, flammable, low acute toxicity	20 ppmv NIOSH	0.75 ppmv OSHA	
Methanol (CH ₃ OH)	H ₃ C— <mark>OH</mark>	Colorless, mild odor, flammable, high toxicity	25,000 ppmv NIOSH	200 ppmv ACGIH	
Toluene (C7H8)	CH3	Colorless, aromatic odor, highly flammable, slight acute toxicity	500 ppmv NIOSH	100 ppmv ACGIH, NIOSH, MSHA	
2-propanol (C ₃ H ₈ O)	н _з с он	Colorless, alcohol-like odor, bitter taste, flammable, low toxicity	12,000 ppmv NIOSH	400 ppmv ACGIH	
n-Butanol (C4H9OH)	н₃с∽∕он	Colorless, vinous odor, flammable, slightly toxicity	8,000 ppmv NIOSH	100 ppmv NIOSH	

Table 1.3 Properties and threshold limit values of VOCs [6], [7], [8], [9].

Remarks:

1. IDLH (immediately dangerous to life or health) is the lowest concentration of VOCs which is immediately dangerous to life or health.

2. TLV (threshold limit value) is defined as the maximum concentration of a chemical permitted during a working day (8 h) for repeated exposure without producing adverse health effects [10].

3. The National Institute for Occupational Safety and Health (NIOSH)

4. Association Advancing Occupational and Environmental Health (ACGIH)

5. Occupational Safety and Health Administration (OSHA)

6. Mine Safety and Health Administration (MSHA)

Among various VOCs, benzene and toluene are highly toxic pollutants detected in both outdoor and indoor air. Benzene is a byproduct of many petrochemical processes and oil refining. It is used in industry as a solvent and a cleaning agent. Toluene is emitted in processes of making gasoline and other fuels from crude oil and the making of coke from coal. Moreover, it is used in productions of paints, paint thinner, fingernail polish, lacquers, adhesives, and rubber, and so on [6], [11] . Physical properties of benzene and toluene are shown in Table 1.4 [12]. For long term exposures, benzene is a well-known carcinogen [13]. While, toluene can cause impairment of the nervous system, hormonal imbalance in male and spontaneous abortion in female [14], [15]. Referring to research studies in Bangkok (Thailand), levels of benzene and toluene gases at a road junction were higher than other gases due to vehicular emission as shown in Table 1.5 [16]. Besides, many air conditioned office buildings in Bangkok presented toluene gas at high concentrations, as shown in Figure 1.2 and 1.3 [17]. Therefore, this research focuses on applying our gas sensors for detecting benzene and toluene gases.

Table 101 Higher Properties of compete and concere [1-]								
Chemical	Molecular weight (g/moll)	Density at 25°C (g/mL)	Boiling point at 760 mmHg (°C)	Vapor pressure at 20°C (mm Hg)	Molecular diameter (Å)	Polarity index		
Benzene	78.11	0.874	80.0	74.6	5.26	2.7		
Toluene	92.14	0.865	110.5	22	5.68	2.4		

Table 1.4 Physical properties of benzene and toluene [12]

 Table 1.5 Comparison of BTEX obtained for different measurement sites in Bangkok. Unit for all species are in ppbv. [16]

Chamical	SIIT (WD)	SIIT (WE)	AREE	Roadside	Junction	Residential	Min [20]
Chemical	[16]	[16]	[16]	area [18]	area [19]	area [18]	WIX [20]
Benzene	0.35-0.86	0.09-0.44	0.35-2.93	0.56-6.27	1.47-8.81	0.38-4.08	0.38-6.21
Toluene	2.77-8.93	0.57-2.32	2.47-30.67	1.57-26.58	8.40-50.10	1.33-35.88	1.33-26.50
Ethylbenzene	0.05-0.76	0.05-0.24	0.25-1.61	0.08-3.00	0.12-5.56	0.05-1.55	0.14-3.02
m-,p-Xylene	0.06-1.23	0.10-0.48	0.41-3.70	0.37-13.38	0.85-24.33	0.32-4.38	0.35-13.29
o-Xylene	0.05-0.48	0.07-0.21	0.21-1.39	0.16-4.15	0.46-3.14	0.99-8.77	0.14-4.22

Remarks:

 SIIT is Sirindhorn International Institute of Technology (14.06°N and 100.61°E) situated at the Rangsit campus of Thammasat University, Pathum Thani, Thailand. The distance from city center is approximately 40 km to the north. It should be noted that there are several industrial estates, within proximity of 20 km of the campus (Industrial Estate Authority of Thailand (IEAT), 2009). Small communities are also scattered in the surrounding area. With this information, it is likely that the air quality observed here is a mixture of suburban characteristics (from industry and households) with impact from urban outflow. WD is weekday and WE is weekend.

2. AREE is a residential area inside Bangkok. Samples were collected where a site is located about 500 m from the main road.

3. Roadside area is in traffic area in Bangkok, Thailand.

4. Residential area is in each district in Bangkok, Thailand.

5. Junction area is in an urban traffic area in Bangkok, Thailand.

6. Mix is the study of aromatic VOCs in Bangkok Metropolitan Area (BMA), located in a tropical region, Thailand which included roadside, residential, and background areas.

For monitoring of benzene and toluene vapors, European Committee for Standardization (CEN) recommends using automatic gas chromatographs as standard measures in its recent directives [21]. Although this measurement technique is very sensitive as well as selective toward the target gaseous molecules, some limitations of this analytical method make it inconvenient for a wide use. Gas chromatography (GC) is a technique necessary to perform in closed laboratory environment due to the complex and bulky instrumentation involved. Moreover, it requires sampling of pollutant analytes and then laboratory analysis. Results may hence differ because the pollutant concentration can be altered during the course of transportation. At last, this method remains very expensive and the time for a complete analysis is long (between 30 min and 1 h depending on carrier gas). Apart from this, other methods such as GC/mass spectrometry, infrared spectroscopy, and fluorescence spectroscopy can also be used to detect VOCs [1]. Some researchers have been developing a portable or compact GC for near real-time BTX (benzene, toluene, and xylene) analysis [22], [23], [24], [25], [26]. However, most of these methods are also expensive and require a pre-concentration system [1], [26]. Using gas/vapor sensors is another attractive choice to develop cheap, portable and easy-to-use devices which could ensure real-time measurements of VOCs in atmosphere [21]. Similarly, the pre-concentrator can be integrated with sensors to enhance their sensitivity for detection of target concentrations as low as several hundreds of ppbv [27].



Figure 1.2 Box plots of indoor and outdoor levels of VOCs for the 17 studied offices. The boundary of the box indicates the 25th and 75th percentile. The solid and dot lines within the box mark the median and arithmetic mean. The solid bar indicates the 10th and 90th percentile. The number represents the arithmetic mean value. PCE = Tetrachloroethylene, TCE = Trichloroethylene, EDC = 1,2-dichloroethane, DCP = 1,2-dichloropropane. n = number of the air samples. The maximum values of toluene concentrations in indoor and outdoor areas were around 0.06 ppmv and 0.02 ppmv, respectively [17].



Figure 1.3 Comparison of arithmetic mean concentrations for aromatic compounds and limonene in offices among oversea studies. The maximum values of toluene concentrations in Thailand was around 0.03 ppmv [17].

1.2 Fundamental gas/vapor sensors

A gas/vapor sensor is a class of chemical sensors containing two basic functional units: a chemically selective receptor and a physical transducer [28]. Roles of the receptor part in the sensor are detection and transformation of chemical information into a form of energy which is measured and transformed into a useable signal by the transducer [29]. The detection and transduction lead to a recordable signal response as shown in Figure 1.4. The operating principle of the transducer for applicable sensors can be categorized by measured parameters as illustrated in Table 1.6. While, the receptor part also depends upon various principles:

- *Physical*, where there is no presence of chemical reaction. For example, measurement of absorbance, refractive index, conductivity, temperature or mass change.
- *Chemical*, in which a chemical reaction with analyte leads to a signal change.
- *Biochemical*, in which a biochemical process provides a signal. It is in case of microbial potentiometric sensors or immunosensors. They may be a subgroup of the chemical ones.



Figure 1.4 A schematic diagram of sensor components (Adapted from [29] and [30]).

Table 1.6 Types of transducers	s (adapted from [29]	and [31])
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Type of device	Physical change	Example
Mass sensitive devices	Mass change at a specially modified	Piezoelectric sensors such as quartz crystal
	surface caused by accumulation of the	microbalances (QCM), surface acoustic
	analyte	wave (SAW), and micro-cantilevers
Optical devices	Optical phenomena such as absorbance,	Optical fibers
	reflectance, luminescence,	
	fluorescence, refractive index and light	
	scattering caused by an interaction of	
	the analyte with the receptor part	
Electrical devices	Electrical properties caused by the	- Metal oxide semiconductor (MOx)
	interaction of the analyte and the	sensors
	receptor	- Organic semiconductor sensors
		- Electrolytic conductivity sensors
Electrochemical devices	Effect of the electrochemical interaction	- Potentiometric sensors
	analyte-electrode	- Voltammetric sensors and amperometric
		devices
Thermometric devices	Heat effect of a specific chemical	Catalytic gas sensors: seebeck effect,
	reaction or adsorption	pellistors [*] , semistors ^{**}

Remarks: * Pellet resistor, and ** one electrode semiconductor gas sensor

Commercial VOCs sensors with various type of transducers such as electrochemical sensors, MOx, optical sensors as UV portable spectrometers, micro-gas chromatograph that combines micro-column with MOx or photo-ionization detectors (PID), electronic noses, etc. [32] can be found for VOCs detection. This research pays attention to the development of mass sensitive devices based on piezoelectric resonant micro-cantilever transducers for gas sensing owing to their sensitivity, miniaturization, portability and low-cost fabrication with screen-printing thick film technique.

1.3 Mass sensing based on piezoelectric transducers

1.3.1 Piezoelectric effects

Piezoelectric materials can transform mechanical energy into electric energy by positive piezoelectric effect, or transform electric energy into mechanical energy by negative piezoelectric effect. When a piezoelectric object deforms under an external force, there are electric charges on the surface. This is called the positive (or direct) piezoelectric effect. On the other hand, when applying an electric field to piezoelectric materials, it deforms. This is called negative (or indirect) piezoelectric effect (Figure 1.5) [33]. These characteristics were discovered by the Curie brothers in 1880 [34].



Figure 1.5 The direct piezoelectric effect causes crystallites in piezoelectric materials to generate electric charges due to the shifting of positive or negative charge centers when the material is under mechanical stresses (Adapted from [35]).

Examples of common piezoelectric materials that are frequently used in sensor technology are lead zirconate titanate (PZT), quartz, and polyvinylidene difluoride (PVDF). Their typical properties are shown in Table 1.7. PZT is a piezoelectric ceramic material which represents direct and inverse piezoelectric effects, high-temperature stability, and large electromechanical coupling coefficients compared to quartz [36], [37], [38]. In contrast, the piezoelectric polymer (PVDF) displays lower piezoelectric properties and lower stability for many applications. For these reasons, despite a lead content, most of piezoelectric transducers employ PZT materials as the main elements [39].

Parameter	Quartz	PZT (hard type)	PZT (soft type)	PVDF
<i>d</i> ₃₃ (pC/N)	2.3	289	593	33
g ₃₃ (10 ⁻³ Vm/N)	57.8	26.1	19.7	380
k_t	0.09	0.51	0.50	0.30
k_p	-	0.58	0.65	-
E33/E0	5	1300	3400	6
Q_m	-	500	65	3-10
T_c (°C)	573	328	193	180

Table 1.7 Typical properties of common piezoelectric materials (in bulk form) [39], [40]

Remarks: d_{33} : piezoelectric charge sensor constant; g_{33} : piezoelectric voltage constant; k_p : electromechanical coupling factor in planar mode; k_i : electromechanical coupling factor in thickness mode; $\varepsilon_{33}/\varepsilon_0$: relative dielectric constant; Q_m : mechanical quality factor; and T_c : Curie temperature.

In general, the gas/vapor detection based on mass sensing system contains mechanical transducers and deposited sensing layer. Adsorption of the analyte's target by the sensing layer induces a shift of the resonant frequency of the mechanical transducers. Thus, the measurement of the resonant frequency shifts can be monitored and the mass loading can be calculated. For all mass sensors, the relation of the mass sensitivity (S_m) and the frequency response is shown in eq. 1.1. For a simple 1D-system Mass/Spring/Damper which assumes that the mass loading (ΔM) is small enough compared to the effective mass (M_{eff}), equation 1.1 becomes equation 1.2 [41].

$$S_m = \Delta f / \Delta M$$
 eq. 1.1

where Δf is the frequency shift, and ΔM is the mass loading.

$$S_m = -f_0/2M_{eff} \qquad \text{eq. 1.2}$$

where f_0 is the resonant frequency and M_{eff} is the effective mass. The effective mass is a single, vibration mode-dependant quantity which allows modeling of the resonator as a simple damped harmonic oscillator [42].

1.3.2 Acoustic wave devices for mass sensing

Certainly, all acoustic wave devices employ piezoelectric materials to generate the acoustic waves. Schematic diagrams of some acoustic wave devices, their operation, and their wave propagation are shown in Figure 1.6, Table 1.8 and Figure 1.7, respectively. Applying a periodic perturbation (electric field/voltage) to the piezoelectric material results in an elastic deformation (strain) that travels through the solid as a wave. These waves propagate in an elastic medium either as longitudinal (compression) or transverse (shear) lattice deformations, or as a combination of both. The acoustic wave device can exhibit different resonant frequencies and vibrational modes depending on the chosen crystallographic orientation. In the field of gas/vapor sensors, these devices operate on a change in the mass at the surface, or in the sheet conductivity of the sensitive layer.



Figure 1.6 The schematic diagrams of (a) a quartz crystal microbalance (QCM), (b) a thin film resonator (TFR), and (c) a surface acoustic wave (SAW) (Adapted from [43]).

Table 1.8 Differen	t operations of some	acoustic wave	devices for	sensors (Adapted	d from [43])
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Devices	Operating frequency range	Detection principle	Wave type
BAW	- QCM (5-30 MHz) - TFR (500 MHz - 20 GHz)	Resonant frequency shift	Bulk waves - Longitudinal (compression)
			- Transverse (shear)
SAW	40MHz-1GHz	 Phase velocity shift Resonant frequency shift 	 Surface waves Rayleigh (both longitudinal and transverse) Shear Horizontal Surface Acoustic Wave, (SH-SAW) Love Wave

Remarks: BAW is the bulk acoustic wave, QCM is the quartz crystal microbalance, TFR is thin film resonator, and SAW is the surface acoustic wave.



Figure 1.7 The schematic diagrams of some lattice point deformations in the acoustic wave devices due to the different wave propagation [43].

A. Bulk acoustic wave (BAW) devices

BAW devices concern acoustic wave propagation through the bulk of the structure. This category of devices includes the quartz crystal microbalance (QCM) and thin-film resonators (TFRs), the latter encapsulating thin-film bulk acoustic resonator (TFBAR) and solidly mounted resonator (SMR) structures. However, QCM and TFR are common devices used in gas sensing. A structure of QCM or TFR generally consists of a thin piezoelectric layer sandwiched between two electrodes. When the electric field is applied towards the two electrodes, mechanical stresses will be induced contributing to deformation of the piezoelectric material and launching acoustic waves. The crystal orientation of the piezoelectric is chosen such that it vibrates in a transverse shear mode when a

voltage is applied to the metal electrodes. For sensing applications, masses that rigidly adhere to the surface will move synchronously with the surface contributing to an effective increase in the devices thickness. Therefore, the mass loading of the surface effectively increases the wavelength, resulting in a fractional decrease in the structure's resonant frequency [43].

B. Surface acoustic wave (SAW) devices

A configuration of SAW devices consists of a piezoelectric substrate, on top of which two metallic interdigital transducers (IDTs) are patterned to form a delay line structure. The separation between the IDT ports determines the delay path between the transmission and reception of the surface wave. With regards to two-port devices, one of the ports is used as the input port and the other as an output. The input signal generates an acoustic wave which propagates to the output port where it is converted to an electrical signal. Conversely for a one- port acoustic device, the single port serves as both the input and output. The SAW devices operate by the application of an alternating voltage to the input IDT, which results in the electrodes becoming alternatively positively or negatively charged, creating an electric field between them. The field distribution induces strain in the piezoelectric substrate, resulting in the generation of surface acoustic waves. The acoustic waves travel along the surface to the output IDT, where the acoustic wave energy is converted into an electrical signal. For gas-sensing applications, the sensitive layer is deposited in between the two IDT ports or over the entire device (if the layer is of low conductivity). The interaction between the analyte and the sensitive layer causes either mechanical or electrical perturbations in the surface boundary conditions leading to the shift in the propagating acoustic mode's phase velocity and resonant frequency [43].

1.3.3 Micro-cantilever devices for mass sensing

A micro-cantilever is the simplest mechanical structure, which is clamped at one end and free at the other end. It is a micro-fabricated rectangular bar shaped structure, longer as compared to width, and has a thickness much smaller than its length or width. In the field of gas/vapor sensors, the micro-cantilever has to be with a deposited sensing layer, which should be selective in order to recognize target molecules in key-lock processes. [30]. In recent years, the use of micro-cantilevers as transducers in chemical and biological sensors have been widely studyied because they have significant advantages of small size and IC compatibility which lead to good performance in chemical sensors such as high sensitivity, particularly at room temperature [44], [45], [46], [47], [48], high integration, miniaturization, mass-production, low cost, and large scale array for multi-target detection [49].

A. Principle operation modes

Two commonly used approaches for the operation of micro-cantilever for gas/vapor sensing applications are static and dynamic modes (Figure 1.8). Their differences are summarized in Table 1.9.



Figure 1.8 The schematic diagrams of major operating modes of micro-cantilever devices for gas/vapor sensing: (a) static-mode exploiting surface stress changes and (b) dynamic mode exploiting resonant frequency changes [50].

Parameters		Sensing modes			
		Dynamic	Static		
Sensing principle		- Measurement of change in resonant	Measurement of cantilever		
		frequency due to change in mass and/or	displacement due to change in		
		spring constant	surface stress		
		- Measurement of resonant frequency due to			
		change in surface stress			
Features		- Receptors are immobilized on either one	- Receptors are immobilized on		
		side or both sides of the cantilever	one side of the cantilever		
		- Sensitivity can be improved by operating	- Sensitivity can be improved by		
		the cantilever at higher mode	incorporating stress concentration		
			regions		
Limitations		- Erroneous due to adsorbate-induced	- Structural nonlinearity due to		
		changes in stiffness	large deflection of the cantilever		
		- Susceptible to fluid damping effect	 Dependence of surface stress 		
		- Susceptible to material damping effect	generation on immobilization		
		- Dependence of change in resonant	protocols		
		frequency on position of the target molecule			
		on the cantilever			
Suitability for measurement					
	- Liquid	Low	High		
	- Air	High	High		
Resolution		Mass: 10 ⁻²⁴ g	Cantilever deflection: 4Å		

Table 1.9 Comparison	of static and dyna	mic sensing mod	des of micro-ca	antilever devices [51	[]
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• Static mode

In this mode, the adsorption-induced deflection of the micro-cantilever is measured. The deflection of micro-cantilever is always due to the surface stress variation. [52].

• Dynamic mode (resonant mode)

In this mode, the adsorption-induced shift in the resonant frequency of the micro-cantilever is measured. Shift in the resonant frequency may originate from either the change in the mass or stiffness (due to the differential stress between the two sides of the micro-cantilever) in the presence of the target molecules [52], [53].

B. Vibration modes of micro-cantilevers

For a rectangular cantilever, its motion is generally described as either out-of-plane or in-plane. Out-of- plane vibrations include transverse (also called bending or flexural), and torsional motions. In-plane vibrations include lateral bending, and longitudinal axial (or extensional) motions as shown in Figure 1.9. Their analytical expressions are summarized in Table 1.10. These equations can be mathematically derived from the following assumptions: the aspect ratio is sufficiently large, the deflection is small compared to cantilever thickness, the geometry is of single-layer uniform rectangular cross-section, and the material is isotropic [54]. Finally, to achieve these motions, different actuation techniques can be chosen thermal, electrostatic, electromagnetic, and piezoelectric.



Figure 1.9 Schemes for (a) a traditional cantilever, (b-e) vibration modes: (b) transverse bending mode, (c) torsional mode, (d) lateral bending mode, and (e) longitudinal axial mode [54].

According to equations in Table 1.10, the resonant frequency of the micro-cantilever device is correlated with the stiffness, geometry, and mass of the cantilever. Consequently, not only attached mass, but also operation conditions dependent on cantilever's stiffness such as viscoelastic properties of the medium and temperature may have effects on the resonant frequency shifts of the cantilever [28], [53].

Mode	Resonant frequency	Constant $(C_{i,n})$	Spring Constant (k _i)	
Transverse	$C_{Tr,n}\sqrt{\frac{k_{Tr}}{m}}$	$rac{\lambda_n^2}{2\pi}$	$\frac{Ew^3t}{12L^3}$	
Torsional	$C_{To,n}\sqrt{\frac{k_{To}}{m}}$	$\frac{2n-1}{4}$	$\frac{Ew^3t}{12L^3}$	
Lateral	$C_{La,n}\sqrt{\frac{k_{La}}{m}}$	$\frac{\lambda_n^2}{2\pi}$	$\frac{Ew^3t}{12L^3}$	
Longitudinal	$C_{Lo,n}\sqrt{\frac{k_{Lo}}{m}}$	$\frac{2n-1}{4}$	$\frac{Ewt}{L}$	

Table 1.10 Summary of cantilever resonant modes in terms of the simple harmonic oscillator model [54]

where i = Transverse(Tr), Torsional (To), Lateral (La), or Longitudinal (Lo) modes, $C_{i,n}$ is a mode-type and mode-order dependent constant, $m = \rho_c Lwt$ is the cantilever mass, ρ_c is the cantilever density, L is the cantilever length, w is the cantilever width, t is the cantilever thickness, E is the Young's modulus of the cantilever, λ_n is the eigenvalue given by the nth positive root of $1 + \cos(\lambda_n) \cosh(\lambda_n) = 0$, and n is a positive integer. The first three eigenvalues are 1.875, 4.694, and 7.855.

C. Readout principles

The deflection and resonant frequency shift of the micro-cantilever can be measured with various techniques. The common techniques are the following:

• Optical readout

In this technique, a laser diode is pointed at the free end of the micro-cantilever. Then, the reflected beam is monitored using position-sensing detector. By this method, small changes (0.1 nm) in the cantilever bending can be detected without electrical contacts [30].

• Capacitive readout

This technique is based on measuring the capacitance between a conductor on the cantilever and another fixed conductor on the substrate that is separated from the cantilever by a small gap. Changes in the gap due to cantilever deformation result in changes in the capacitance between two conductor plates [28].

• Piezoresistive readout

Piezoresistivity is the variation of the bulk resistivity with the applied stress. The resistance of the piezoresistive material integrated on a cantilever can change when the cantilever is stressed with the deflection. This deflection can be caused by changes in absorption-induced stress or by thermal stress [30].

• Piezoelectric readout

This technique needs to have the piezoelectric layer on the cantilever in order to perform the direct or inverse piezoelectric effect. Piezoelectricity can be used for both cantilever actuation and detection. For piezoelectric micro-cantilevers, they are actuated via the negative piezoelectric effect by applying an electric AC voltage to the piezoelectric layer. Then, sensing of mechanical deformation is presented by transient charges [28], [50]. For high resolution detection of the deflection, it is necessary to operate the cantilever in the dynamic mode because the voltage produced by the static force cannot be maintained by the thin film piezoelectric material. Thus, the piezoelectric read-out is primarily utilized in resonance mode [45].

D. Resonant micro-cantilever devices based on piezoelectric materials

The resonant micro-cantilevers containing piezoelectric layer have been becoming an interesting candidate for using as resonant transducers in the field of chemical and biological detection due to their sensitivity, portability, highly parallel analysis systems [28], [45]. In fact, the read-out and actuation for resonant cantilever which can be both achieved with piezoelectric effect is also attractive. Generally, piezoelectric micro-cantilevers are multilayer structures consisting of a PZT piezoelectric layer on a cantilever substrate. Two electrode layers, insulated from each other, provide electrical contact. An identical structure is usually integrated into the rigid chip body to provide a reference for the piezoelectric signals from the cantilever. When the piezoelectric micro-cantilever is vibrating with an adding mass, its resonant frequency usually shifts towards a lower value and a mass change can be calculated. This approach is attractive to sense a small mass, but the dynamic mode operation in a liquid environment poses problems such as high damping of cantilever oscillations due to high viscosity of the surrounding media [30], [53]. Therefore, various research studies focus its application on gas/vapor detection by deposition of some sensing layer onto its structure.

At the beginning of development, the PZT film was fabricated onto a single-crystal silicon (Si) cantilever in order to be both an actuator and a sensor for resonant-based mass sensing applications. For example, Lu *et al.* [55] prepared the cantilever based on a 5.25-mm-thick silicon-on-insulator (SOI) wafer, as shown in Figure 1.10-1.11. The Q-factor and sensitivity of the obtained cantilever could be markedly improved by partially covering the cantilever with the PZT film. Under atmospheric pressure, excellent Q-factor of 808 was achieved by a 30-µm-wide 100-µm-long cantilever at fundamental resonant mode. Moreover, the high-mode vibration was successfully demonstrated using the proposed structure for the pursuit of higher mass-detection sensitivity.



Figure 1.10 Schematic views of cantilever fabrication process [55].



Figure 1.11 SEM image of the fabricated silicon cantilever partially covered with PZT film [55].

The group of Tae Song Kim developed the actuation-detection cantilevers to detect a small mass by coating thin PZT onto silicon nitride cantilevers for bio-sensing. Their PZT micro-machined cantilever (100 μ m wide, 200 μ m long, and 2.1 μ m thick) had a gravimetric sensitivity of 300 cm²/g, which enabled detection of 5 ng mass using Au metal deposition [56]. Their devices were improved to detect bio-materials such as the C-reactive protein (CRP) [37], the prostate-specific antigen (PSA) [57] and the Hepatitis B virus DNA [58]. An example of their cantilever is shown in Figure 1.12.



Figure 1.12 Example of resonant piezoelectric cantilever with PZT thin film on the Si substrate (a) fabrication steps and (b) SEM image of the obtained cantilever applied to bio-sensing [57].

Moreover, Park *et al.* screen printed PZT thick films on Si-based substrates (Figure 1.13) in order to improve actuation efficiency. The harmonic oscillation response (resonant frequency) was measured using an optical laser interferometric vibrometer. The mass sensitivities of these devices were measured with subsequent Au deposition and the sensitivities through resonant frequency measurement were discussed in terms of cantilever geometry. Mass sensitivities are estimated to be 30.7, 57.1 and 152.0 pg/Hz for the 400×380 μ m², 400×480 μ m² and 400×580 μ m² cantilever, respectively. According to the obtained results, these devices were considered to be a strong candidate for biosensor applications [59].



evaporator & patterning using lift-off

Figure 1.13 Example of resonant piezoelectric cantilever with screen-printed PZT thick film on the Si substrate (a) fabrication steps and (b) SEM image of the obtained cantilever applied to bio-sensing [59].

Zhao et al. [60] demonstrated the PZT/stainless cantilevers for detection of vapor of dimethyl methylphosphonate (DMMP) at room temperature. This cantilever consisted of a PZT layer 0.7 mm long, 1.8 mm wide, and 0.127 mm thick bonded to a 0.05 mm thick stainless steel layer using a conductive epoxy. The 1.9-mm-long-stainless steel was coated with microporous SiO₂ (MIPS) or mesoporous Al_2O_3 (MEPA) synthesized by the sol-gel method. A schematic of a coated cantilever is presented in Figure 1.14(a). The MIPS and the MEPA had a specific surface area of ≈800 and \approx 380 m²/g and an average pore size of 10 and 61Å, respectively. The coating was achieved by repeatedly depositing 1 μ L of a 3 mg/mL metal oxide powder suspension. The resonant frequency shift of the cantilever under DMMP vapor was monitored using an impedance analyzer (Agilent 4294A, Agilent, Palo Alto, CA). For array sensing, the impedance analyzer was connected to a switch box. They found that the array PZT/stainless steel cantilever sensors coated with different metal oxide adsorbents can be used to detect DMMP at room temperature with different responses. The MEPA-coated cantilever exhibited a decrease of the resonant frequency which did not saturate after an hour (Figure 1.14(b)). The MIPS-coated cantilever sensor exhibited a sharp resonant frequency decrease which saturated within a minute or two with the mass sensitivity 2.5×10^{-8} g/Hz. (Figure 1.14(c)). The resonant frequency of the uncoated PZT/stainless cantilever remained stable under DMMP vapor, but it displayed a larger resonant frequency shift than the MIPS-coated cantilever under NH_3 vapor (Figure 1.14(d)), indicating the potential to selectively identify DMMP in mixed gas conditions through pattern recognition.



Figure 1.14 (a) A schematic diagram of piezoelectric cantilever coated with microporous silica (MIPS) at the tip; (b) resonant frequency shift vs. time of array PZT/stainless steel cantilevers: uncoated (open squares), 19.2- g-MIPS-coated (open circles) and 19.2- g-MEPA-coated (open diamonds) when 10 mL of DMMP was sprayed into the chamber; (c) resonant frequency shift vs. time of the uncoated (open squares) and 18-g-MIPS-coated (solid squares) cantilever after spraying 10 mL liquid DMMP in a large chamber (66 L). Also shown are the relative humidity (open up triangles) and temperature (open down triangles) in the chamber during the test; and (d) resonant frequency shift vs. time of an uncoated PZT/stainless steel (open squares) and a 6-g-MIPS-coated PZT/stainless steel (full squares) cantilever when 10 mL of a 5N ammonia solution was introduced in the chamber [60].

In the field of VOCs detection, Ahmed *et al.* [61] employed a sensor device with an array of eight piezoelectric micro-cantilevers for VOCs analysis. The array contained two micro-cantilevers coated by polyacrylic acid (PAA), two micro-cantilevers coated by polyethylenimine (PEI), two micro-cantilevers coated by polyethylene glycol (PEG), and two uncoated cantilevers used as reference measurement. Their work employed a single micro-cantilever beam arrangement (length 200 μ m × width 100 μ m, thickness 2 μ m), with one end glue-bonded onto the electrode. Microcantilevers were fabricated and assembled on a silicon-on-insulator wafer. Structure of the obtained cantilever is shown in Figure 1.15. The electronic connection between the micro-cantilever and chip carrier were made by wire bonding. Polymer layers were spotted (density 1g/cm³, and thickness 50 nm) onto the tip of each cantilever using the FEMTO (Fluidics Enhanced Molecular Transfer Operation) process with a Nano eNabler molecular printing system. The response for both control and coated micro-cantilevers also correlated with the change in environmental stimuli i.e. decreasing temperature (sensitivity of 0.05 Hz/°C), and increased relative humidity (sensitivity of 0.1 Hz/%rH). By measuring the frequency shift of the resonating micro-cantilevers, results of acetone, ethanol, octane are distinguishable from one another, with a measurement limited of detection of 1568, 383, and 87 ppmv, respectively. PAA has the weakest response, and PEG the strongest response, with the exception of octane where PEI shows the strongest response above 263 ppmv. The uncoated control micro-cantilever interacts with acetone above 4737 ppmv, whereas for ethanol, the control remains unresponsive throughout all concentrations (measured up to 5789 ppmv). Similarly, an increase for the control micro-cantilever is also shown for octane above 396 ppmvv (Figure 1.16). The overall high intensity of PEG (compared to PAA and PEI) for polar VOCs may be due to hydrogen bonding on the O-H termini of the PEG polymer surface, whereas the comparatively lower intensity for octane due to its low polarity and therefore low chemical affinity, may only exhibit weak Van der Waals forces due to its low chemical affinity for the PEG surface. Chemical interactions, which are based on solubility properties of the polymer coating, cause swelling and deswelling and therefore changes in resonance.



Figure 1.15 Left: the top and side view plan of a single micro-cantilever for a non-coated micro-cantilever, and Right: an image ($\times 10$ magnification) of the sensor chip ($10 \text{ mm} \times 10 \text{ mm}$) with multiple cantilevers with a single micro-cantilever highlighted in red [61].



Figure 1.16 The $\Delta f/f_0$ responses of the cantilever array with different polymer coating as a function of time and vapor concentration of (a) acetone, (b) ethanol, and (c) octane [61].

1.4 Sensing layer

Regarding section 1.2, one of the main importance in gas sensor developments is selection of molecular recognition materials that exclusively interact with the target species, and that alone are responsible for the selective detection. In ordinary, these materials should be sensitive, selective, stable, and provide short response time in harsh environments [62], [63], [64]. Organic or inorganic coatings or even composites can be used as sensing layers for gas detection with resonant sensors [47]. The partition coefficient (K) which can be defined via eq. 1.3 and high specific area, for instance, are considered to achieve good selectivity and/or high sensitivity [65]. The different kinds of organic and inorganic sensitive coatings allow reversible adsorption/desorption of target species but their major drawback is their partial selectivity for an individual device and, in many cases, their lack of sensitivity for detecting gases at trace levels. To overcome the problem of selectivity, a multi-sensors approach in which micro-cantilever arrays are coated with different sensing layers can be used [66], [67]. Furthermore, integration with the pre-concentrator is another alternative to improve sensor's sensitivity [27]. According to Potyrailo's report, [68] classification of sensing materials and gas-response mechanisms of various sensing materials are presented in Table 1.11. Table 1.12 summarizes recent results obtained with resonant transducers coated with different sensitive layers and tested under different gas species.

$$K = \frac{C_{coating}}{C_{gas}} = \frac{\Delta m}{LbtC_{gas}}$$
 eq. 1.3

where Δm , *L*, *b* and *t* are the mass variation in the sensitive coating due to gas adsorption, the length, width and sensitive layer thickness of the cantilever; and C_{gas} and $C_{coating}$ are the analyte concentration (mass per unit volume) in the gas phase and in the coating, respectively.

Sensing material	* * *	Gas-response mechanisms		
Organic Material Dielectric polymer (i.e., polyethylcellulose		Dispersion, polarizability, dipolarity, basicity, acidity,		
	poly(ethyl acraylate), and poly(etherurethane))	and hydrogen-bonding interactions		
	Conjugated (conducting) polymers (i.e., polypyrrole, polyaniline, and poly(3,4- ethylenedioxythiophene)	Changes in density and charge carrier mobility, swelling, and conformation transitions of chain		
	Macrocycles (i.e., metalloporphyrins, metallophthalocyanines)	Hydrogen bonding, polarization, polarity, metal center coordination interactions, π -stacking, and molecular arrangements		
	Cavitands	Intracavity host–guest complexation with hydrogen bonding, CH- π , and dipole–dipole as the main specific interactions		
Inorganic Material	Zeolite, mesoporous silica	Molecular discrimination by size, shape, molecular kinetic diameter		
	Metal-organic frameworks	Van der Waals interactions of the framework surface, coordination to the central metal ion, hydrogen bonding of the framework surface, size exclusion		
	Metal oxides	Physisorption, chemisorption, surface defects, and bulk defects depending on operation temperatures (ambient to ca.1000 °C) and utilizing different metal oxides and dopants		
	Monolayer-protected metal nanoparticles	Electron tunneling between metal cores, charge hopping along the atoms of ligand shell		
	Carbon nanotubes	Charge transfer from analytes and polarization of surface adsorbates, gas-induced Schottky barrier modulation		
	Graphene	Charge transfer induced by adsorption/desorption of gaseous molecules acting as electron donors or acceptors, leading to changes in conductance		
	Molybdenum disulfide	Charge-transfer mechanism involving transient doping of sensing layer		
Organic/Inorganic composite	Plasmonic nanoparticles with soft organic layers	Changes in interparticle spacing, refractive index of the organic layer, and reflectivity of the metal nanoparticle network film		
	Plasmonic nanoparticle/metal oxide nanocomposite films	Charge exchange with the nanoparticles, change in the dielectric constant surrounding the nanoparticles, dependent on the type of a metal oxide and its morphology for operation at $300-800$ °C		
	Colloidal crystals from core/shell nanospheres	Vapor-induced changes of optical lattice constant of colloidal crystal with cores and shells of nanospheres responding to diverse vapors		
	Iridescent scales of tropical Morpho butterflies	Lamella/ridge nanostructures with gradient of surface chemistry induce spatial control of sorption and adsorption of analytes and probed with light interference and diffraction		
	Bioinspired photonic interference- stack nanostructures	Chemically functionalized nanostructures with weak optical loss induce spatial control of sorption and adsorption of analytes probed with light interference and diffraction		

Table 1.11 Some gas-response mechanisms of representative sensing materials [68]

Resonant gas sensor	Sensing layer	Target species	Limit of Detection,	Ref./Year
Cuertz Crystel	Eunctionalized CNT	Mathanol	LOD (ppillv)	[70]/2005
Microbalance (OCM)	HDMSO	Methanol	5	[70]/2003
Wherobalance (QCWI)	HDMSO/O2	Ethanol	5	[/1]/2014
	11DW30/02	Bonzono	4	
		Chloroform	5	
	Matal organia framaworks	Panzana	0 15	[72]/2020
	Au Decorated ZnO poroug	Dibutyl Dhthalata	0.13	[72]/2020
	Au-Decorated Zito porous	Dibutyi Philialate	0.001	[75]/2015
		Nitur and diamida	1	[74]/2015
	110 ₂ nanostructures	Nitrogen dioxide		[74]/2015
Surface Acoustic	PIB ONT	Octane	N/C	[75]/2011
wave sensor (SAW)	PIB-CN1	Toluene	7.4	1(2)/2012
	PECH/PECH-CNT	Octane	/.4	[63]/2012
	PEUT/PEUT-CNT	Toluene	1.7	
	Graphene Oxide	Ethanol	N/C	[76]/2016
	Mesoporous TiO ₂ and SiO ₂	Ethanol, Toluene	N/C	[77]/2011
Micro-cantilever	Peptide	2.4 DNT	0.00043	[78]/2011
	ZnO nanotubes	DEA	10	[79]/2014
	ZnO nanorods			
	HM-β -cyclodextrin	DMN	0.00017	[80]/2001
		TCE	0.28	
	Cyclodextrins	2,3 DHN	0.125	[81]/2003
		TriCE	0.98	
	HM-β -cyclodextrin	2,3 DHN	N/C	[82]/2002
	HDATB-β-cyclodextrin			
	None	DIMP	0.0012	[83]/2012
	PEUT	Toluene	80	[48]/2013
	Metal oxides	DMMP	N/C	[60]/2006
	PEO, PVA, PEVA	Hexane, Octane,	N/C	[49]/2010
		Toluene, Benzene,		
		Acetone, Ethanol		
	Zeolite	o-Nitrotoluene	1	[84]/2009
		Toluene	11	
	Functionalized-CNTs	Benzene	1	[69]/2016
	-COOH functionalized	Ammonia	0.005	[85]/2018
	mesoporous silica	Aniline	mg/L level	[86]/2018
	nanoparticles (MSNs)			
	-COOH functionalized	Ammonia	tens of ppb	[87]/2011
	SBA-15 mesoporous silica		· FF ·	
	Hexafluoro-2-propanaol-	Trinitrotoluene	ppt level	[87]/2011
	functionalized SBA-15		TT	
	mesoporous silica			
	*	1	1	1

Table 1.12 Performances of resonant gas sensors coated with different sensing layers (adapted from [69])

Remarks:

1. The limit of detection (LOD) is the lowest concentrations of the analytes that can be detected. It is defined as the value of sensor sensitivity.

2. Abbreviation's definitions:

CNT: carbon nanotubes, HDMSO: Hexamethyldisiloxane, Au: gold, PIB: polyisobutylene, PECH: polyepichlorohydrin, PEUT: polyetherurethane, HM- β -cyclodextrin: Heptakis-6-mercapto- β -cyclodextrin, HDATB- β -cyclodextrin: heptakis (2, 3-O-diacetyl-6-O-tertbutyl-dimethylsilyl)- β -cyclodextrin, PEO: polyethyleneoxide, PVA: polyvinylalcohol, PEVA: polyethylenevinylacetate, - COOH: carboxyl groups, and SBA: Santa Barbara Amorphous structure.
1.4.1 Mesoporous materials

Meso is the Greek prefix meaning "in between". It has been adapted by the International Union of Pure and Applied Chemistry (IUPAC) to define porous materials which have the pore size in between micro-pore and macro-pore [88], [89]. According to IUPAC classifications, porous materials are classified by the internal pore width (diameter) into three classes; micro-pore (diameter < 2 nm), meso-pore (diameter 2-50 nm), and macro-pore (diameter > 50 nm) [90] which can be categorized into Table 1.13.

Tuble fille for the classification of porous materials							
Definition	Micro-pore	Meso-pore	Macro-pore				
Pore size (nm)	< 2 nm	2 nm - 50 nm	>50 nm				
Example	Zeolites	MCM-41	Sponge				

 Table 1.13 IUPAC Classification of porous materials

Since the discovery of a M41S family of ordered mesoporous silica such as MCM-41, MCM-48, etc. (Figure 1.17) by Mobil Oil Company researchers in 1992 [91], [92], there is a large increase of interest in synthesis of new mesoporous materials as shown in Figure 1.18. [93]. Mesoporous structures are presented by a wide class of substances such as silica, metal oxides, metal hydroxides, metal salts, carbon structures, and hybrid materials, organic structures. The detailed classification of mesoporous materials is presented in Figure 1.19 [93].



Figure 1.17 Structures of M41S family [94].

Many researchers pay attention to the mesoporous material's applications in various fields such as ion exchange, separation, catalysis, biological molecular isolation, purification, absorbents, and sensor [90] because the mesoporous materials possess some outstanding properties which other porous materials do not have. These properties are the following:

- Well-defined pore system: high surface area, pore sizes and shape, narrow pore size distribution and adjustable in the range of ≈2 to ≈50 nm, existence of micro-pores in the amorphous wall (for those thicker wall materials)
- Various wall (framework) compositions obtained from direct synthesis, or post-treatment or modification
- High thermal and hydrothermal stability if properly prepared or treated
- Various controllable regular morphologies in different scale from nanometers to micrometers
- Application potentials such as large-molecule catalysis, biological process, selective adsorption, functional materials [95].



Figure 1.18 Chemical classification of mesoporous materials [93].



Figure 1.19 Time scale of the discoveries of mesoporous materials [93].

1.4.2 Mesoporous silicas (MPS)

Mesoporous silicas (MPSs) are a nontoxic inorganic solid having a variety of structural characteristics. Examples of well-known MPSs and their characteristics are given in Table 1.14. Many types of MPSs and their functionalization were developed to be VOCs adsorbents because the special features of MPSs are that their regularly large pore size (diameter of 2-50 nm) which is enough to absorb VOCs molecules [96], high surface area, open pore structure, and reliable desorption performance [96], [97], [98], [99], [100]. However, the high concentration of silanols (Si-OH) on the amorphous walls surface of MPSs led to hydrophilic behavior and decreased the adsorption efficiency of VOCs under humid environment. Therefore, most of MPSs are functionalized before using in an adsorption field [99]. With these features, the MPSs and functionalized MPSs are considered to be used as the sensing layer for VOCs detection in sensor systems.

Mesoporous silica	Template	Pore structure	Pore diameter (nm)	Reference
MCM-41	CTMA ^a	2D hex. channels (p6mm)	2-10	[92]
SBA-15	P123 ^b	2D hex. channels (p6mm)	5-30	[101]
MCF	P123 ^b	Meso-cellular foam	10-50	[102]

Table 1.14 Examples of well-known MPS

Remarks: ^a CTMA: $C_nH_{2n+1}(CH_3)N^+$, n = 8-18 and ^b EO₂₀PO₇₀EO₂₀

A. MPS sensing layer based VOCs detection

In 2016, K. Hamdi *et al.* [103] monitored adsorption of volatile benzene, toluene, and p-xylene (BTX) in real-time by UV spectroscopic analysis. Rapid preconcentration and recovery were achieved with mesoporous silica nanoparticles films (thickness of 1.5- 1.8μ m) dip-coated on a quartz plate. These films illustrated high transmittance and allowed the detection of toluene up to 1 ppmv within a minute and a regeneration of the sensor in less than 30 seconds. However, the affinity of benzene and p-xylene molecules with the mesoporous silica layer was linked to their polarity in vapor phase. Therefore, BTX adsorption may occur in mesoporous silica nanoparticle film at different energy levels since the sites of adsorption are displaying different curvatures and accessibilities. However, the presence of humidity in volatile toluene induced a dramatic degradation of the sensor response (Figure 1.20). Grafting with hexamethyldisilazane on mesoporous silica nanoparticles resulted in a complete loss of toluene sensitivity. Thus, the application of the sensor in humid air was made possible by the introduction of a gas dryer before the measurement cell



Figure 1.20 (a) TEM image of the synthesized silica nanoparticles, (b) Absorbance variation at 267 nm wavelength as a function of time during exposition (3 min) and regeneration (1 min) cycles in the presence of (i) 20 ppmv toluene in dry air, (ii) 20 ppmv toluene in 50% humidity air and (iii) 20 ppmv toluene initially in 50% humidity air and dried through a gas dryer before the sensor cell. Film thickness $\approx 1.8 \pm 0.08 \mu m$ (three layers) [103].

Liu et al. [104] revealed the use of carbon functionalized MPSs co-operated with AT-cut QCM crystals (diameter 8.0 mm) transducers for detection of indoor volatile organic compounds. Different types of the mesoporous silicas (SBA-15, SBA-16, KIT-6, MCM-41, and MCM-48) with uniform carbon coating on the internal surface of silica meso-pore channels were synthesized via a simple template-carbonization strategy. Although the obtained mesoporous silica-carbon nanocomposites (denoted as SBA-15-C, SBA-16-C, KIT-6-C, MCM-41-C, and MCM-48-C) showed decreases of surface area, pore volume, and pore size after functionalization, they presented improved hydrophobicity and anti-interference capacity to environmental humidity, as shown in Figure 1.21(a) and (b). The sensing performances of the mesoporous silica–carbon nanocomposites to ethylbenzene, methylbenzene, benzene, methanol, acetone, formaldehyde, dichloromethane and tetrahydrofuran, were systematically investigated. The mesoporous silica-carbon nanocomposites of SBA-15-C exhibited outstanding performance at room temperature to benzene and acetone with high responses, short response (2–3 s) and recovery (16–19 s) time, and long-term stability (less than $\approx 5\%$ loss of the frequency shifts after 42 days), as shown in Figure 1.21(b-d) because it had bigger pore sizes and higher carbon contents compared to MCM-41-C and MCM-43-C. Moreover, SBA-15-C with 2D hexagonal microstructures showed significant higher responses to organic gases than SBA-16-C and KIT-6-C which possess 3D cubic pore characteristics with the similar surface area, pore diameter and carbon contents. SBA-15-C with well-ordered straight cylindrical mesopores could facilitate the diffusion and transportation of organic gas molecules (Fig. 1.22(a)). On the contrary, the spherical cavities of the mesoporous SBA-16-C nanocomposite with 3D bodycentered cubic meso-structure which are connected via small holes, and the bi-continuous cubic meso-structure of KIT-6-C with tortuous pore channels were unfavorable to the diffusion and transportation of organic gas molecules (Fig. 1.22(b-c)). This is because more energy was needed for organic gas molecules adsorption onto the curved meso-pore surfaces with large interfacial curvature. Therefore, the adsorption efficiencies of the mesoporous SBA-16-C and KIT-6-C nanocomposites are lower than those of SBA-15-C at room temperature.



Figure 1.21 Response and recovery curves of the (a) mesoporous silica SBA–15 and (b) mesoporous silica– carbon nanocomposite SBA–15–C-1 sensors to benzene within the relative humidity of 97.6 rH%, (c) response and recovery curve of the SBA–15–C-1 sensor to acetone for three times, and (d) stability curve of the nanocomposite SBA–15–C-1 sensor to benzene. All the samples were tested with the same acetone concentration of 1000 ppmv at room temperature [104].



Figure 1.22 Diffusion and transportation of organic gas molecules (e.g. acetone) in the meso-pore channels of (a) 2D hexagonal (space group, p6mm) meso-structure, (b) 3D body-centered cubic (space group, Im3m) meso-structure, and (c) 3D bi-continuous cubic (space group, Ia3d) meso-structure [104].

Currently, Bao et al. [86] reported detection of VOCs in solution with the mesoporous silica sensing layer constructed on the resonant cantilever transducers (Figure 1.23(a-b)). The closed-loop fluid part was used to circulate the sample solution in the sensing micro-system (Figure 1.23(c-d)). They developed Si-cantilever with two types of modified mesoporous silica nanoparticles (MSNs) to detect aniline and acetic acid gases. Both gases were isolated from their solution by evaporation through a commercial waterproof and breathable expanded polytetrafluoroethylene (ePTFE) film. -COOH modified MSNs and -NH₂ modified MSNs were used as sensing layers for detection of aniline and acetic acid gases respectively. The base-line of detection was done by injection of 20 mL deionized water into the sample cell for half an hour in order to stabilize the sensor cavity via water vapor. With piezoresistive-readout, water vapor caused a decrease of the resonant frequency of the sensor compared to under ambient environment. However, the O-factor changed very little from 276 to 255, which means that the mass sensing resolution of the sensor has no obvious change. Injecting 100 mg/L of aniline solution into a sensing chamber dropped the frequency by \approx 36 Hz (Figure 1.24 (a)). While, the 100 mg/L acetic acid solution, decreased the frequency of ≈ 60 Hz (Figure 1.24 (b)). At the end or during the sensing experiment, 0.5 mL of DI water was injected into the sample cell for almost fully recovering to the base-line. Moreover, these sensors showed the same frequency shift when they were tested at 20 and 25°C, but this value changed of 10Hz at 50°C (Figure 1.24 (c)).



Figure 1.23 (a) Photograph and (b) SEM image of the resonant micro-cantilever with functionalized MSNs loaded, (c) Cross sectional (left) and 3D (right) schematic view of the sensing chamber of the platform, (d) Photos of the main components of the sensing platform, where arrows show the fluid flow direction [86].



Figure 1.24 (a) Repeatable responses of the functionalized cantilever sensor to aniline solution of 100 mg/L concentration, (b) Sequential responses of the cantilever with- NH_2 functionalized MSNs to acetic acid solutions of 50 mg/L and 100 mg/L concentrations, and (c) Sensing signals of the cantilever at different temperature conditions [86].

Liu *et al.* [85] was successful to synthesize carboxyl group (-COOH) functionalized mesoporous silica nanoparticles (C-MSNs) with specific surface areas and pore diameters around 1100 m²/g and 2.2 nm, respectively. For detection of ammonia (NH₃) vapor, 10 mg of the C-MSNs was dispersed into 1 mL deionized water to form a crude suspension. Then, 0.1 L of the suspension is precisely loaded onto surface of the Si-cantilever by using a commercial inkjet printer (SonoPlot Microplotter GIX II, USA). Figure 1.25 shows synthesized C-MSNs and C-MSNs loaded onto the Si-cantilever and Figure 1.26 presents response of the resonant cantilever under different concentrations of ammonia vapor. The limit of detection (LOD) of the C-MSNs sensor was 5 ppb in real air atmosphere. Besides, the sensor outputs responses indicates a satisfactory repeatability and selectivity.



Figure 1.25 (a) TEM image of the prepared C-MSNs and (b) SEM image of the C-MSNs loaded resonant microcantilever sensor [85].



Figure 1.26 (a) Micro-gravimetric sensing curve of the C-MSNs loaded resonant microcantilever sensor to ammonia vapor with concentrations, (b) three-cycle repeat detection of the sensor to ammonia with 120 ppb concentration, (c) cross-response of the sensor to eight kinds of interfering gases compared with the response to 300 ppb of NH₃ [85].

B. Possibility of using Meso-cellular foam silica (MCF-Si) as sensing layer for VOCs detection

Meso-cellular foam silica (MCF-Si) is one type of mesoporous materials which is attractive to use in various applications due to the following reasons:

- It has the ultra-large pore size (up to 50 nm) and large pore volume (> 2 cm³/g) in a unique feature of uniform spherical cells interconnected with uniformly sized windows (a continuous 3D meso-pore system) [102], [105]. Its morphologies are shown in Figure 1.27 [106].
- In comparison with MCM-41 and SBA-15, MCF materials presented a better product diffusion due to overcoming internal mass transfer limitations [107], [108].
- With silanol groups (Si–OH) as similar as other types of MPS, MCF-Si can be modified by functionalization for improvement of its properties [109], [110].

In previous studies, MCF-Si was generally synthesized to be a drug carrier [93], [111] or a supporter for enzymatic immobilization in biosensors [93], [112], [113], [114] or metal catalyst in catalytic processes [115], [116]. Some research applied MCF-Si for carbondioxide capture [117]. In addition, MCF-Si was studied to exploit in the field of effective absorbents for removal of selected pollutants such as Ni²⁺ [118], Hg²⁺ [119], and 2,4-dichlorophenoxy acetic acid. However, MCF-Si have never been used as sensing layer onto PZT cantilever transducers for the VOCs detection. Consequently, this is an interesting alternative for development of PZT cantilever transducers in this work.



Figure 1.27 (a) SEM and (b) TEM images of MCF-Si [106].

1.5 Developed cantilever transducers for VOCs detection at IMS laboratory

Silicon (Si)-based materials are favorably used to fabricate the cantilevers due to their low energy dissipation, resonating with high quality factor values [54], and their availability and easy integration with silicon-based technology [120], [121]. Thus, Si-cantilevers transducers with different sensing layers were developed for comparing VOCs detection. Polymer sensing layer performed high distinctive selectivity. For example, Si cantilever with sprayed poly-etherurethane (PEUT) sensing layer (Figure 1.28) under ethanol and toluene vapors presented the limit of detection (LOD), accounting for 263 ppmv and 43 ppmv, respectively. While, with hydrophilic zeolite sensing layer, the difference of LOD values was just 2 ppmv between ethanol and toluene. These cantilevers were actuated due to Laplace electromagnetic force leading to a transverse vibration. The read-out of the resonant frequency was piezo-resistive [65].



Figure 1.28 Schematic representation and picture of the Si cantilevers [65].

In 2009, IMS laboratory began to develop piezoelectric transducers by using screen-printing thick film technology associated with sacrificial layer technique. They achieved to fabricate resonant free-standing Au/PZT/Au cantilevers transducers ($8 \times 2 \times 0.08 \text{ mm}^3$), as shown in Figure 1.29. Their fabrication process was simple and low cost with fewer steps compared to Si-cantilevers preparation. The cantilever was actuated via inverse piezoelectric effect while the resonant frequency was measured by direct piezoelectric effect and the vibration of in plane (31 longitudinal mode) owing to the symmetry of the cantilever (PZT layer comprised between the two Au electrodes). With a dropped PEUT sensing layer, the obtained devices demonstrated a LOD of 15 ppmv under toluene vapor for the first vibration mode. It was noticed that lead borosilicate glass

frit was the sintering aid of PZT and epoxy-based strontium carbonate was the sacrificial layer. The free-standing structure was released after sintering at 850°C for 15 min including the dissolution of the sacrificial layer in a diluted H_3PO_4 aqueous solution. The density of this sintered PZT film was 5.4 g/cm³ [122].



Figure 1.29 Fabrication and flow chart of PZT cantilever (with glass frit sintering aid) for selfactuating/sensing (a) thick-film deposition of sacrificial layer based on epoxy-SrCO₃, (b) multi-stage screenprinting Au/PZT/Au, (c) sacrificial layer elimination with H₃PO₄ after firing at 850°C, and (d) photograph of the obtained cantilever after firing [122].

A few years later, Lakhmi *et al.* [123] compared the quality factor for 31 longitudinal resonant mode of screen-printed Au/PZT/Au cantilevers ($8 \times 2 \times 0.095 \text{ mm}^3$). The cantilevers were densified at 900 °C for 2 hours with different kinds of sintering aid: lead borosilicate glass frit and ternary mixture of Li₂CO₃, Bi₂O₃ and, CuO (abbreviated as LBCu). As in previous work, both cantilevers were using the same materials for sacrificial and sensing layers [122]. The sintered PZT cantilever with LBCu sintering aid gave the highest quality factor (≈ 330) for the first vibration mode, although it had higher porosity ($\approx 35\%$). To be noticed that the quality factor and porosity of the PZT cantilever with glass frit sintering aid were around 320 and 25% respectively. Furthermore, the results were compared with those of the Si-cantilever studied at IMS for toluene detection and PEUT sensitive layer. The PZT cantilever with LBCu sintering aid (Figure 1.30) which was operated in longitudinal vibration mode showed higher sensitivity (15.0 mHz/ppmv at 70 kHz and quality factor ≈ 940) [48].



Figure 1.30 The PZT cantilever (with LBCu sintering aid) (a) its photograph, (b) its cross-sectional drawing, and (c) its resonant frequency shift under toluene gas [48].

With the same PZT compound and sacrificial layer materials used in Lakhmi's work, Clément et al. [69] fabricated screen-printed PZT cantilevers sandwiched between Au electrodes. However, the top electrode of this cantilever was interdigitated pattern in order to generate double transduction. This structure was called "ID-cant" microcantilever (Figure 1.31(a)). The actuation was still applied between the electrode e_1 and e_2 and the resonant frequency was simultaneously monitored between these electrodes. Alternatively, oxygen plasma treated multi-wall carbon nanotubes (named O-MWCNTs) was used as sensing layer. It was sprayed on the top electrode. Figure 1.31(b) shows the cantilever covered by the O-MWCNTs layer. The resistance of the sensing layer was measured between electrodes e_2 and e_3 which have a gap of 200 μ m. The responses towards volatile benzene, carbon monoxide and nitrogen dioxide concentrations are shown in Figure 1.31(c) and (d). Positive and negative shifts of the resonant frequency were observed at low and high gas concentrations due to domination of stress and mass effects respectively. The detection limit values calculated from shifts of resistance were higher than those of resonant frequency. The LOD values with resistive measurement of benzene vapor, carbon monoxide, and nitrogen dioxide were 2 ppmv, 30 ppmv, and 0.05 ppmv, while the LOD values with resonant frequency measurement of these three gases were 1 ppmv, 5 ppmv, and 0.05 ppmv, respectively.



Figure 1.31 (a) Scheme of top view of the new "ID-cant" microcantilever allowing the double transduction method where the bottom electrode is e_1 and the top interdigitated electrodes are e_2 and e_3 , (b) the O-MWCNTs dropped on the microcantilever, (c) sensor responses in frequency and (d) sensor responses in resistance toward different gases with SR = x/x_{air} (where x is the resonant frequency or resistance difference under air and contaminants) [69].

Grall *et al.* [124] also studied the Au/PZT/Au cantilevers for gravimetric sensors (pattern geometries in the range of $1 \times 1 \times 0.1$ mm³ to $8 \times 2 \times 0.1$ mm³) with LBCu sintering aid onto a new sacrificial layer material (polyester) for gravimetric sensor. An example of the sintered specimen is shown in Figure 1.32. As a result of decomposition of polyester during sintering at 900°C, the densification of the PZT films was improved (% porosity is approximately 6.2) compared to the PZT cantilever of Lakhmi [48]. Moreover, with inkjet deposition of a known mass, an experimental mass sensitivity of 85 Hz/µg was estimated against 330 Hz/µg in theory for a $1 \times 2 \times 0.1$ mm³ microcantilever geometry. The corresponding LOD was ≈ 70 ng. Theoretical sensitivities of 740 Hz/µg were calculated for the smallest geometry $1 \times 1 \times 0.1$ mm³.



Figure 1.32 The sintered Au/PZT/Au cantilever in size of $2 \times 1 \times 0.1 \text{ mm}^3$ (a) its photograph and (b) the shifts of resonant frequency (f_0 = blue line) and quality factor (Q = red line) during the inkjet deposition test on the cantilever, where the deposited mass was around 1.88 µg [124].

1.6 Conclusions

Regarding previous studies of IMS laboratory, with for some of these studies, collaborations with colleagues from Spain for the sensitive coating [65], [69], [125], the simple technology of screenprinting thick film associated with sacrificial layer technique were employed to fabricate PZT cantilever transducers. Their performances are summarized in Table 1.15. These devices were a new alternative of mass sensors for VOCs detection with PEUT and O-MWCNTs sensing layer. However, the remained porosity in the screen-printed PZT cantilever (\approx 35%) should be decreased in order to improve the cantilever performance. According to section 1.4.2, there are still few research focusing on the use of MPS as sensing layer in the VOCs mass sensors. Furthermore, no study was found on the development of resonant PZT cantilever transducers with MPS sensing layer; especially, functionalized MCF-Si. Therefore, the major objectives of this research are as follows:

- The densification improvement of the screen-printed PZT specimens
- Optimization of the PZT cantilever size to use as transducers for VOCs detection
- Study of the VOCs detection via the mass sensor composed of the optimized PZT resonant cantilever transducers and the functionalized MCF-Si sensing layer

Cantilever type and size	Vibration mode	Sensing layer	Target vapor	LOD (ppmv)	Ref/Year
Si-cantilever					
(5×0.4×0.06 mm ³)		PEUT		43	
(5×1.0×0.06 mm ³)	Out of allows	PECH		36	
(4×0.6×0.06 mm ³)	floyural	PIB	Toluene	28	[65]/2012
(4×0.2×0.06 mm ³)	пехита	Zeolite (LTA structure)		21	
(3×0.2×0.02 mm ³)		Zeolite (FAU structure)		26	
(5×0.2×0.06 mm ³)		Silicalite		160	
PZT cantilever	In-plane longitudinal	PEUT	Toluene	15	[122]/2009
(8×2×0.08 mm ³)					
Si cantilever	Out-of-plane	PEUT	Toluene	47	[48]/2013
(5×0.4×0.059 mm ³)	flexural				
PZT cantilever		PEUT	Toluene	80	[48]/2013
(8×2×0.095 mm ³)	In-plane				
PZT cantilever	longitudinal	O-MWCNTs	Benzene	1	[69]/2016
(8×2×0.1 mm ³)		Zeolite (DAY structure)	Benzene	*0.306	[125]/2014
				(Hz/ppmv)	

 Table 1.15 VOCs detection of cantilever transducers with different sensing layers developed by IMS laboratory and co-workers

Remarks: 1. PEUT is poly-etherurethane, PECH is poly-epichlorohydrin, and PIB is poly-isobutylene, 2. *Sensitivity

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CHAPTER 2: Transducer fabrication: material selection, paste preparation, transducer design, and used equipment

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2.1 Introduction

Fabrication is a significant procedure for forming piezoelectric (micro) ceramic (so called piezo ceramic) thick films acting as transducers in this work. Its process involves paste preparation, shaping of the paste onto a substrate, drying of the deposited films, and sintering of the obtained films [1], [2], [3]. Among various methods of structuring ceramic thick films, screen-printing thick film technology is an interesting alternative for fabricating transducers because of the following reasons:

- It is a simple technique used in microelectronic components manufacturing with reduced critical process parameters. This results in low cost production.
- The thickness of the obtained thick films (1-100 μ m) is well suitable for some sensor, actuator or transducer applications.
- It provides flexibility in choices of paste compositions, substrate materials, and patterns.
- Multilayer circuits can be obtained (with same or different nature) with firing between each deposition or co-firing after all layer depositions and drying
- It can be integrated with conditioning electronics in hybrid electronic systems.

Final properties of fired screen-printed thick films strongly depend upon their microstructure [4] which are mainly correlated with:

- The properties of the used materials in the multilayer: paste ingredients such as active materials and sintering aid, particle size of starting powders, supporting substrate, etc.
- The time-temperature-atmosphere conditions during firing.

Among piezo ceramics, lead zirconate titanate or $Pb(Zr,Ti)O_3$, or PZT is very often preferred for transducer applications because of its excellent dielectric and piezoelectric properties [5], [6], [7], despite its hazardous lead content. The printed PZT thick films with high densification and no chemical reaction between the printed film and the substrate majorly perform good quality. To receive these requirements, sintering at low temperature (<1000°C) with fine grain of ceramic powders and the addition of a few weight percent of sintering aids are favorable ways [1]. However, thick films are normally bound to the substrate. This causes constrained densification because the printed and dried layer mostly shrinks in only direction perpendicular to the substrate [1]. Also, for some applications (actuating or energy harvesting), the passive substrate correlates closely with the global performances of the device.

As mentioned in Chapter 1, the objectives of this work are not only preparing the PZT cantilever transducers for VOCs sensors, but also improvement in the screen-printed PZT microceramic thick film properties. This challenging target involves different choices of constituting materials detailed in next section. For this study, in addition to cantilever structures, PZT disks are also studied because of fewer fabrication steps, and easier characterization.

2.1.1 Constituting material choices

A. Substrates

The basically required properties of substrates are high values in electrical resistivity, mechanical strength, dielectric strength, thermal shock resistance, and thermal conductivity [4]. For the thick films needing high temperature in production, ceramic substrates are normally used to integrate multilayer films because they can stand without bending or decomposition during processing. Furthermore, other considered factors for selecting substrates are the coefficient of thermal expansion (CTE), surface roughness, chemical properties of substrate, and price. The coefficient of thermal expansion of the substrate should be matched with the crucial elements mounted on it. The proper surface roughness helps paste transfer during screen-printing. The chemistry of substrate can influence film properties and adhesion due to interaction between the film and the substrate [4].

In this work, two kinds of the ceramic substrates: (1) aluminum nitride (AlN) and (2) aluminum oxide also called alumina (Al₂O₃) with 96% of purity (in length × width × thickness of 2 inch × 2 inch × 250 μ m) manufactured by Maruwa Co., Ltd. are used for mechanical supporting the printed PZT films which will be fired at 900°C. Alumina is mostly used in hybrid electronic application because of the good compromise cost-physical properties. AlN, more expensive, is preferred for power applications. Also, chemistry of the pastes may be different for CTE matching and final layer adhesion. The substrate's properties are summarized in Table 2.1.

- Aluminum nitride (AlN) substrates are allowed to support the printed disk (both with and without electrodes) because both specimens can release from this substrate easily.
- Alumina (Al₂O₃) of 96% purity substrates (other compositions are related to lead containing glasses for densification improvement [8]) are allowed to integrate the cantilever transducers because it can fix the PZT anchor with enough adhesion.

	Condition	Unit	AlN	Al ₂ O ₃ (96%)
Color			Grey	White
Bulk density		g/cm ³	3.30	3.75
Surface roughness Ra		μm	0.3	0.4
Bending strength	3-point method	MPa	450	400
Modulus of elasticity		GPa	320	330
Coefficient of thermal expansion (CTE)	40-800°C	10 ⁻⁶ /K	5.2	7.8
Thermal conductivity	25°C	W/(m.K)	180	24
	300°C	W/(m.K)	120	12
Specific heat	25°C	J/(kg.K)	720	750
Dielectric constant	1MHz	10-3	9.0	9.8
Volume resistivity	25°C	Ω.cm	>1014	>10 ¹⁴
Price			Expensive	Inexpensive

Table 2.1 Properties of AlN and Al_2O_3 substrates (maruwa-g.com)

B. Sintering aids

According to IMS laboratory's research of Debéda *et al.* [9], Lakhmi *et al.* [10], and Grall *et al.* [11], PZT thick films with 3 wt.% of sintering aid (a ternary mixture of lithium carbonate (Li₂CO₃), bismuth trioxide (Bi₂O₃), and cupric oxide (CuO) abbreviated as LBCu) could be used for sensitive gravimetric gas transducers. They were indeed presenting higher piezoelectricity after firing at 900°C for 2 hours compared to PZT thick films sintered with a borosilicate glass-frit (usual sintering aid found in thick film compositions additive). These components were co-sintered with printed Au

electrodes. Besides, Medesi *et al.* [12], prepared and characterized tape-casting thick films of PZT multilayers with internal pure silver (Ag) electrodes fired at 900°C in air. Effect of ten different kinds of liquid phase sintering aids (Li₂O, Li₂CO₃, PbO, MnO₂, V₂O₅, CuO, Bi₂O₃, eutectic mixtures Cu₂O.PbO and PbO.WO₃ and LBCu ternary system) on the density and piezoelectric properties were studied. The LBCu system presented the best results. The PZT film with 5 vol% LBCu showed an average relative density of 97%, while PZT with 2 vol% LBCu expressed the highest averaged piezo-electric charge constant (d_{33}) of 181 pC/N.

Therefore, LBCu is a potential choice for using as sintering aid in this study. However, the ratios of LBCu mixtures referred to both research teams are different (Table 2.2). Hence, in this work, two PZT pastes prepared from the non-milling PZT powder and mixed with two different LBCu compositions have been studied for optimization.

Research team	Li ₂ CO ₃	Bi ₂ O ₃	CuO
IMS laboratory team [11]	1.0	1.5	1.2
Medesi team [12]	1.0	1.0	3.7

Table 2.2 Ratios of LBCu sintering aid from different research teams

Remarks

1. Li_2CO_3 , Bi_2O_3 , and CuO were milled by planetary mill before mixing together for IMS research.

2. There was no information about milling in the case of Medesi team.

C. Piezoelectric starting powders

For conventional sintering processes, decreasing the size of the powder particles leads to an increased driving force and sintering kinetics which manifests itself in enhanced sintering and the ability to process films at lower temperatures [13]. Moreover, the higher surface/volume ratio of the fine particles also contribute to a higher density at lower sintering temperature [1].

Therefore, in this work, effect of decreased PZT particle sizes on the PZT films' densification is studied. A commercial PZT powder with typical hard properties (Pz26 (Navy I) Hard relaxor type PZT) manufactured by FerropermTM Piezoceramics (Table 2.3 and Appendix A-1) is used for nonmilling powder. This material is milled by either planetary mill or attritor mill to define two groups of milled PZT powder. Therefore, overall of three different PZT powders are as follows:

- Non-milling powder
 (Pz26, the distribution of particle size ≈1-100 μm, D_{0.5} ≈10 μm with powder agglomeration)
- Milled powder by planetary mill (The distribution of particle size ≈ 0.2 -4.0 µm, $D_{0.5} \approx 0.4$ µm with powder agglomeration)
- Milled powder by attritor mill (The distribution of particle size $\approx 0.4-0.9 \ \mu m$, $D_{0.5} \approx 0.6 \ \mu m$ with powder dispersion)

To be noticed that $D_{0.5}$ is the volume median diameter.

	Material p	Symbol	Pz26	
Electrical				
	Relative dielectric	permittivity at 1 kHz	K_{33}^T	1300
	Dielectric dissipat	ion factor at 1 kHz	$tan \delta$	3 × 10 ⁻³
	Curie temperature		T_c	>330 °C
	Recommended wo	orking range		<280 °C
Electromechanical				
	Coupling factors Planar (<i>p</i>) vibration mode		k_p	0.56
		Thickness (t) vibration mode	k_t	0.47
	Piezoelectric charge coefficient			300 pC/N
Mechanical				
	Mechanical Quality Factor		Q_m	>1000
	Density		ρ	7.7 g/cm^3

Table 2.3 Properties of Pz26 (Navy I) Hard relaxor type PZT (FerropermTM Piezoelectric)

D. Electrodes

Various metals can be used as electrodes in thick film hybrid circuit such as gold (Au), platinum (Pt), silver (Ag), palladium (Pd), and binary or ternary alloy combinations of these metals. However, Au, Pd, and Pt are very expensive. Other metals such as silver (Ag), its binary (Ag/Pd) or ternary (Ag/Pd/Pt) systems are consequently preferred in an industrial level. With high conductivity, but easy migration during the co-firing at \approx 750°C of Ag [14], PZT films with Ag electrodes presented a failure of electrical properties [15]. Therefore, Pd or glass additives such as PbO, Bi₂O₃, SiO₂ in an Ag-rich Ag/Pd system are added in its system to minimize the Ag migration. Moreover, some of the glass additives of Ag/Pd systems can act as sintering aids for PZT inducing a rise in densification and electrical properties at low co-firing temperature (700-820°C) [14].

In this work, two kinds of electrode materials (Au and Ag/Pd), as shown in Table 2.4 are used to compare releasing of the printed disks from the substrates. This is because Au could be used as the electrode matching with releasing the PZT free-standing cantilevers on the Al_2O_3 substrates in previous work. While, Ag/Pd is a new choice produced by the industrial partner (EXXELIA). It is exploited to improve releasing of the PZT disks on the AlN substrates. Moreover, properties of the PZT disks with different electrode materials are also studied.

I I I I I I I I I I I I I I I I I I I						
Paste	Au electrode ¹ (ESL) [16]	Ag/Pd electrode ² (EXXELIA)				
Active material	Au	Ag/Pd: 90/10 (wt%/wt%)				
Additive	Glass frit	Low permittivity oxide MgTiO ₃				
Solvent	Terpineol	Kerosene (aliphatic solvent)				
Organic binder	No information	Cellulose binder				

Table 2.4 Compositions of electrode pastes

Remarks: ¹ the commercial paste of ElectroScience Laboratory (ESL) and ² the paste prepared by the industrial partner EXXELIA.

E. Sacrificial layer materials

The sacrificial layer is a temporary layer created for supporting a movable part of the active structure during the fabrication process. During or at the end of process, this layer will be eliminated by chemical or heat treatment in order to release the free-standing structure. Referring to [9] and [10], the screen-printing thick film technology associated with sacrificial layer technique was

successfully used to prepare the free-standing cantilever transducers for gas sensors. These cantilevers were based on a printed PZT thick film sandwiched between printed Au electrodes.

By using a composite paste based on strontium carbonate (SrCO₃) and epoxy as the sacrificial layer and sintering at 900°C, the epoxy was decomposed (at 275°C) whereas the SrCO₃ was stable (it was still stable until 1100°C [17]). The free-standing part of the cantilevers could be performed after dissolution of the rest SrCO₃ in diluted phosphoric acid. Nevertheless, the obtained cantilevers presented residual porosity (35%) because the residue of SrCO₃ powder below the sintered Au/PZT/Au stack inhibited the lateral shrinkage of the PZT. Recently, PZT screen-printed cantilevers for gravimetric sensors with a polyester sacrificial layer were successfully developed in IMS laboratory [11].

To sum up, in order to improve the printed PZT films' densification, some materials performing the complete decomposition during the sintering are considered as the sacrificial material; particularly, the materials having a decomposition temperature lower than 600°C. This is because the PZT film begins shrinking at this temperature [16]. As a result, the proper sacrificial layer materials should contribute to the free-standing structure during the sintering process without dependent shrinkage and further steps. Instead of epoxy-SrCO₃ based sacrificial layer, the polyester and homemade corn starch/epoxy pastes become interesting candidates for acting as the sacrificial layer in this work. The commercial polyester paste is generally used in electronics manufactures, while the corn starch is a simple, green and cheap material for food production. The decomposition temperature of the polyester and homemade corn starch/epoxy pastes are approximately 450°C and 550°C, respectively. The compositions of both sacrificial layer materials are presented in Table 2.5.

Paste	Polyester paste	Corn starch/epoxy paste [17]
Active material	Polyester	Corn starch
Solvent	Butyl di-glycol acetate	Butyl di-glycol acetate
Organic binder	No information	Epoxy (ether of bisphenol A diglycidyl and anhydride
		acid)

 Table 2.5 Compositions of sacrificial layer materials

2.1.2 Scopes of fabricating PZT films in this work

As a result of several parameters related to properties of the printed PZT thick films, to make it easy, the printed films are fabricated in disk and cantilever shapes with different objectives. Disks are formed to study the film densification and to observe releasing behaviors of the printed films of PZT sandwiched between printed electrodes from substrates. Then, the effective PZT paste giving high densification specimens is chosen to fabricate PZT cantilever transducers for gas sensing. This is because the screen printing steps of the disk transducers have fewer steps (no anchor part) compared to those of the cantilever transducers. Furthermore, sintered disks with typical design have no bound areas which is convenient to investigate the release of the disk transducers from the substrates (especially the bottom electrode quality). The author classified the studied factors related to the printed structures (Figure 2.1). This chapter will explain both printed film structures, used screen-printing pastes, preparing methods of the homemade pastes; used screens; and substrates, fabrication processes and exploited conditions, and concerning equipment.



Figure 2.1 Study of (a) densification improvement by the disk structure and (b) sensitivity of cantilever structure.

Besides, possibility of using corn starch as sacrificial layer is studied. Its paste is fabricated on the AlN substrates in order to support the structure of PZT disks. The characteristics of the obtained disks are compared to the one prepared onto polyester sacrificial layer.

2.2 General principles of screen-printing

The screen-printing is one of many common and low cost techniques for depositing materials in a form of thick film layer (with thickness in the range of 1-100 μ m) on substrates. This technique is nowadays developed for manufacturing of smart sensors due to its ability to produce miniaturized circuits. Furthermore, it can integrate the electronics on a particular substrate and it is flexible to prepare multilayer including sacrificial layer for supporting other layers during fabrication process. The basic screen-printing process is shown in Figure 2.2.



Figure 2.2 The basic screen-printing process (a) the paste is placed on the mesh screen, (b) the paste is forced through the opening areas in the screen by the squeegee which depresses the screen to contact the substrate, and (c) the paste is deposited onto the substrate; the pressure is released resulting in the snap off between the screen and substrate [4]. The fabrication via the mesh screen with different patterns is given in Section 2.2.3.

After printing, the deposited wet film in a desired pattern on the substrate is allowed to stand in air for few minutes to let the paste level off [2]. This step will help removing mesh traces when using a mesh screen. Then, the printed wet film is dried to remove solvents. For printing a piezoelectric ceramic thick film, the rest binder is always finally removed from the film during the firing (traditional method) at high temperature leading to densification of the film. For polymer thick films, drying introduces cured films and no further thermal step is needed.

2.2.1 Paste Rheology

In order to shape the thick film by the screen-printing, an active material is necessary to be in a paste (ink) form. The paste will be pressed by a squeegee through the open areas of a screen onto the substrate. By typical rheology behaviors of the paste, its viscosity is decreased by the applied shear force (pseudo-plastic or shear thinning behavior), but it also recovers more viscous after deposition (thixotropic behavior) relating to settling with uniform thickness and geometry of a printed wet film. A change of the paste viscosity during screen-printing is shown in Figure 2.3(a-b). Generally, the paste viscosity depends on the ratios of powders, resins, and solvents. Resins dissolved in the solvents yield the organic vehicle, whose viscosity affects that of the paste [8].



Figure 2.3 Rheology behaviors of the printed paste (a) relation between viscosity and shear rate of the paste during the screen-printing process as a function of time. Stages: I – Rest; II – Squeegee; III – Mesh; IV – Recovery [18], [19] and (b) viscosity as a function of shear rate. Stages: 1– shear thinning flow during the screen-printing process; 1 and 2 – thixotropic flow during settling.

2.2.2 Screen-printing machine

Screen-printing machine of DEK (HORIZONTAL 03iX) is used to shape the transducers. Its compositions and additional tools are shown in Figure 2.4. The operation procedures of this machine begins from putting the substrate inside a square hole of a shim placed on a substrate holder to lock movement of the substrate with vacuum system. The thickness of the shim should be similar or close to the substrate thickness plus a pre-deposited film thickness. Then, that substrate holder is put on DEK's transport rails. With an operation of a camera controlled by a monitor, the related positions of the fiducials (alignment marks) on the screen pattern and the substrate are automatically read and aligned. This leads to accurate positions of the deposited films.



Figure 2.4 (a) Compositions of DEK (HORIZONTAL 03iX) and additional tools.

2.2.3 Screen characteristics

The roles of the screen are to define the pattern of the printed film and to control its thickness on the substrate [20]. Favorable screens used in electronic industries are a mesh screen or a stencil. Both kinds of the screens are produced to print multilayer films in this thesis. The stencil is particularly used for printing piezoelectric resonance layers which have higher thickness than other constituted layers. Examples and drawing of the used mesh screen and stencil are shown in Figure 2.5- 2.6. The mesh screens contain woven stainless steel wires with a square opening, whereas no wires are placed in the open area of the stencil.



Figure 2.5 Examples of the used (a) mesh screen and (b) stencil.



Figure 2.6 Drawing of compositions and screen-printing operation of mesh and stencil screens when T_e , T_m , d_w , O_m , and T_{ss} are emulsion thickness, mesh thickness, wire diameter, mesh opening, and stainless steel thickness respectively.

A. Mesh screen preparation

To make various patterns (open areas) over the mesh screen, the patterns are designed by CLE software and printed on a transparent film with black color. Next, the suitable mesh screen is coated with a light-sensitive emulsion (MS Capillary Film - Murakami, Tokyo, Japan) which has thickness

in the range of 15-50 μ m. The transparent film featuring the pattern is then laid onto the emulsioncoated screen before exposing them by an intense ultraviolet (UV) light source. The UV light hardens the emulsion due to curing, but some areas covered by the black pattern remain soft and can be dissolved in water because the UV light cannot go through these areas. So, those soluble areas are removed from the screen by water in order to perform the screen pattern. The fiducial patterns appear on all screens for alignment before printing each layer. For the mesh screens, the fiducial patterns are filled with ESL 1901, an Ag-epoxy paste, manufactured by Electro-Science Technologies (Appendix A-1) and are dried at 80°C for a night in order to make contrast between the fiducials printed on the substrate. With different mesh screens and emulsion thickness, the theoretically printed wet thickness can be calculated from eq. 2.1 [21]. The difference of mesh screen characteristics used for each layer provides different thickness of the printed wet films as shown in Table 2.6.

$$T_{mw} = [(1/W) - d_w]^2 (T_m + T_e) \times W^2$$
 eq. 2.1

where T_{pw} is the thickness of the printed wet film, W is the number of wire per inch, d_w is the wire diameter, T_m is the mesh thickness, and T_e is the emulsion thickness.

Screen characteristics		Printed layer				
		Fiducial	Anchor	Sacrificial	Electrode	
		Fiuuciai	Anchor	layer	(Top and bottom)	
The number of wire per inch* (so called mesh)	-	400	200	70	325	
Wire diameter $(d_w)^*$	μm	18	36	65	24	
Mesh thickness $(T_m)^*$	μm	40±1	80±2	140±3	52±2	
Mesh opening $(O_m)^*$	μm	45	90	300	53	
Emulsion thickness (T_e)	μm	15	50	50	15	
Theoretically printed wet film thickness (T_{pw})	μm	≈28	≈67	≈128	≈32	

Table 2.6 Mesh screen characteristics and theoretically printed wet layer thickness of constituted layers

Remarks:

1. * Information is from DEK society information.

2. The screen characteristics' definitions can be explained by the drawing below.



B. Stencil preparation

For the stencil made of a stainless steel sheet with thickness of 150 μ m, the designed patterns are punched by a laser cutting, while their fiducials are shallowly dug by DB Products Company.

2.3 Structures of the printed films

2.3.1 Disk structures

The disk structure contains a PZT layer sandwiched between top and bottom electrodes. It is supported by a sacrificial layer deposited on a substrate during screen-printing as shown in Figure 2.7 (a-b). The bottom and top electrodes are designed with the same diameter to provide the symmetric electromechanical coupling for testing piezoelectric properties. Diameter of screen patterns for printing the PZT disks is 9 mm. It is 1 mm wider than its electrode in order to avoid short circuits. Apart from this, a PZT disk without electrodes containing only a PZT layer supported by the sacrificial layer on the substrate is also prepared for density measurement as shown in Figure 2.7 (c-d).

2.3.2 Cantilever structures

The cantilever structure contains a PZT anchor for fixing one side of the cantilever on the substrate and a PZT piezoelectric layer (the screen pattern dimensions are varied in the length of 3-6 mm and in the width of 1-2 mm) sandwiched between top and bottom electrodes. The cantilever is also supported by the sacrificial layer deposited on the substrate during screen-printing as shown in Figure 2.7 (e-f). To avoid short circuits, the patterns of electrode are shorter than those of the piezoelectric cantilever (300 μ m and 150 μ m in width and length, respectively).



Figure 2.7 Drawing of the disk transducer (a) cross-sectional view, (b) top view; the piezoelectric disk without electrodes (c) cross-sectional view, (d) top view; and the cantilever transducer (e) cross-sectional view, (f) top view.

2.3.3 Pattern dimensions of all constituted layers

Table 2.7 and Figure 2.8 present dimensions of the patterns and thickness of the emulsion on mesh screens and the stencil for printing whole layers, while Figure 2.9 and 2.10 shows the designed patterns in real size in this work.

			Group				
Shape	Pattern dimension (mm)		I	II	III	VI	
Disk							
 Piezoelectric layer* 	Diameter	D_D	9.00	-	-	-	
- Electrode layer		E_D	8.00	-	-	-	
- Sacrificial layer	Length×Width		11.70×11.70	-	-	-	
Cantilever							
 Piezoelectric layer* 		$CV_L \times CV_w$	6.00×1.00	3.00×1.00	6.00×2.00	3.00×2.00	
 Anchor layer 	I on other Width		11.50×3.00	11.50×3.00	11.50×3.00	11.50×3.00	
- Electrode layer	Length×width	$E_L \times E_w$	5.85×0.70	2.85×0.70	5.85×1.70	2.85×1.70	
- Sacrificial layer			6.50×6.00	3.50×6.00	6.50×6.00	3.50×6.00	

 Table 2.7 Various-pattern dimensions for fabrication thick films in this work

Remarks *The free standing part



Figure 2.8 Dimensions in mm of various patterns: (a) disk, (b) cantilever with bottom electrode, and (c) cantilever with top electrode. Note that D_D is disk diameter, E_D is electrode diameter, CV_L is cantilever length, E_L is electrode length, CV_W is cantilever width, and E_W is electrode width.



Figure 2.9 Designed patterns of the disk structure for printing on the transparent film.



Figure 2.10 Designed patterns of the cantilever structure for printing on the transparent film.
2.4 Printable paste preparation

2.4.1 Procedure of preparing printable pastes

In order to prepare some printable pastes in our laboratory, the active powder (a solid part) is placed in a mortar. Then, the organic vehicle (a viscous liquid part) is added before pre-blending by a pestle (Figure 2.11(a)). After that, agglomerates of the obtained mixture is broken and homogenized by a three-roll mill (EXAKT 80S). The used equipment is shown in Figure 2.11(b). This is a basic method for mixing and dispersion compositions of semi-viscous materials by the shear forces generated between the adjacent rolls. The material is placed between a feed roll (roll no. 1) and a center roll (roll no. 2). Each adjacent roll rotates at progressively higher speeds. For example, the feed roll may rotate at 30 rpm, the center roll at 60 rpm and the front roll (roll no. 3) at 90 rpm. With different speed and rotation's direction rolls, the material is transferred from the center roll to the front roll, as presented in Figure 2.11(c). In this work, the corn starch paste and the various PZT pastes are prepared by this procedure (Figure 2.12).



Figure 2.11 The mixing equipment (a) the mortar and pestle, (b) the three-roll mill (EXAKT 80S), and (c) the side view's drawing of the three-roll mill operation.



Figure 2.12 The procedure of preparing printable pastes.

In case of the PZT pastes, the particle size of the solid part containing PZT and the sintering aid $(Li_2CO_3, Bi_2O_3, and CuO)$ powders need to be decreased for densification improvement. As a result, two additional steps are practiced before preparation of the printable pastes which are the following:

• Decreasing particle size of each ceramic powder

The used milling equipment for solid powders and their details are explained in section 2.4.2.

• Preparing active powder (mixed powders of PZT, Li₂CO₃, Bi₂O₃, and CuO)

In this step, all ceramic powders, eight zirconium grinding beads (5 mm diameter), and 60 mL of ethanol media are put in the container and mixed by a 3-dimentional- shaker/mixer turbula (Type

T2F, Willy A. Bachofen AG Maschinefabrik) for 12 hours. The equipment is shown in Figure 2.13. Then, the mixture is poured into a beaker, the grinding beads are removed. Finally, the ethanol is evaporated from the wet mixture by drying in an oven at 60°C for four nights. The dried-powder mixture is ready to use as the active powder in the PZT paste. The summarized steps of preparing the PZT paste are shown in Figure 2.14.



Figure 2.13 The 3-dimentional- shaker/mixer turbula for mixing the PZT powder and LBCu sintering aid.



Figure 2.14 Preparation of the PZT paste.

2.4.2 Milling tools for solid powders

Two milling tools employed to decrease the particle size of solid ceramic powders in this research are a planetary mill and an attritor mill. The differences of both tools are presented in Figure 2.15 and Table 2.8.



Figure 2.15 The schematic diagrams of (a) planetary mill (rot_d is rotation of the supporting disk and rot_c is rotation of containers) [22] and (b) attritor mill [23].

• Planetary mill

The counter-rotation of a supporting disk and milling containers in this tool originates centrifugal forces leading to movement of milling balls along, across the wall of the container before impacting on the opposite side. With shear, friction, and impact forces accelerate grinding of material powder [22]. This equipment is used for decreasing the particle size of the neat PZT, Li₂CO₃, Bi₂O₃, and CuO powders.

• Attritor mill

Inside of an attritor container with materials, grinding balls and a media, rotation at high speed of a vertical shaft with cross arms (impellers) leads to a different movement between the milling balls and material powder. This process gives both shear and impact forces on the powder contributing to the dispersion and decrease of material particle size [24]. This equipment available at LUSAC Cherbourg is used for decreasing the PZT particle size only.

	Equipment	Planetary miller (Retsch®)	Attritor (LUSAC laboratory)
	Tank size (mm ³)	7.5	-
	Ball type	Agate ball	Yttria stabilized zirconium ball
	Ball diameter (mm)	0.8	0.8
n	The number of ball	13	-
litic	Media	Ethanol	Water
puc	Ceramic powder/media	30g/40g	-
ŭ	Milling time (h)	18	0.5
	Surfactant	None	Dolapix CA
	Speed (rpm)	400	-
	Drying condition	7 h at 60°C (oven)	One night under infrared lamp

Table 2.8 Milling tools

2.5 Selected materials for screen printable pastes

To shape materials by screen-printing, the materials need to be in a form of printable pastes. Thus, instantly commercial and IMS labmade pastes are used in screen-printing. Furthermore, in the case of printing multilayer films with critical geometries and positions, an automatic screen-printing machine with high accurate printing positions is required. By a vision system, the screen-printing machine can capture and process the correct printing positions from relation of alignment marks (fiducials) located on the substrates and screens. Therefore, deposition of the alignment marks onto the substrates is a necessary step. It is done before printing active materials. High contrast between the alignment marks and the substrate helps the machine work well. In this research, the deposited alignment marks are also done by the screen-printing machine. As mentioned above and in the constituted layers of transducers section, used screen-printing pastes can be classified by their roles, as shown in Table 2.9.

Function	Paste choices	Manufacture or producer
Alignment marks	- ESL 8836 (Au) ESL 4024 (blue dialectric)	Electro-Science Laboratories (ESL)
~	- ESL 4924 (blue dielectric)	
Sacrificial layer	- ESL 244-T (polyester)	- ESL
	 Corn starch/epoxy paste 	- Mixing pastes by IMS laboratory with
		commercial corn starch obtained from
		EXXELIA and epoxy (ESL CV59)
		manufactured by ESL
Electrode	- ESL 8836 (Au)	- ESL
	- Ag/Pd (90% wt/10% wt)	- EXXELIA
	paste	
Piezoelectric disk	- PZT paste	Mixing pastes by IMS laboratory with the
and cantilever		following ingredients:
shapes		- Commercial PZT powder (Pz26 (Navy I))
Anchor layer (only in	- PZT paste	manufactured by Ferroperm
the cantilever		- Li ₂ CO ₃ , Bi ₂ O ₃ , and CuO powders (LBCu
structure)		sintering aid) manufactured by Sigma Aldrich
		- Organic vehicle (ESL 400) manufactured by
		ESL

 Table 2.9 Used screen-printing pastes

Remark: Details of commercial materials are presented in Appendix A-1.

2.5.1 Instantly pastes

A. Alignment mark pastes

• ESL 8836

A major material in this paste is gold (Au). With its high conductivity, it is normally used as electrodes in transducer field. It shows high contrast and good adhesion after firing when it is deposited on (gray) AlN substrates. Consequently, it is also exploited for printing alignment marks onto this kind substrate. Although Au paste is not developed for AlN substrate, its adhesion on this ceramic substrate is suitable for the alignment mark application.

• ESL 4924

This paste is a blue dielectric with non-porous characteristic composition (Appendix A-1) designed to insulate unabraded, unoxidized, ferritic steels for the thick film on steel application. However, the contrast between this paste and the (white) alumina substrate is high. Therefore, this paste is used for printing alignment marks on the alumina substrates [17] in this work.

B. Electrode pastes

• ESL 8836 (Au)

This commercial paste with aluminosilicate glass frit [16] leads to thin Au conductive layers suitable to ultrasonic wire-bonding (Appendix A-1). According to previous studies of [11] and [16], this paste can be used as electrode for the cantilever transducers. Thus, it is used to be one kind of electrode in this work.

• *Ag/Pd* (90/10)

This paste is prepared by EXXELIA for thin internal electrodes in multilayer capacitors. It contains a low permittivity oxide based on magnesium titanate (MgTiO₃) matching the coefficient of thermal

expansion of PZT ceramics, without affecting dielectric properties of capacitors [25]. Therefore, it is used as another kind of electrode for studying release behaviors and piezoelectric properties of the disks from the AlN substrates.

C. Sacrificial layer pastes

• ESL 244-T (the transparent polyester resin)

This paste is industrially produced for protecting silver polymers on glass substrates. This material is thermosetting and cures by cross linking at 125°C (Appendix A-1). It is chosen to be the sacrificial layer since it can be completely decomposed during the firing process reaching the temperature of 900°C in this work [26].

2.5.2 IMS Labmade pastes

A. Sacrificial layer paste

• Corn starch paste

This paste contains a 36 wt.%-commercial starch (active powder) and a 64 wt.%-epoxy ESL CV59 (viscous liquid part, Appendix A-1). They are blended together by the procedure described in section 2.4.1.

B. PZT pastes

Various PZT pastes are prepared in order to improve densification and optimize piezoelectric properties of the obtained specimens. Majorly basic ingredients of prepared PZT pastes are summarized in Figure 2.16. Difference types of the PZT powders are shown in Figure 2.17.



Figure 2.16 Ingredients of the PZT paste.



Figure 2.17 The PZT powder types (the particle size is observed by a laser granulometer of Horiba, pratica 950 and $D_{0.5}$ is the volume median diameter. The results of measurement are shown in Appendix A-2.

• Active (ceramic) powders

They are a part of active piezoelectric compound containing piezoelectric material and its sintering aid as follows:

- Non-milling or milled PZT powder (Pz26 (Navy I)) manufactured by Ferroperm
- Sintering aid with the ternary mixture of Li₂CO₃, Bi₂O₃, and CuO (LBCu). All materials were manufactured by Sigma Aldrich.

In this section, various groups of the active powder are prepared for different purposes which are the following:

For optimizing LBCu composition

Two groups of the active powder are prepared from the non-milling PZT powder (Powder A) and the 3 wt.%-milled sintering aid powders. The composition of the sintering aid is different. One LBCu formula (Type I) is from IMS team with 26.7 wt.% Li₂CO₃, 40 wt.% Bi₂O₃, and 33.3 wt.% CuO [11]. Another formula (Type II) is from Medesi team with 8.9 wt.% Li₂CO₃, 55.9 wt.% Bi₂O₃, and 35.2 wt.% CuO [12]. The ceramic compositions of each group of the active powder are shown in Table 2.10.

Coromio	Dowdon milling	Particle size, D _{0.5}	% Weight			
Ceranne	rowder minnig	(µm)	Туре І	Type II		
PZT (Powder A)	None	≈10	97.00	97.00		
Li ₂ CO ₃			0.80	0.27		
Bi ₂ O ₃	Planetary mill	2-5	1.20	1.68		
CuO			1.00	1.05		

Table 2.10 Ceramic compositions in two different groups of the active powder

Remark: The particle size is observed by a laser granulometer of Horiba, pratica 950.

For densification improvement

The optimized composition of LBCu sintering aid (3 wt.%) is mixed with two types of milled PZT powder obtained from the planetary mill (Powder B) and the attritor mill (Powder C).

• Organic vehicle

The commercial organic vehicle of ESL 400 based on texanol solvent and ethyl cellulose binder manufactured by Electro-Science Laboratories (Appendix A-1) is employed in this work. The content of organic vehicle added in the active powder to form the printable paste is related to the screen type. The stencil screen is used for printing PZT-disk and PZT-cantilever layers in order to avoid non-smoothing of obtained films with thickness around 100 μ m in one printing time. The mesh screen is used for printing a PZT-anchor layer with lower thickness. The weight ratios of the PZT powder and organic binder in each PZT paste are presented in Table 2.11.

Table	2.11	The contents	of	organic	vehicle	in	the	PZT	nastes
I able .	4.11	The contents	01	organic	venicie	ш	une	L L I	pasies

	PZT paste				
Compositions	Disk or cantilever layer	Anchon lover			
	(movable part)	Allehor layer			
Dried active powder (PZT + LBCu sintering aid) (wt.%)	88	84			
Organic vehicle (wt.%)	12	16			

Remark: The rheology of the PZT pastes are shown in Appendix A-3.

2.6 Multilayer printing and thermal treatment

2.6.1 Substrate preparation

To use the ceramic substrates for integrity of printed multilayer with the vision mode of the screen printing machine (DEK), the alignment marks (fiducials) on the substrates are required. In this work, the fiducials (1 mm in diameter) are printed onto the blank substrates by a manual mode before drying at 120°C for 20 minutes and firing at 850°C for 20 minutes in order to fix the fiducials and clean the substrates at the same time. Examples of used substrates are shown in Figure 2.18. The fired substrates are cracked in size of (1 inch×1 inch×250 μ m) before printing the multilayer transducers.



Figure 2.18 Examples of (a) AlN substrate, (b) Al_2O_3 substrate, (c) fired AlN substrate, and (d) fired Al_2O_3 substrate.

2.6.2 Deposition of constituted layers and drying

Multilayer disks and cantilevers are deposited by the differences of the screen-printing steps as shown in Figure 2.19. Their printing condition is detailed in Appendix A-4.

A. Screen-printing steps for the multilayer disks

Figure 2.19(a) shows printing of the piezoelectric disk sandwiched between electrodes. The sacrificial layer is printed on the ceramic substrate before the bottom electrode, the piezoelectric layer, and the top electrode respectively. For the disk without electrodes, printing of electrode layers is ignored.

B. Screen-printing steps for the multilayer cantilevers

In this case, printing direction affects a continuity of deposited layers. This is because the piezoelectric resonance cantilever with sandwiched electrodes is supported by two different parts (the anchor and the sacrificial layer) as it can be seen in Figure 2.19(b). A junction between the anchor layer and the sacrificial layer sometimes causes cracking of the cantilever owing to presence of a gap between them. Another reason is an excessive difference of their thicknesses [17]. For this work, the anchor layer is firstly printed to be a fixed part standing on the ceramic substrate. Then, the sacrificial layer is printed followed by the bottom electrode, the piezoelectric movable PZT layer, and the top electrode respectively. Their printing directions are presented in Figure 2.19(b).

C. Drying

After the screen-printing of each layer, the anchor layer, sacrificial layer, bottom electrode, and top electrode are dried in a conventional oven at 120°C for 30 minutes. The piezoelectric movable layer is dried in a progressive oven to avoid thermal shock and cracked propagation due to solvent evaporation. In this step, the temperature is increased from 25°C to 120°C with a 1°C/min heating rate and held at 120°C for an hour before natural cooling down to 25°C.



Figure 2.19 Screen-printing steps.

2.6.3 Isostatic pressing and sintering

After screen-printing and drying, the green specimens are packed in plastic part (two foil bags) with vacuum system before pressing with isostatic pressure at 40 MPa and 65°C for 4 minutes. This additional step is well known for improving density [27], [28]. It is done at EXXELIA, Pessac, France. The equipment is shown in Figure 2.20.



Figure 2.20 Isostatic pressing equipment available at EXXELIA Pessac

Then, the obtained specimens are sintered by co-firing at 900°C for 2 hours. This process also leads to releasing of the movable part of disk and cantilever multilayer films from their substrates due to decomposition of the sacrificial layer. The special furnace designed by IMS laboratory and manufactured by AET technologies (Figure 2.21) allows to fire the specimens under air flow with a controlled temperature profile. The specimens are put on a covered alumina tray inserted in tray channels of the tray holder. A K thermocouple located under the tray channel measures temperature. This furnace uses a computer with Labview to control temperature conditions around a tray holder by movement of a quartz tube in vertical directions (up or down direction). The temperature profile is set to fire all specimens at the same conditions as shown in Figure 2.22. It is similar to previous research of our team [11]. The phenomena occuring during the different temperature steps are expressed in Table 2.12.



Figure 2.21 The vertical furnace manufactured by AET technologies with IMS laboratory design: (a) outside with a computer for controlling the quartz tube movement and temperature monitor showing the maximum furnace temperature, (b) inside of its mechanical room, (c) the tray holder, and (d) the tray for putting specimens.



Figure 2.22 Co-firing temperature steps

Stop	Temperature	Heating rate	Holding time	Objective
Step	(°C)	(°C/min)	(hour)	Objective
1	25-250	40	-	Elimination of the residual solvent and the
				sacrificial layer
2	250-450	1	-	Elimination of the binder and the sacrificial
				layer
3	450-900	40	-	Formation of liquid phase of the sintering
				aid and beginning of densification of the
				PZT film
4	900	-	2	PZT sintering
5	900-25	40	-	Cooling down

Table 2.12 Steps of the co-firing cycle and objectives of each temperature range

2.7 Conclusions

The screen-printed PZT transducers are fabricated following the summarized process in Figure 2.23. According to the objectives of this thesis subject, the effects of the PZT pastes compositions, sacrificial layer materials, and electrode materials on various properties of the obtained PZT disks will be studied in Chapter 3. The optimized PZT paste and sacrificial layer material will be used to form the PZT cantilever transducers for VOCs sensors in Chapter 4.



Figure 2.23 Overall fabrication.

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CHAPTER 3: Optimization of screen-printed PZT transducers fabrication and microstructural and electromechanical characterization

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In general, ceramic properties majorly depend on its microstructure. PZT is a piezoceramic material which is screen-printed into a free-standing cantilever form for transducer application. However, plenty of remained pores in its microstructure were found. In order to improve densification of the screen-printed PZT films, several factors correlated to their microstructure such as compositions of PZT compound and PZT particle size are studied in this chapter. The release of PZT disks from two kinds of sacrificial layer are observed. The printed disks with electrodes (disk resonators) are fabricated to determine dielectric and electromechanical properties. Then, an effective PZT compound and an adequate sacrificial layer material will be selected for fabrication of free-standing-micro-cantilever with different geometries. The appropriate size of micro-cantilever with acceptable properties will be chosen for transducer application in Chapter 4. Some results in this chapter was published in Journal of Electroceramics [1].

3.1 Study of densification of screen-printed PZT disks

3.1.1 Principle of sintering

The densification process of ceramic powders (particles) by heat treatment at a high temperature (below the melting temperature) is commonly called sintering. This process is able to decrease the amount of pores within specimen structures due to bounding particles through mass transfer mechanisms, and leads to grain growth and binding among grains [2].

A. General sintering mechanisms

For conventional sintering (firing under air or controlled atmosphere), the sintering mechanisms can be widely divided into two types as the following:

• Solid phase sintering

Consolidation is induced in only solid phases. Mass transfer in this system is completed via diffusion of atoms or vacancies migrate along surface, interface or within material body [2]. The sintering stages in this case contain three stages [3], as shown in Figure 3.1.



Figure 3.1 Solid phase sintering (https://www.industrialheating.com).

At an initial stage, the main process is the formation of a neck between neighboring particles, pore geometry is open and interconnected. An increase in neck areas is responsible for changes in material properties associated with sintering. Continuous pores are performed by interconnected structure during intermediate stage. At the last stage, some pores are closed and grain growth is evident. The pores gradually decrease by diffusion to the grain boundary region. This densification is sensitive to grain size and the connection of pores to the grain boundary [3].

• Liquid phase sintering

In general, the diffusion in solid state sintering of ceramic particles (without sintering aids) is slow, although its process is done at high temperature (for instance, >1250°C for bulk PZT). The addition of liquid phase (sintering aids) enable to accelerate mass transfer rates and densification of ceramics. The liquid phase can come from melting of one component or formation of an eutectic. Then, it acts as a lubricant to allow rearrangement of the particles. The capillary force allows rapid compaction. This leads to a better compacity and an improvement of density of the sintered specimens at lower sintering temperature compared to the solid phase sintering [4], [5]. The microstructure changes during liquid phase sintering is presented in Figure 3.2. The mixed powders of piezoelectric ceramic and its additive (sintering aid) are heated leading to formation of liquid phase inducing grain rearrangement (particles movement, and decreasing porosity until forming a closed structure). Then, additional densification occurs by dissolution of the solid in the grain contact. Finally, grains grow and compact together contributing to a decrease in the porosity due to minimizing surface energy in its system [4], [6], [7].



Figure 3.2 A schematic diagram of the microstructure changes during liquid phase sintering (Adapted from [5]).

For finer particles, larger capillary pressure and specific surface could provide larger driving force for densification than that for coarse particles. The sintering shrinkage's model for liquid phase sintering giving a first sense of the particle size role is shown in eq.3.1.

$$\left(\frac{\Delta L}{L_0}\right)^n = K \frac{t^2}{D^m}$$
eq. 3.1

where $(\Delta L/L_0)$ is the sintering shrinkage, *K* is a mechanism dependent parameter for sintering shrinkage, *t* is the sintering time, *D* is particle size, and the constants m and n are mechanism dependent exponents, with m = 4 and n = 6 for grain boundary diffusion [5].

B. PZT sintering

• Bulk PZT ceramics

For PZT bulk ceramics, they are normally sintered at temperature above 1250° C; however, this extreme temperature range causes evaporation of volatile components relating to changes of composition of PZT and migration of the electrodes [4]. To relieve these problems, supplementation of metal oxide additives, for instance, MnO₂ [8], combination of Li₂CO₃ and Na₂CO₃/Bi₂O₃ [9], combination of PbO and Cu₂O [4], or a mixture of LiBiO₂ and CuO [10] is used to drop the sintering temperature.

Corker *et al.* [4] reported that for a commercial PZT (Pz26, $D_{0.5} = 1.7 \ \mu\text{m}$) ceramic, adding 5 wt.% of sintering aid (Cu₂O:PbO in a ratio 1:4) allowed sintering at 800°C with acceptable densification (7.65 g/cm³). However, low effective electromechanical coupling coefficient in planar mode ($k_p = 43.1\%$) was received. Figure 3.3 presents an eutectic of solid solution system of Cu₂O-PbO (mixed oxides) with a melting point of around 680°C, which is lower than conventional sintering temperature. This resulted in the formation of a liquid phase at an early stage of firing. The acceleration of densification occurred due to a wetting action of the powder particles by this liquid phase. Apart from this, improved electromechanical properties ($k_p = 51.7\%$) and densification (7.83 g/cm³) were obtained from using finer PZT particle ($D_{0.5} = 1.1 \ \mu\text{m}$) and an addition of 3 wt.% of sintering aid at sintering temperature of 850°C.



Figure 3.3 Solid solution system Cu₂O-PbO [4].

Wang *et al.* [10] demonstrated that PZT ceramics could be densified at as low as 800°C by incorporation of 1wt.%-LiBiO₂ and 0.06wt.%-CuO (LBCu) as the sintering aid. It exhibited high dielectric constant (1000-1300) and coupling factor (55-60%) over a wide temperature range 800-1000°C. The optimum properties were gained for the ceramics sintered at 880°C for 2 h. Generally, if only LiBiO₂ is employed, the optimal properties could be obtained at sintering temperature higher than 1000°C. When one more CuO component is used, the sintering temperature at which the optimal properties are presented is shifted to below 900°C. Figure 3.4 presents that the densification of PZT adding 1.06 wt.% LBCu started at \approx 600°C and approached its end at \approx 950°C. This supported that LBCu could motivate the densification.



Figure 3.4 Shrinkage behavior of $Pb(Zr_{0.53}Ti_{0.47})O_3$ with and without LBCu additive (1.06 wt.%): (a) linear shrinkage versus temperature, (b) shrinkage rate versus temperature [10].

• PZT thick and thin films

According to previous literatures, in cases of PZT thick and thin films, sintering at low temperature also restricts chemical reaction between the film and the substrate. The presence of a liquid sintering aid helps releasing of the shear stress through a process of particle rearrangement owing to enhanced transport via a stress-supported dissolution-precipitation mechanism [6]. Examples of the sintering aids used in the densification of lead containing piezoelectric films include PbO [11], Bi₂O₃-Li₂O [12], Cu₂O:4PbO [13], Bi₂O₃-ZnO [14], borosilicate glass [15], Li₂CO₃-Bi₂O₃-CuO (LBCu) [16], [17].

In 2014, Medesi *et al.* [17] achieved using LBCu sintering aid formula developed by Wang *et al.* [10] for sintering at 900°C of PZT fabricated by tape casting. The obtained specimen with 5 vol.% LBCu gave density 7.4 g/cm³. Moreover, IMS laboratory could also sinter screen-printed PZT thick film at 900°C with dissimilar formula of LBCu sintering aid. With 3 wt.% LBCu, density of sintered film was around 7.0-7.2 g/cm³ [16], [18], [19].

Regarding piezo-ceramic thick films, another route for decreasing processing temperature and improving densification in thick film technology is the decrease in size of ceramic powder. Small particles of ceramic ingredients contribute to large surface areas of the powder and the accompanying high surface reactivity. However, too small particles (diameter < 1 μ m) would be detrimental for the piezoelectric properties of the material [20]. Additionally, similarly as in ceramic process, a pressure step introduced before sintering can also improve density and piezoelectric properties of the PZT thick films [21].

To study the densification of screen-printed PZT thick films in this work, the PZT disks are fabricated on polyester sacrificial layer deposited on AlN substrates. Particle sizes of raw ceramics are measured by a laser granulometer (Horiba, pratica 950) and Scanning Electron Microscopy (SEM, JEOL-JSM-6100). Green bodies and sintered PZT specimens' sizes are observed and measured by an optical microscope (WILD HEERBRUGG TYP 327616) linked with a NIKON acquisition's system in order to calculate shrinkage. The density of the sintered PZT disks with different composition of LBCu sintering aid are determined by helium gas pycnometer (Micrometrics accupyc 1330). 3D images created from scanning with an optical profilometer (ALTISURF 500) are employed to determine thickness of green bodies and observe warpage of the sintered specimens. For microstructural observation, the sintered specimens are cross-sectioned and traditionally polished. Then, the electrode and PZT thickness are measured by the optical microscope. Next, the polished specimens are coated with carbon before analysis by SEM (JEOL-JSM-6100). With SEM images of cross-sectional areas, the porosity of the PZT films is estimated with ImageJ. Moreover, SEM (HITACHI S-3400 N) linked with EDS (EDAX-Octane Elect Plus) is used to identify some elements in the PZT layer and at interface between the PZT and the bottom electrode layers.

3.1.2 Sintering aid compositions effect

In this research, the ternary mixture of Li_2CO_3 , Bi_2O_3 , and CuO (LBCu sintering aid) is used to sinter the screen-printed PZT thick films at 900°C. As mentioned in section 2.1.1B of Chapter 2, the effect of LBCu compositions on film's densification is studied. The constant values of total percentage of LBCu (3 wt.%) in PZT compound and temperature profile are used for all specimens.

Photographs of the released PZT disk without electrodes prepared from PZT pastes containing raw PZT powder (particle size $\approx 10 \ \mu$ m) and 3wt.%-milled LBCu sintering aid (particle size $\approx 2-5 \ \mu$ m) on polyester sacrificial layer are shown in Figure 3.5. Microstructures of the PZT disks with different LBCu composition are revealed in Figure 3.6. Their lateral shrinkage, density, and porosity are presented in Table 3.1. Whole results indicate that the LBCu composition of IMS laboratory (Type I) is still appropriate to fabricate the PZT disks with high shrinkage, acceptable densification ($\approx 7.0 \ \text{g/cm}^3$), and lower porosity (19%) compared to outcomes of another LBCu composition. Therefore, this LBCu composition is selected to prepare the PZT cantilevers.



Figure 3.5 Example of sintered disk (Type I, see Table 3.1): (a) top and (b) bottom sides.



Figure 3.6 SEM images of polished areas of the sintered disks: (a) Type I (developed by IMS laboratory team) and (b) Type II (developed by Medesi team), see Table 3.1.

Type of PZT compound	LBCu ratio (Li ₂ CO ₃ /Bi ₂ O ₃ /CuO)	Lateral Shrinkage (%)	Density, ρ_p (g/cm ³)	Porosity (%)
I (IMS laboratory team)	26.7/40.0/33.3	12	7.0	19
II (Medesi team)	8.9/55.9/35.2	10	5.5	32

Table 3.1	Lateral	shrinkage	density	and no	orosity	of the	sintered	disks	with	different	LBCu	composition
Table 3.1	Lateral	sinnkage,	uchisity,	and p	orosity	or the	sincicu	uisks	W ILII	uniterent	LDCu	composition

Remarks:

1. The same powder sizes of raw (non-milling) PZT powder ($D_{0.5} \approx 10 \ \mu\text{m}$) and milled Li₂CO₃, Bi₂O₃, CuO ($D_{0.5} \approx 2-5 \ \mu\text{m}$) are used in both cases.

2. Density is determined by pycnometer.

3.1.3 PZT particle size effect

Although the PZT paste prepared from the PZT-compound Type I (the formula developed by IMS laboratory team) with raw (non-milling) PZT powder (Paste A) is suitable to shape cantilevers, the residual porosity in a sintered disk is still found (Section 3.1.2). In order to improve densification, the raw PZT powder is milled with two different methods (planetary mill and attritor mill). SEM images of PZT powders with distinct milling histories are shown in Figure 3.7(a-c). Two new PZT pastes (B and C) with the 3 wt.%-LBCu sintering aid (composition type I developed by IMS Laboratory team) are prepared, shaped onto polyester sacrificial layer, and sintered. Microstructures of the sintered PZT disks gained from different particle size of PZT powders are shown in Figure 3.7(d-f). Their characteristics are illustrated in Table 3.2.



Figure 3.7 SEM images of PZT powders with different milling methods (a) non-milling (Powder A), (b) planetary mill (Powder B), and (c) attritor mill (Powder C); polished areas of the sintered micro-disks obtained from printing onto polyester sacrificial layer and different PZT powders (d) Powder A, (e) Powder B, and (c) Powder C [1].

Table 3.2 Lateral shrinkage, density, and porosity of the sintered disks with difference in milling (each paste is mixed with the 3 wt.%-LBCu sintering aid developed by IMS laboratory team with the Li₂CO₃/Bi₂O₃/CuO ratio of 26.7/40.0/33.3 (Type I)

Samula/Desta	A B		С	Commercial Pz26	
Sample/Faste	(non-milling)	(Planetary mill)	(Attritor mill)	Ceramic	Thick film
Powder characteristic					
- Particle size of PZT powder, $D_{0.5}$ (µm)	≈10	<1	<1	-	-
- The distribution of particle size (µm)	1-100	0.2-4.0	0.4-0.9	-	-
	(Powder agglomeration)	(Powder agglomeration)	(Powder distribution)		
Disk characteristic					
- Lateral shrinkage (%)	12	15	14	-	-
- Porosity (%)	19	6	6	-	-
- Density (g/cm ³)				7.7ª	5.0 ^b
• Pycnometer (ρ_p)	7.0	7.4	7.5		
• SEM (ρ_{SEM})	6.2	7.2	7.2		

Sources a Pz26 datasheet, and b V. Ferrari et al. [22], [23]. and M. Prudenziati [24]

Remarks: The density estimated from SEM images (ρ_{SEM}) is calculated by $\rho_{\text{SEM}} = (1-\text{porosity}) \times \rho_{ref}$ where ρ_{ref} is the density of non porous PZT. In this case, the density of a bulk PZT (7.7 g/cm³) given by the manufacture (Ferroperm) is considered for the reference value. Besides, the porosity obtains from analyzation of SEM images with Image J [16], [25].

The sintered PZT disks prepared from three different PZT powders: A (non-milling powder), B (milled powder by planetary mill), and C (milled powder by attritor mill) are called A, B, and C samples, respectively. SEM micrographs in Fig 3.7(d-f) of the sintered disks show some partially distributed pores resulting from solvent evaporation during drying and binder decomposition during sintering. Sample A prepared from raw PZT powder (non-milling with particle size, $D_{0.5} \approx 10 \,\mu\text{m}$) reveals a lot of pores whereas B and C samples prepared from milled PZT powders (particle size, $D_{0.5} < 1 \,\mu\text{m}$) show dense zones and few pores. Basically, the smaller PZT particles have better packing and are responsible for accelerated densification process compared with bigger PZT particles [26], [27]. This is in accordance with the results shown in Table 3.2, where B and C samples show lower porosity, higher density, and higher shrinkage than Sample A. In addition, black particles related to a copper element (Figure 3.8) are found in the PZT layer of all samples. It clearly shows that the distribution of LBCu powder, i.e. melting, is not homogeneous.



Figure 3.8 EDS spectrum of the black particle.

In summary, with screen-printing associated with sacrificial layer technique, the sintered PZT disks prepared from PZT paste Type I (3 wt.% LBCu sintering aids: Li₂CO₃/Bi₂O₃/CuO in a ratio of 26.7/40.0/33.3) present lower residual porosity compared to PZT paste Type II (3 wt.% LBCu sintering aids: Li₂CO₃/Bi₂O₃/CuO in a ratio of 8.9/55.9/35.2). Furthermore, using the nano-scale of PZT powders improve microstructural packing and decrease the residual porosity in the printed disks. Consequently, PZT paste Type I is selected to prepare resonators in this work.

3.2 Study of using sacrificial layer based corn starch

Polyester (commercial) paste has been used as sacrificial layer for the preparation of the freestanding PZT cantilever in recent and current research because it can completely decompose during sintering process at 900°C. However, the corn starch/epoxy based paste is another interesting material for this function because the corn starch is green and a cheap material. Therefore, its paste is prepared in our laboratory (as mentioned in Section 2.5.2A of Chapter 2) in order to study the tendency of using as the sacrificial layer.

Figure 3.9 shows decomposition temperature of polyester and corn starch/epoxy (ESL CV59) based pastes determined by TGA analysis. There are two steps for decomposition of the polyester paste (Figure 3.9(a)). The initial mass loss (\approx 70%) is related to solvent evaporation, while the final mass loss (\approx 30%) is linked to the thermal decomposition of polyester. This material completely disappears at approximately 450°C. The corn starch/epoxy based paste has a 3-step process of decompositions (Figure 3.9(b)). In the first step (mass loss \approx 37%) between 50-150°C, the solvent are lost. Then, based on TGA analysis of epoxy (Figure 3.9(c)), the combined thermal decomposition of the corn starch and epoxy major occurs in the second step (mass loss \approx 50%). The third weight loss (\approx 13%) may the pyrolysis of complex segments obtained from decomposition of the corn starch in the second step. However, the corn starch/epoxy based paste completely decomposes at around 550°C. The decomposition temperature in each step of the corn starch/epoxy based paste is slightly shifted compared to the epoxy (ESL CV59) alone (Figure 3.9(c)) [28].



Figure 3.9 TGA curves of (a) polyester tested in this work, (b) corn starch/epoxy (ESL CV59) based paste tested in this work, and (c) epoxy (ESL CV59) paste obtained from previous work [28].

With completely decomposition at temperature lower than 900°C of polyester and corn starch/epoxy based pastes, both sacrificial layer materials are screen-printed on the substrate with the same conditions. The thickness and roughness of dried sacrificial layer of polyester and corn starch are observed by ALTISURF 500 profilometer. The cured deposits of the polyester and the corn starch/epoxy based pastes have thickness of around 40 μ m and 90 μ m, respectively. With more

solvents, the polyester-based paste has a thinner cured layer. Figure 3.10 reveals roughness of both layers. The average roughness (R_q) of the polyester and the corn starch-based pastes are 0.8 µm and 4.8 µm, respectively.

SEM images (Figure 3.10) of sintered PZT disks with the paste of PZT compound Type I (3 wt.% LBCu sintering aids: Li₂CO₃/Bi₂O₃/CuO in a ratio of 26.7/40.0/33.3) and Powder B (milled PZT powder by planetary mill) printed onto each sacrificial layer are used to estimate their porosity and density. The results are shown in Table 3.3. The disks printed on corn starch present an improvement in density. This could be due to a higher decomposition temperature of the corn starch/epoxy based paste compared to the polyester one. Consequently, the PZT disks printed onto the corn starch/epoxy layer has stand a longer time on this kind of sacrificial layer during the sintering. This retards a contact between the bottom disk and the substrate where interdiffusion may occur. Thus, the shrinkage of the obtained disk could be easier; especially, if there is no chemical reaction between the PZT disk and the sacrificial layer as in the case of corn starch/epoxy sacrificial layer.



Figure 3.10 Roughness profiles and SEM images of (a) polyester sacrificial layer (b) corn starch sacrificial layer.

 Table 3.3 Porosity and estimated density of sintered disks with different sacrificial layer materials from SEM images

Sacrificial layer	Porosity (%)	Density , ρ_{SEM} (g/cm ³)
Polyester	6.0	7.2
Corn starch	2.2	7.5

Remarks:

1. The density estimated from SEM images (ρ_{SEM}) is calculated by $\rho_{\text{SEM}} = (1\text{-porosity}) \times \rho_{ref}$ where ρ_{ref} is the density of non porous PZT. In this case, the density of a bulk PZT (7.7 g/cm³) given by the manufacture (Ferroperm) is considered for the reference value [16], [25].

2. The porosity obtains from analyzation of SEM images with Image J.

However, high roughness of corn starch layer should be decreased by milling of corn starch powder before mixing with epoxy. Otherwise it will introduce defects in the bottom electrode if the disk resonators sandwiched between electrodes are prepared.

In summary, corn starch based paste could be used as sacrificial layer. Nevertheless, the particle size needs to be decreased to obtain a smoother surface. Thus, in this work, the polyester paste is kept to prepare the sacrificial layer with a flat surface for further screen-printing of the resonators. One should pay attention to this factor because it will affect the surface quality of the bottom electrode of the resonators and also the electrical properties of the printed devices.

3.3 Study on characteristics of PZT disk resonators

3.3.1 Releasing of the PZT disk resonators from substrates

A. Warpage

The free-standing PZT disks with electrodes visibly show small warpages and defects. They have a total thickness of $\approx 150 \ \mu\text{m}$. In the field of micro-thin films, warpage corresponds to a residual stress, including thermal stress, interfacial stress, and intrinsic stress which depend upon processing parameters and mismatch characteristics of each material in a sample structure [29], [30]. The tiny warpage of the obtained disks (Figure 3.11) is also caused by an increase of thermal stress owing to the difference of coefficients of thermal expansion (CTE) between the electrodes and the PZT layers during the co-firing. The CTE values are shown in Table 3.4.



Figure 3.11 3D-thickness profiles of sintered PZT microdisks prepared from Paste C: (a) the sample with Au electrodes and (b) the sample with Ag/Pd electrodes.

Material	CTE (ppmv/°C)
^a Pure Gold (Au)	14.6
^a Pure Silver (Ag)	19.2
^a Pure Palladium (Pd)	11.2
Ag/Pd system [31]	17
MgTiO ₃ [32]	4.9
PZT Ceramic [33]	4.1

Table 3.4 The coefficient of thermal expansion (CTE) of some materials used in this process

^a The approximate ranges at room temperature to 100°C [24].

An asymmetry in thickness of the multilayer can also be a cause of deformation. At the beginning of the experiment, when one layer of Au bottom electrode was printed, discontinuity of the electrode was observed because of partial dissolution of the gold in the sacrificial layer during the printing process. Consequently, two layers of the Au bottom electrodes are printed to avoid this problem. For the Ag/Pd electrode (with high solvent content), two layers are necessarily screen-printed to achieve continuous electrodes for further polarization and electromechanical characterizations. After the co-firing, the layer thicknesses within the sintered specimens are measured and shown in

Figure 3.12. The asymmetrically sintered specimens with Au electrodes result in more warpage compared with the symmetrically sintered specimens with Ag/Pd electrodes. S. L. Kok [34] reported that an increase of the bottom electrode thickness developed the maximum stress related to elastic modulus in a sample. The asymmetry of the sintered samples with Au electrodes possibly induces more residual stress and more warpage in their structures compared to the samples with Ag/Pd electrodes. Figure 3.12 also shows that the PZT-layer thickness is correlated with the particle size and morphology of starting powder. Powder "A" (non-milling) produces a thicker PZT layer in comparison with B and C powders.



Figure 3.12 Thickness of each layer assembly as sintered PZT microdisks: (a) the samples with Au electrodes, and (b) the samples with Ag/Pd electrodes. Remarks: A, B, and C samples are prepared from PZT powders with different milling histories of non-milling powder, milled powder by planetary mill, and milled powder by attritor mill, respectively. The PZT compound for fabrication of each sample contains 3 wt.% LBCu sintering aids: Li₂CO₃/Bi₂O₃/CuO in a ratio of 26.7/40.0/33.3 (Type I).

B. Releasing

Typical releasing behaviors of the sintered specimens from the substrates are observed as shown in Figure 3.13 (Sample A, B, and C show similar behavior of releasing). The top electrodes of the samples with Au and Ag/Pd electrodes are smooth since these surfaces are free from overlapping by another layer, as shown in Figure 3.13(a) and (b). However, the bottom electrodes are imperfect, especially in the case of the Au bottom electrodes. Figure 3.13(c) reveals a defect appearing at the edge of the electrodes. This defect is caused by sticking between the bottom Au electrode and the substrate. It can be explained by differences in solvent compositions (Table 3.5) and warpage. Solvents within the Au electrode and the sacrificial layers are polar. This possibly induces diffusion between the Au bottom electrode and the sacrificial layer during the printing process. In contrast, the Ag/Pd electrode contains a nonpolar solvent. Thus, it is insoluble in the sacrificial layer during the process. No sticking is observed in Figure 3.13(d) when the Ag/Pd paste is used as the bottom electrodes. The Au bottom electrode roughness is observed in Figure 3.13(e). By comparison, the flat Ag/Pd bottom electrode is shown in Figure 3.13(f).



Figure 3.13 Optical Microscope images of the sintered samples (Sample B) with different electrode materials (a) Au, (b) Ag/Pd top electrodes; (c) Au, (d) Ag/Pd bottom electrodes; polished areas of the samples with (e) Au, (f) Ag/Pd electrodes.

1 01									
Screen-printing paste	Commercial name	Active element	Solvent or binder						
Polyester sacrificial layer	ESL 244-T	Polyester	Butyl diglycol acetate						
PZT paste	Pz26 and ESL V400	PZT	Organic binder with texanol solvent						
Au electrode	ESL 8836	Au	Terpineol						
Ag/Pd electrode	-	Ag/Pd:90/10	Kerosene						

Table 3.5 Information of solvent in screen-printing pastes

C. Interfaces

Figure 3.14(a) shows a discontinued interface between the Au bottom electrode and the PZT layer. This is probably caused by the polar differences in their solvents and residual stresses between their layers, despite presence of glass frit additives in the Au electrode [35]. Conversely, a completely continuous interface of the Ag/Pd bottom electrode and the PZT layer is shown in Figure 3.14(b). This good interface may be attributed to the following contributions:

- The inter-diffusion between Ag/Pd and PZT layers as confirmed by EDS analysis in Figure 3.14(c)
- Presence of MgTiO₃ (an additive in Ag/Pd electrode) promotes a better matching between the Ag/Pd electrode's and the PZT layer's shrinkage. This is due to the coefficients of thermal expansion (CTE) of PZT and MgTiO₃ that are very close as shown in Table 3.4. Hence, this contributes to a better chemical interface.



Figure 3.14 SEM images at interfaces between the bottom electrode and PZT layers: (a) the sample with Au electrodes, (b) the sample with Ag/Pd electrode, and (c) EDS line scan results at the interface between the bottom Ag/Pd electrode and the PZT layer.

3.3.2 Electrical characterization

A. Poling treatment

Poling treatment (or polarization) is a process inducing the presence of piezoelectric effect (an uniform orientation of dipoles in direction of the electric field) in piezoelectric materials by applying the d.c. electric field. A remanent polarization (P_r) is thus achieved within the material after the removal of the electric field (Figure 3.15).



Figure 3.15 Diagrams of the domains in lead zirconate titanate (a) before, (b) during, and (c) after polarization. Where ΔS is change in length during polarization and ΔSr is residual changing length after the polarization process [36].

• Electrical contacts

In order to apply the d.c. electrical field to the sintered PZT disk with electrodes, the platinum wires (0.0508 mm diameter) are connected to top and bottom electrodes of the sintered disk by a drop of Ag-epoxy based paste (ESL 1901 of Electroscience, Appendix A-1), as shown in Figure 3.16. This connection (drop size < 1 mm in diameter for all specimens) does not affect significantly piezoelectric properties of the specimens (Appendix B-1).



Figure 3.16 Example of wires connection of PZT micro-disk with electrodes.

• Poling

Figure 3.17 displays AET Technologies furnace designed by IMS laboratory. This furnace is employed to polarize all PZT resonators in this work. The PZT disks with wires are connected with two metal wires (diameter ≈ 1 mm) to a ceramic cell placed in the chamber of AET Technologies furnace. The poling procedure is the following:

- Vacuum is done at room temperature before introducing nitrogen gas.
- The chamber is heated to 280°C (Curie temperature of Pz26 is 330°C). This working temperature will ease the dipoles alignment.
- Vacuum is done again to remove residual humidity in the chamber before introducing nitrogen gas. This step is done in order to prevent breakdown of the dielectric material.
- The polarization is conducted across the specimens for 10 min with an increasing electric field of ≈ 1.5 kV/mm. During this process, the current is controlled to be kept lower than 10 μ A in order to avoid breakdown of the specimens.
- The specimens are subsequently cooled down to room temperature ($\approx 2^{\circ}C/min$) while maintaining the electric field
- Finally, the electric field is cut off, and the specimens are moved for measuring remanent polarization (*P_r*) by TF Analyzer 2000E and piezoelectric and dielectric properties by an Agilent E5063B network analyzer.



Figure 3.17 AET Technologies furnace.

B. Electromechanical and dielectric properties

Commonly, there are two vibration modes of disk resonators which are planar and thickness modes. In this subject, the electromechanical and dielectric properties are measured with the first planar vibration mode at room temperature. The phase angle θ spectra are observed to evaluate the poling capacity. The resonant frequency (f_r) and anti-resonant frequency (f_a) can be extracted from an impedance modulus spectrum at the lowest and highest peaks respectively [37], [38]. The effective electromechanical coupling coefficient is calculated using eq. 3.2. This factor quantifies the efficiency of the samples associated with the mechanical to electrical energy conversion of the piezoelectric transducer [39], [40]. The B(G) admittance circles are plotted in order to estimate dielectric and mechanical losses of the resonators (the equivalent circuit of the admittance circle of piezoelectric resonators is illustrated in Appendix B-2. Capacitance (C_p) values are also measured to calculate the relative permittivity (ε_r) according to eq. 3.3. [41].

$$(k_{eff})^2 = (f_a^2 - f_r^2)/f_a^2$$
 eq. 3.2

where f_a and f_r are from the impedance spectra.

$$\varepsilon_r = C_p d / \varepsilon_0 A$$
 eq. 3.3

where C_p is the capacitance measured at 1 kHz, *d* is the PZT thickness, *A* is the electrode area, and ε_0 is the vacuum permittivity whose value is 8.85×10^{-12} Fm⁻¹.



Figure 3.18 (a) Phase angle θ , (b) Impedance as a function of frequency for the samples with different electrodes, (c)) k_{eff} of the samples with different electrodes (the standard deviation are calculated for 3 samples), and (d) The admittance circle B(G) for the samples with Ag/Pd electrodes (first planar vibration mode measurement).

According to the ideal poling state of piezoelectric materials without the energy loss, the phase angle θ reaches a peak at 90° in the frequency range between the resonant and anti-resonant frequencies [42], [43], [44]. The phase angle θ as a function of frequency in Figure 3.18(a) shows that A, B and C samples with Au electrodes have the phase angle θ of 61°, 84°, and 79° respectively, while the samples with Ag/Pd electrodes reach a peak at the same value (≈88°) with broader frequency ranges. These results prove that the defect and asymmetry of the Au electrodes convey a decline of the poling efficiencies. Figure 3.18(b) shows differences of the resonant frequency f_r taken by impedance modulus spectra. The f_r of the planar vibration mode is inversely proportional to the sample's radius [45], [46]. Hence, a sample with a wider diameter shows a f_r at a lower frequency. As mentioned in Section 3.1.3, the different PZT particle sizes lead to different shrinkage affecting the diameter of the sintered samples, although they are shaped with the same screens. The highest f_r is generated by Sample B, followed by Sample C, and Sample A with samples' diameter of approximately 7.5 mm, 7.7 mm, and 7.9 mm, respectively. Regarding an effect of electrode materials on the impedance spectra in Fig 3.18(b), single-peak spectra are obtained from the samples with Ag/Pd electrodes. Conversely, an inhomogeneity of the bottom Au electrodes contributes to multiple-peak spectra. This makes it difficult to indicate the f_r and f_a accurately. However, these values are estimated and converted to the k_{eff} , as shown in Figure 3.18(c). With symmetric electrodes and thicker PZT layers, the samples with Ag/Pd electrodes obviously present higher values of the k_{eff} . Besides, a lower standard deviation is noticed for the Ag/Pd electrodes because of a greater reproducibility with homogeneous bottom electrodes compared to those with Au electrode. Therefore, to determine the effect of the PZT particle sizes on dielectric and electromechanical properties, we will focus the discussion on the obtained results from the samples with Ag/Pd electrodes.

Figure 3.18(d) and Figure 3.18(e) illustrate the admittance circles G(B) measured for each sample and the abscissa of the left hand of each admittance circle respectively. These abscissa values correlated with dielectric losses ($1/R_d$ when R_d is the dielectric resistance) are similar for all samples close to zero. Furthermore, the diameter of the admittance circle is in inverse proportion to the mechanical resistance (R_m) related to the mechanical losses of the resonator. Large circles are obtained from samples B and C compared to Sample A. This is coherent as samples B and C share similar microstructural characteristics. On the other hand, the small circle observed for Sample A can be due to decreases of the density, and the apparent large pores which result in higher R_m .

Table 3.6 compares the printed samples made of the different PZT grain sizes with Ag/Pd electrodes, commercial ceramic (Ferroperm), and PZT thick films in other works in terms of k_{eff} and ε_r . Sample A represents the lowest values of k_{eff} and ε_r owing to highest porosity compared to B and C samples. Moreover, the k_{eff} and ε_r of B and C samples are very close due to their similar densification (Table 3.6). In comparison, slightly higher values are obtained with the commercial Pz26 ceramic sintered at around 1200-1300°C. Moreover, samples B and C have the significantly higher ε_r value compared to the thick films based on Ferroperm Pz26 in other research studies. These outcomes reflect the developed dielectric permittivity of Sample B and C with a densification promoted by the use of the LBCu sintering aid and the nanometric PZT powders. In addition, using Ag/Pd electrodes and polyester sacrificial layer are another important factor attributed to improved piezoelectric and dielectric properties of the printed samples with the uniform releasing.

· · · ·						
Sample	keff (%)	$C_p(nF)$	Er			
A (non-milling)	40	2	900			
B (Planetary mill)	45	3	1200			
C (Attritor mill)	42	3	1200			
Pz26 ceramic (Appendix A-1)	57 (k_p) 44 (k_t)	-	1300			
Pz26 thick film [23]	-	-	570			
TF2100 (PZT thick film based on Pz26) [24]	-	-	520			

Table 3.6 Electromechanical and dielectric parameters of the samples with Ag/Pd electrodes

Remarks: k_p and k_t are the planar and thickness coupling factors, respectively.

C. Comparison between PZT disks obtained from screen-printing and commercial ceramic

In this part, the screen-printed disks with Ag/Pd electrodes fabricated are compared to the commercial PZT disk with Ag electrodes manufactured by PI ceramic (hard PZT PRYY+1113) with a 10-mm diameter and a 0.2-mm thickness in terms of P(E) loop and admittance identification.

• P(E) hysteresis loop

A typical hysteresis loop and the corresponding measured switching currents for the screen-printed PZT disks with Ag/Pd electrodes and the commercial PZT disk with Ag electrodes are illustrated in Figure 3.19. The current peaks indicate that the electrical field is high enough to switch the dipoles into the grains. At hysteresis frequency of 0.1 Hz, the printed and commercial disks present the remanent P_r of $\approx 33.19 \ \mu\text{C/cm}^2$ and $\approx 41.79 \ \mu\text{C/cm}^2$, respectively. Similarly, the switching current peaks at coercive field (E_c) of the printed disk ($+E_c \approx 1.59 \text{ MV/m}$ and $-E_c \approx 1.55 \text{ MV/m}$) are lower than those of the commercial disk ($+E_c \approx 1.78 \text{ MV/m}$ and $-E_c \approx 2.41 \text{ MV/m}$). Although the screen printed disk shows lower capacity than the commercial disk, it displays a normal hysteresis loop of usable piezoelectric. These slight deterioration of the remanent polarization and higher switching current may be due to the residual porosity causing a decrease in permittivity for the printed sample [47].



Figure 3.19 (a) Hysteresis loops and (b) switching current peaks of the printed PZT disk (Sample C) with Ag/Pd electrodes and commercial PZT disk with Ag electrodes (tests at hysteresis frequency is 0.1 Hz by Elorprintec, Pessac, France).

• Admittance identification

Figure 3.20 shows that the printed and commercial disks have similar admittance characteristics planar vibration mode), but different amplitudes. The maximum and minimum magnitudes of the printed disk take place at higher frequencies than those of the commercial disk. This is because the printed disk has smaller diameter. Moreover, the printed disk has lower quality factor (\approx 400) and lower phase angle θ (\approx 88°) compared to the commercial disk with (\approx 1900) and (\approx 90°), respectively. This is probably because of differences in densification and electrode materials (thin sputtered electrode for the commercial specimen).



Figure 3.20 Admittance identification of the printed PZT disk with Ag/Pd electrode (Sample B) and the commercial PZT disk with Ag electrode (a) magnitude and (b) phase (measurements by Associate Pr. Alexis Brenes (ISEP, LISITE Paris) and Pr. Elie Lefeuvre (Université Paris-Saclay, C2N-Palaiseau).

In comparison with the commercial specimens, the piezoelectric coupling factors of the planar vibration mode k_p are extracted by the relationship plotted in Figure 3.21 (using IRE standards on Piezoelectric Crystal [48]). Besides, with the measured resonant frequency, similarly as for Au/PZT/Au cantilevers with an in-plane vibration mode [35], Young's modulus of the PZT material with Au electrodes can be calculated for the disks from eq. 3.4. The calculated values are reported in Table 3.7 and compared to commercial values and other works. The obtained results exhibit that k_p of the printed disks on polyester sacrificial layer are higher compared to the disk printed on an

epoxy-SrCO₃ sacrificial layer in previous work [49]. This value of our printed disk is also close to the obtained value of the printed film of commercial PZT paste based on Pz26 (TF2100, Appendix A-1) which was bound by a substrate. This corresponds to improved densification due to the use of polyester sacrificial layer for avoiding constrained shrinkage. However, our printed disk still has lower k_p than that of the commercial bulk ceramic disk. The difference is mainly attributed to microstructures differences (see table 3.2, density part). The nature of electrodes (pure thin electrodes) may also impact the electromechanical properties as reported in [50]. A similar trend is noticed for Young's modulus. The Young's modulus of our printed-disk is more two times higher than the PZT disk sintered on epoxy-SrCO₃ layer. In addition to residual porosity, to be noticed that the thickness and Young's modulus values used in calculations introduce errors which could explain some differences from Young's modulus of the bulk ceramic.



Figure 3.21 Planar coupling factor of thin disk, where $f_p = f_a$ and $f_s = f_r$ due to $Q_m > 50$ [48]. To be noticed that the curve is valid for the piezoelectric materials which have Poisson's ratio (σ^E) in the range of 0.29-0.33 and Poisson's ratio of PZT is around 0.3 [51].

$$f_0^i = \frac{(2i-1)}{4L} \sqrt{\frac{E_{PZT}h_{PZT} + E_{Electrode}(h_{top \ Electrode} + h_{bottom \ Electrode})}{\rho_{PZT}h_{PZT} + \rho_{Electrode}(h_{top \ Electrode} + h_{bottom \ Electrode})}}$$
eq. 3.4

where f_0^i is the resonant frequency, *L* is the resonator length (for this case, it is equal to the diameter of the disk), *E* is Young's modulus, and *h* is thickness, The Young's modulus and density of Au electrode are 55 GPa and 18500 kg/m³ [35], respectively.

In summary, with screen-printing process and using polyester as the sacrificial layer, the freestanding PZT disks sandwiched between electrodes achieve to release from substrates during the co-firing. However, the Ag/Pd electrode gives more uniform surface compared to the Au electrode. Decreasing PZT particle sizes increases density of the disks. This leads to the improvement of electromechanical properties of the printed disk resonators.

	^a Bulk ceramic disk		Screen-printed disk					
			Sacrificial layer material					
			None	Epoxy-	Dxy-PolyesterCO3(This work)			
				SrCO ₃				
	PRYY		Sample	Sample	Sample	Sample	Sample	
			^{a,b} TF2100	A	A	В	В	С
	+	Pz26		with	with	with	with	with
	1113			Au	Au	Au	Ag/Pd	Ag/Pd
				electrode	electrode	electrode	electrode	electrode
Outer diameter (mm)	10	-	-	-	7.9	7.5	7.5	7.7
Total thickness (mm)	0.2	-	-	-	0.148	0.140	0.141	0.138
f_a (kHz)	-	-	-	-	262.599	275.202	331.174	318.356
f_r (kHz)	227	-	-	166 [49]	254.156	261.319	295.965	288.537
k_p	0.56	0.57	0.29	0.14 [49]	0.28	0.43	0.47	0.46
Young's modulus	-	95.6	70	36	^a 85	^a 103	-	-
(GPa)		[20]	[24]	[52]				

Table 3.7 Piezoelectric coefficients and Young's modulus of PZT disks

Remarks: f_a and f_r are the anti-resonant frequency and is the resonant frequency, respectively. For printed disk,

1. PZT density obtained from SEM images is used to calculate Young's modulus of the disks sandwiched between Au electrodes.

2. Young's modulus of the disks with Au can be calculated, but one with Ag/Pd electrodes cannot be calculated because we do not have information on Ag/Pd Young's modulus.

For commercial disk,

1. ^aThe commercial material, ^bthe bound film (commercial Pz26 paste for screen-printing) onto substrate, their information comes from their datasheets.

Piezo components of PRYY+1113 are made of ferroelectric hard piezo material (PIC181). Its datasheet presents the coupling coefficients in radial mode. The actual value can deviate by ±5% (below 2000 kHz) or ±10% (from 2000 kHz).

3.4 Study on characteristics of PZT cantilever transducers

According to Section 3.1.3, PZT pastes (B and C) with ceramic compound of PZT powder (particle size $< 1 \ \mu$ m) and 3 wt.% LBCu sintering aid (Li₂CO₃:Bi₂O₃:CuO in a ratio of 26.7:40.0:33.3) give printed PZT disks with almost similar properties. Therefore, they are fabricated into cantilever forms. An example of 3D-thickness profiles of the PZT cantilever with Au electrodes before sintering is shown in Figure 3.22. Photographs of sintered PZT cantilevers with different geometries and different electrode materials are presented in Figure 3.23



Figure 3.22 3D-thickness profiles of the PZT cantilever (6×1×0.1 mm³) with Au electrodes before sintering.



Figure 3.23 Photographs of some sintered PZT cantilevers (a) the varied geometries of the cantilevers with Au electrodes (Paste B), (b) comparison between cantilevers (Paste B) sandwiched by different electrodes (Au and Ag/Pd electrodes), and (c) comparison between cantilevers fabricated from Paste B and Paste C. To be noticed that in order to achieve polarization, the bottom Au electrode are twice repeatedly printed, but the bottom Ag/Pd electrode are thrice repeatedly printed.

According to Figure 3.23(a), for Au electrode and PZT paste B, the smallest cantilever $(3 \times 1 \times 0.1 \text{ mm}^3)$ presents cracking at a 4-overlaid-layer area (PZT/Au/PZT/Au layers). This area impedes electrical poling of the cantilever. However, other cantilever sizes do not show any open-circuit on the electrode. In case of the smallest cantilever with Ag/Pd electrodes, the structures have continuity on the electrode area (Figure 3.23(b)). Therefore, these defects are mainly due to higher CTE differences between PZT and Au compared to Ag/Pd.

In addition, for Paste C, all fired cantilevers are completely cracked as shown in Figure 3.23(c). This is due to higher shrinkage of the PZT occurring during sintering correlated to the uniformly finer PZT particle size. Grall [53] reported that a decrease in heating rate (10° C/min instead of 40° C/min) during the sintering process could decline this problem. However, we have chosen in this work to maintain the same conditions for PZT sintering. Consequently, only the cantilevers with Paste B are further characterized in the next section.

Observation of morphology and shrinkage of the sintered cantilevers is done by the method studied for the PZT disks. Electromechanical properties of the cantilever are still measured by the Agilent E5063B network analyzer.

3.4.1 Releasing of PZT cantilevers from substrates

Free-standing sintered PZT cantilevers are presented, as shown in Figure 3.24(a). An example of cross-sectional area of sintered PZT cantilever is shown in Figure 3.24(b). The interface between Au electrode and PZT layers is continuous. This result is opposite to the PZT disk showing discontinued interface. The cantilever structure has smaller area touching sacrificial layer compared to the disk structure. Moreover, one side of the cantilever is bound up with the substrate. These
make it easier releasing of the free end cantilevers compared to the disk structure. Curvature (socalled bulking of the micro-beams) of the free-end area of cantilevers is corresponded to asymmetry in material shrinkage and clamping part bound to the substrate. The thicknesses of constituting layers of the cantilever are shown in Table 3.8. The thickness of the Au bottom electrode is higher than those of the Au top electrode because two layers of the Au bottom electrode are screen-printed. These two layers are necessary to avoid electrical discontinuity due to partial Au dissolution with polyester sacrificial layer.



(a)

(b)

Figure 3.24 (a) Examples of the sintered Au/PZT/Au cantilevers with two different geometries ($6 \times 1 \times 0.1$ mm³ and $3 \times 1 \times 0.1$ mm³) and (b) SEM image of cross-sectional area of the movable part of PZT cantilever ($6 \times 1 \times 0.1$ mm³).

Table 3.8 Thickness of each layer assembling as movable part of the PZT cantilever after sintering

Layer	Thickness (µm)				
	Before sintering (µm)*	Sintered specimen (µm)**			
Anchor	23	No measurement			
Polyester sacrificial layer	23	-			
Au Top electrode	11	11			
PZT cantilever	124	102			
Au Bottom electrode	28	25			

Remarks: *measurement by 3D profilometer, and **obtained from Optical microscope photos

Table 3.9 presents the lateral shrinkage of cantilevers with different geometries. Short cantilevers have more shrinkage than long cantilevers. This result is similar to Grall's work [16] explaining that a shorter cantilever via a smaller contact area between cantilever and sacrificial layer leads to ease of separation between them during firing. According to Table 3.8, the thickness shrinkage of PZT layer is around 17% for all cantilevers.

Table 3.9 The lateral shrinkage of cantilever with different geometries

Cantileve	Shrinkage	
Length (mm)	Width (mm)	(%)
6	1	13
6	2	12
3	1	16
3	2	16

3.4.2 Electromechanical properties

In order to characterize electrical properties, the PZT cantilevers are connected with wires (Figure 3.25) and polarized as mentioned in Section 3.3.2 before measuring electromechanical and dielectric properties by the network analyzer. Figure 3.26 shows examples of the conductance and susceptance as a function of the frequency for in-plane 31-longitudinal vibration mode. The resonant frequency (f_0) can be extracted from a conductance spectrum at the highest peak. The mechanical quality factor (Q_m), mass sensitivity (S_{th}), and limit of detection (LOD) can be calculated from equations 3.5, 3.6, and 3.7, respectively [16], [53].

$$Q_m = f_0 / (f_2 - f_1)$$
 eq. 3.5

where Q_m is the mechanical quality factor, f_1 and f_2 are highest and lowest peaks received from the susceptance spectra.

$$S_{th} = -f_0/2m \qquad \qquad \text{eq. 3.6}$$

where *m* is cantilever mass.

$$LOD = 3\sigma/S_{th}$$
 eq. 3.7

where σ is the standard deviation of the resonant frequency. In this work, σ is evaluated in the range of 20-40°C and 50%rH for an hour of each temperature and the mean is then calculated.



Figure 3.25 Example of PZT cantilever connected to wires.



Figure 3.26 (a) Conductance and (b) susceptance as a function of frequency of the PZT cantilever with Au electrodes (length×width×thickness: $6 \times 1 \times 0.1 \text{ mm}^3$).

Table 3.10 presents effect of cantilever geometries and electrode materials on properties of the PZT cantilevers. The maximum and minimum of mass sensitivity are obtained from the 3×1-cantilever (\approx 44.2 Hz/µg) and 6×2-cantilever (\approx 6.8 Hz/µg), respectively. These results are related to the cantilever mass. The cantilever with lower mass has higher sensitivity. In addition, PZT cantilevers with Ag/Pd electrodes are also fabricated (3×1×0.1 mm³). However, the obtained cantilever cannot be polarized with a two-layer printing of both top and bottom electrodes. Thus, three electrode layers are printed. Then, the obtained cantilever can be polarized. It gives the higher resonant frequency (289.455 Hz), higher Q_m (\approx 1100), and higher capacitance (\approx 300 pF) compared to the same cantilever size with Au electrodes. Figure 3.27 presents the admittance circles of the PZT cantilevers with different electrode materials. By comparison, the cantilever with Ag/Pd electrodes has bigger diameter than the one with Au electrodes. This is possibly related to lower mechanical losses due to less defects on Ag/Pd electrodes and the PZT layer matching between layers of the PZT and Ag/Pd electrodes, as mentioned in Section 3.3.1. Therefore, the PZT cantilevers with Ag/Pd electrodes are another interesting candidate for using in transducer technology. However, for VOCs detection application, the cantilever with Au material is still chosen to be electrodes because of its chemical stability and possibility of grafting for bio-applications.

	C	Cantilever geometries: Length (mm) ×Width (mm)					
Parameter		Au ele	ctrodes		Ag/Pd electrodes		
	6×1	6×2	3×1	3×2	3×1		
f_r (kHz)	144.284	143.633	236.754	233.149	289.455		
Q_m	460	380	660	610	1100		
PZT information							
• Length (µm)	5404.50	5034.18	2517.09	2505.85	-		
• Width (µm)	843.50	1628.71	932.29	1707.33	-		
• Thickness (µm)		1	02		-		
• Density (kg/m ³)		72	200		-		
• PZT mass (mg)	3.35	6.02	1.72	3.14	-		
Au information							
• Length (µm)	5121.37	4899.33	2404.72	2393.48	-		
• Width (µm)	596.05	1404.06	595.32	1448.91	-		
• Thickness (µm)		3	36		-		
• Density (kg/m ³)		18	500		-		
• Au mass (mg)	2.03	4.58	0.95	2.31	-		
Total mass, <i>m</i> (mg)	5.38	10.60	2.67	5.45	-		
S_{th} (Hz/µg)	13.4	6.8	44.2	21.4	-		
σ(Hz)			1		-		
LOD (ng)	224	441	68	140	-		
C_p (pF)	400	1000	200	600	300		
Er	1600	1700	1600	2000	2100		

Table 3.10 Electromechanical and dielectric properties of cantilevers with different geometries

Remarks:

1. The cantilevers are connected to Ag wires (diameter = 100 μ m) for polarization and characterization with network analyzer at -45 dBm for f_r and Q_m , measurements and at 0 dBm for C_p and ε_r measurements, where dBm is the power ratio expressed in decibels (dB) with reference to one milliwatt (mW).

2. Density of Au and PZT layers are from Grall's et al. [16] because we use the same screen-printing pastes.



Figure 3.27 The admittance B(G) circles of the $3 \times 1 \times 0.1$ mm³ PZT cantilevers with different electrode materials.

In summary, the highest mass sensitivity of the printed PZT cantilever with Au electrodes is obtained from the $3\times1\times0.1$ mm³ geometry. However, with inappropriate firing condition, most of this cantilever size have the open-circuit due to cracking of the PZT layer. Moreover, its area is too small to drop sensing material by hand. Consequently, the wider cantilevers ($3\times2\times0.1$ mm³) with acceptable sensitivity are selected to be used as transducers for VOCs detection in Chapter 4.

3.5 Conclusions

In this chapter, screen-printing thick film process associated with sacrificial layer technique has been used to fabricate PZT disks sandwiched between electrodes. The influence of two commercial electrodes with different compositions (Au and Ag/Pd pastes) and the PZT particle sizes on processing and electromechanical properties has been studied. The PZT disks have been successfully released during the co-firing by using the polyester sacrificial layer. The solvent incompatibility between the Ag/Pd electrode and the sacrificial layer pastes has resulted in the uniform releasing. The surface electrode is more uniform compared to the Au electrode. The decrease of the PZT particle sizes from micro- to nano-scales by planetary miller or attritor, and the use of the LBCu sintering aids (Li₂CO₃:Bi₂O₃:CuO in a ratio of 26.7:40.0:33.3) have developed microstructural packing and decreased the residual porosity ($\approx 6\%$). Improved dielectric and electromechanical properties of the PZT disks have been obtained. The highest values of k_{eff} and ε_r of the PZT disks with Ag/Pd electrodes and PZT paste B approach the values of the commercial Pz26 ceramic. The effective fabrication process has been demonstrated for disk preparation which could be applied to sensing, actuating, and Structural Health Monitoring (SHM) systems. This fabrication with the same process conditions is also extended to the fabrication of resonant cantilevers for gravimetric applications such as gas and particles sensing. The small cantilever gives higher mass sensitivity compared to the bigger sizes. The cantilevers in size of $3 \times 2 \times 0.1$ mm³ are chosen to be used as transducers in VOC detection due to its satisfied properties and its appropriate size for drop casting of sensing material.

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CHAPTER 4: PZT cantilever transducers with functionalized MCF sensing layer for VOCs detection

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This chapter presents the application of the PZT cantilever transducers for VOCs detection. Functionalized MCF-Si is synthesized and applied as a sensing layer. Thus, the first section of this chapter will explain how to synthesize and functionalize the MCF-Si. Then, effects of temperature, humidity, and VOCs on shifts of the blank transducers are observed and used as references. Finally, influences of temperature, humidity, and VOCs on the PZT cantilever transducers with functionalized MCF-Si are studied. Note that results concerning characterization of MCF-Si have been published in Solid State Phenomena [1].

4.1 Preparation of functionalized MCF-Si sensing material

4.1.1 Introduction

In this thesis, mesocellular foam silica (MCF-Si) is synthesized by sol-gel method of a hydrothermal process. The fundamental procedures of such method are as follows [2], [3], [4]:

- Firstly, surfactants are dissolved in aqueous solution.
- Secondly, swelling agents are added and dissolve in oil-in-water micelles. The added oil swells out surfactant chains until saturation, and then pure oil cores are formed at the center of micelles. To cover the oil droplets with minimum amount of surfactant chains, the micelles become more spherical.
- Thirdly, silicate sources are added into the solution where they undergo hydrolysis catalyzed by an acid catalyst and transform to a sol of silicate oligomers. As a result of the interaction between these oligomers and surfactant micelles, cooperative assembly and aggregation provide precipitation from a gel. During this steps, micro-phase separation and continuous condensation of silicate oligomers occur [2].
- Then, the gel is treated hydrothermally for further condensation, solidification and reorganization of the material to an ordered arrangement [2], [3], [4].
- Finally, after certain time the resultant product is cooled, filtered, washed and dried. Ordered mesostructured silica material is obtained from this as-synthesized solid after the removal of surfactant through solvent extraction or calcination.

Basically, chemical structure of MCF-Si contains a high concentration of silanols (Si-OH). The surface silanol groups can be in various forms as shown in Figure 4.1(a). The silanols cause a decrease of VOCs adsorption owing to their hydrophilic behavior. Consequently, functionalized MCF-Si by hexamethyldisilazane (HMDS) is prepared in order to improve hydrophobicity and VOCs sensitivity. The chemical reaction between MCF-Si and HMDS is written from one of widely basic forms presented in Figure 4.1(b). The next section describes the experimental procedure in this work.



Figure 4.1 Schemes for (a) surface functional groups of silica (adapted from [5]) and (b) the reaction of MCF-Si with hexamethyldisilazane (HMDS) and chemical structure of the HMDS functionalized MCF-Si (Adapted from [6]).

4.1.2 Synthesis of HMDS functionalized MCF-Si

A. Preparation of MCF-Si material

The chemicals used in this part are presented in Table 4.1. MCF-Si is synthesized according to Thananukul *et al.* [7] which begins from dissolving of 2 g of Pluronic P123 in 75 mL of 1.6 M HCl under stirring at 35-40°C for 1 hour to get a transparent solution. Then, 5 g of TMB is added, and the stirring is kept for another 2 hours before 4 g of TEOS is added. The mixture is stirred for 5 more minutes at the same temperature. After that, the resulted mixture is left standing in a Teflon bottle at 40°C for 20 hours; then, the temperature is raised to 100°C and kept for 24 hours. The precipitates are filtrated and washed with 50 mL ethanol followed by 50 mL deionized water. The obtained material is consecutively dried at room temperature for a day and at 60°C for 1 hour. In order to remove the surfactant template, ethanol extraction is done by refluxing 1.5g MCF-Si with a mixture of 100 mL ethanol and 1 mL concentrated HCl for 24 h at 90°C using a soxhlet extractor. The schematic synthesis of MCF-Si is shown in Figure 4.2.

Function	Chemical name	Abbreviated name	Manufacture
Triblock copolymer	poly(ethylene oxide)-	Pluronic P123	BASF
surfactants (as a	poly(proplylene oxide)-		
template)	poly(ethylene oxide) with		
	PEO20PPO70PEO20 formula		
Silica source	Tetraethoxysilane (98%)	TEOS	Sigma-Aldrich
Swelling agent (oil)	1,3,5- Trimethylbenzene	TMB	Suspelco
Catalyst	Hydrochloric acid	HCl	J.T. Baker
Solvent for extraction	Ethanol	-	Sigma-Aldrich

Table 4.1 Chemicals for preparation of MCF-Si



Figure 4.2 A schematic synthesis of MCF-Si (Adapted from [8] and [9]).

B. Functionalization of MCF-Si with HMDS

MCF-Si (0.5 g) is added into a 3-round neck bottle flask, and is heated to 573 K for 1 h. Then, the system is cooled down to room temperature before a 2-hour humidity evacuation at constant temperature by a vacuum pump. After 2 h at constant temperature, Nitrogen gas is next purged through the flask for 30 minutes. 20 mL of anhydrous toluene with HMDS (99.9%, Aldrich) are prepared. The mixture of HMDS-toluene is injected into the MCF-Si contained flask at varied HMDS:MCF-Si (molar ratios from 0.05-0.20). The material contained flask is warmed again at 383 K for 3 h. Finally, functionalized materials are taken out and are washed with anhydrous toluene before drying at room temperature. The experimental setup is shown in Figure 4.3 Valve 1 is connected to a nitrogen gas tank, Valve 2 is free for outing gas and adding chemicals, and Valve 3 is connected to the vacuum pump. The gas flow in this system can be controlled by these three valves. A schematic diagram of the functionalization procedure is illustrated in Figure 4.4.



Figure 4.3 A schematic diagram of experimental setup for preparation of HMDS functionalized MCF-Si (humidity evacuation step).



Figure 4.4 A schematic diagram for preparation of HMDS functionalized MCF-Si.

4.1.3 Characterization

A. Physical and chemical characteristics

Pristine MCF-Si and the HMDS functionalized MCF-Si are characterized by various tecniques. TGA (Mettler Toledo, TGA/SDTA 851) is used to observe the adsorbed water. FTIR (Perkin Elmer 1760x) is used to study chemical structures. Nitrogen gas adsorption (Quantachrome autosorb-1) is used to observe pore characteristics. The surface areas and pore volumes of synthesized materials are analyzed by Brunauer-Emmett-Teller (BET) [10] and Barrett-Joyner-Halenda (BJH) [11] models, respectively. While the pore and window size analyses are conducted from the adsorption–desorption isotherms using Broekhoff-de Boer-Frenkel-Halsey-Hill (BdB-FHH) model [12]. Field emission scanning electron microscopy (FE-SEM; JEOL JSM7800F Prime) and TEM (JEOL JEM-2010) are used to study respectively microstructure and nanostructure, of the materials.

B. Benzene adsorption

• Preparation of benzene stock gas

In order to prepare the benzene stock gas, 0.728 ml of benzene solution is injected into a 10 liter Tedlar bag. The injected bag is allowed to reach equilibrium at room temperature for a week. With these procedures, the calculated concentration of the benzene stock gas is 20,000 ppmv.

• Testing of benzene adsorption

The pristine and HMDS functionalized MCF-Si are dehydrated in an oven at 100° C for 24 h. Then, 20 mg of each material is placed in 10 ml glass vials with septa caps. The required amount of benzene stock gas is drawn from the stock bag and is injected to the vials by a gas-tight syringe. The injected vials are shaken for 5 min before left standing at room temperature for 3 h. Finally, 20 μ l of the head-space gas within the vials is drawn using the gas-tight syringe in order to check the remained benzene concentrations by gas chromatography-mass spectrometry (GC-MS).

4.1.4 Results and discussion

SEM and TEM images of the pristine MCF-Si and HMDS functionalized MCF-Si powders are shown in Figure 4.5 and 4.6. Although HMDS grafted molecules on MCF-Si powders cannot be observed by these techniques, the obtained images reveal the maintained porosity with interconnected spherical pore structure of the MCF-Si powders after functionalization by HMDS.



Figure 4.5 SEM images of (a), (b) the pristine MCF-Si, and (c) HMDS functionalized MCF-Si with HMDS:MCF-Si ratio of 0.15.



Figure 4.6 TEM images of (a) the pristine MCF-Si, (b) the HMDS functionalized MCF-Si with HMDS:MCF-Si ratio of 0.15.

Figure 4.7(a) shows TGA curves of the pristine MCF-Si and the HMDS functionalized MCFs-Si powders. At the dehydration step (between 0-200°C), the pristine MCF-Si powder shows the highest amount of water molecules adsorbed on the surface. The different HMDS functionalized MCF-Si powders present a significant decrease of the water contents, as shown in Table 4.2. In the HMDS:MCF ratio of 0.15, the sample shows the lowest water adsorption. It implies that the optimized ratio of HMDS is 0.15 with the highest improvement of the materials hydrophobic behavior.

Considering the weight losses in the high temperature range (200-800°C), the decomposition of the HMDS changes nearly in line with the rising ratio of the HMDS:MCF. The sample with the maximum amount of the HMDS functionalized (HMDS:MCF ratio of 0.20) shows the largest weight loss in this high temperature range.



Figure 4.7 (a) TGA and (b) FTIR results of the pristine MCF-Si and the HMDS functionalized MCF-Si powders.

HMDS-MCE S:	Weight loss (%)			
HWIDS:WICF-SI	0-200°C	200-800°C		
Pristine	7.174	5.225		
0.05	4.883	7.432		
0.10	4.548	6.552		
0.15	2.703	10.150		
0.20	4.074	11.900		

Table 4.2 Weight loss at low and high temperature ranges for the pristine and functionalized MCFs-Si

The pristine MCF-Si and the HMDS functionalized MCF-Si FTIR spectra are shown in Figure 4.7(b). The silanol peak (Si-OH) of MCF-Si spectrum is at $\approx 3500 \text{ cm}^{-1}$. Their intensity steadily decreases with increasing concentration of the HMDS. Conversely, the peak of the trimethylsilyl (TMS) group (-Si-(CH₃)₃) at $\approx 1000 \text{ cm}^{-1}$ is not presented in the pristine MCF-Si, but moderately increases with HMDS concentration. These results indicate that the HMDS is successfully grafted on the surfaces of the MCF-Si with the increasing amount of TMS functional group by the risen ratio of HMDS:MCF-Si.

Figure 4.8 illustrates nitrogen adsorption-desorption isotherms of the pristine and the HMDS functionalized MCF-Si materials. All isotherms show the same characteristic of hysteresis loops correlating to mesoporous structure of all samples. These results support that the pore structure remains the same before and after functionalization. The analysis results of Nitrogen gas adsorption-desorption isotherms of the MCF-Si materials are expressed in Table 4.3. The decreases of BET surface areas and the BJH pore volumes with increasing HMDS ratio are observed. However, the pore sizes and the window sizes have not significantly changed after functionalization. Considering the HMDS:MCF-Si ratio of 0.20 with the biggest pore size, this is likely due to the inhomogeneity of the pristine MCF-Si itself which is not as a consequence of the HMDS functionalization [7].



Figure 4.8 Adsorption-desorption isotherms of the pristine MCF-Si and the HMDS functionalized MCFs-Si.

HMDS:MCF	BET Surface Area (m²/g)	BJH Pore Volume (cc/g)	BdB-FHH Pore Size (nm)	BdB-FHH Window Size (nm)
Pristine	622	1.070	6.56	5.51
0.05	560	0.914	6.56	5.44
0.10	532	0.917	6.45	5.59
0.15	484	0.906	6.59	5.53
0.20	437	0.901	7.48*	5.50

Table 4.3 Physical characteristics of the pristine and functionalized MCFs-Si

Remark * This point is probably an error measurement.

Figure 4.9 shows benzene adsorption of MCF-Si functionalized with different HMDS ratios. It exhibits a little improvement in ability to adsorb benzene vapor after functionalization with all HMDS ratios. The highest benzene adsorption appears with the HMDS ratio of 0.15. Considering the high error bar, the benzene sorption properties of the functionalized MCF-Si with the HMDS ratio of 0.20 is assumed that its sorption is quite similar to the functionalized MCF-Si with the HMDS ratio of 0.15. This is probably because they have similar pore volume as shown in Table 4.3. However, the best benzene sorption capacity fits well with the TGA result (Figure 4.7(a)) which shows the lowest amount of adsorbed water with the 0.15 ratio. Thus, the ratio of 0.15 is selected for further experiments under vapors.



Figure 4.9 Percentages of benzene adsorption by MCF-Si at various ratios of HMDS:MCF-Si.

4.1.5 Conclusions of preparing sensing material

Although, the functionalization of MCF-Si with HMDS drops the surface area and pore volume of the modified materials, the pore and window sizes of all functionalized MCF-Si is stable compared to the pristine MCF-Si. After three hours of benzene adsorption test, the residual benzene concentrations are analyzed by the gas chromatography-mass spectrometry (GC-MS). The amount of the benzene adsorbed is improved by the functionalization. The highest benzene adsorption of the HMDS functionalized MCF-Si is at the HMDS:MCF-Si ratio of 0.15. This indicates that the HMDS functionalized MCF-Si could be used as a sensing material for benzene detection.

4.2 Acquisition devices for environmental and VOCs detection

Two different acquisition devices, which are an open cell and a closed cell are used for distinct purposes in this work. The open cell allows to study influences of various environment conditions (temperature and relative humidity) on the sensor behavior. While, the closed cell is exploited to observe the sensor responses under low concentration of water vapor and VOCs.

4.2.1 Open cell

The sensor assembled in this cell is allowed to be exposed to various environmental conditions. The cell contains two polylactic acid (PLA) parts for being a sample holder and a printed circuit board (PCB) support. This PCB holds the electric contact pins and subminiature coaxial connectors version B (SMB) for connecting to the network analyze. The contact pins are spring-mounted with the fixed height of the sample holder allowed to adapt the stable pressure of the pins on the sample. The cantilever sensor is placed on the bottom PLA part overlaid with the top PLA part and the PCB, respectively. These three components are conjugated together with screws. However, the used wires for connecting between the acquisition device and network analyzer are quite heavy and high compared to the open cell. Therefore, the open cell need to be fixed on the metal plate before connecting wires to the network analyzer (Figure 4.10). The overall connection is presented in Figure 4.11.



Figure 4.10 The assembled acquisition device for the open cell: (a) schematic diagram, (b) photograph, (c) separated components, and (d) the assembled acquisition device with the metal plate.



Figure 4.11 A schematic diagram of overall connection of the open cell, Agilent E5063B network analyzer, and the recorder (laptop).

4.2.2 Closed cell

The sensor assembled in this closed cell (volume of $\approx 17 \text{ cm}^3$) is allowed to be exposed to the target vapor flowing through the cell by inlet and outlet pipes (Figure 4.12). The cell contains a polytetrafluoroethylene (PTFE) chamber for controlling vapor path, and the printed circuit board (PCB) holding and connecting the sensor thanks to the silver wires (diameter 150 µm). The PCB is dig with the deepness of 1 mm with the length and width of 12.7 mm each for putting the sensor. The circuit is linked with the electrical cable type plugged in conjugated towards the banana plug for connecting to the network analyzer by wires, as shown in Figure 4.13. The cell is finally connected to the network analyzer, as shown in Figure 4.14.



Figure 4.12 A schematic diagram of the side view of the closed cell.



(b)

Figure 4.13 PZT cantilever sensor integrated with the PCB (a) components, and (b) constructed cell and its connection.



Figure 4.14 A schematic diagram of overall connection of the cell for using under gas flow, Agilent E5063B network analyzer, and the recorder (laptop).

4.3 Sensing system set up

Two different machines are exploited to generate various conditions for studying the response of the PZT cantilever sensor. The artificially environmental conditions with distinct temperature and relative humidity are done by Climate EXCAL chamber. While, the low concentration values (in ppmv level) of the target vapor are done by the vapor generator PUL110. The ambient temperature in this case is controlled by an air conditioner. Their system and connection are explained in this part.

4.3.1 Sensing system connecting with Climate EXCAL chamber

The $3\times2\times0.1$ mm³-cantilever sensor is linked with the network analyzer for monitoring the resonant frequency by using an open cell as mentioned in section 4.2.1. This system is placed in Climate EXCAL 1411-HE chamber (Figure 4.15) for studying effects of temperature and relative humidity on the resonant frequency of the cantilever sensor. The Climate EXCAL can generate various static conditions by heating water in a big water bath. Air circulation in a chamber is flown by a high temperature fan. Air is drawn in and conditioned in the technical compartment then sent back into entire test volume. This solution leads to homogeneity on temperature and humidity treatments within the chamber. The overall sensing connected with the Climate EXCAL is shown in Figure 4.16.



Figure 4.15 Climate EXCAL 1411-HE chamber.



Wires for transferring electrical signals from the cantilever towards the network analyzer

LaptopNetwork analyzerClimate EXCAL chamberThe constructed acquisition deviceFigure 4.16Photographs of the sensing system for testing in Climate EXCAL chamber.

4.3.2 Sensing system connecting with PUL110 vapor generator

Figure 4.17(a) shows the vapor generator (Calibrage, PUL110) which is used to generate the target vapor in ppmv level. This equipment heats a cylinder container filled with liquid of desired analyte. A constant flow rate of nitrogen (100 mL/min) is used as a carrier of evaporated vapor. This corresponds to the initial concentration of the taken vapor. Then, the taken vapor is diluted by the nitrogen gas in order to make the different vapor concentrations, as shown in Figure 4.17(b). The overall of the sensing system connected with the vapor generator (PUL110) is shown in Figure 4.18. The PZT sensor linked with this system is operated at room temperature ($\approx 20^{\circ}$ C) via the air conditioner. However, the vapor temperature and humidity need to be monitored by a thermometer/hygrometer. Indeed, the sensor is sensitive to these environmental effects (temperature and humidity) that will be removed from the raw results before calculation of the sensitivity as it will be shown in Section 4.5.1 (eq. 4.8).



(b)

Figure 4.17 (a) The vapor generator (Calibrage, PUL110): (a) photographs and (b) schematic diagram.



Figure 4.18 Photographs of the overall of sensing system connected with the vapor generator (PUL110).

Figure 4.19 presents the flow charts of the vapor pathway and used element analyzers for studying the responses of the PZT sensor. For water vapor, the sequences concentration values flows through the cell containing the PZT sensor and thermometer/hygrometer at room temperature (20°C) before emitting to the environment. However, in the case of VOCs, a Figaro gas sensor (model of TGS 2602 connected with SR-D1A, Appendix B-3) is added for confirming that VOCs is flowing in the system. This commercial sensor needs air flow for operation whereas this work uses nitrogen gas as a carrier. Thus, the obtained parameters from Figaro sensor only allow to observe the tendency of VOCs flow. They do not reflect the accurate concentration of VOCs (an example of this sensor response is presented in Appendix B-3).



Figure 4.19 Flow chart of sensing connection for target vapor detection by PUL110.

4.3.3 Set conditions and recording

A. Studying environment effect

• Temperature effect

Five different temperatures are generated by the climate EXCAL in order to study the effect of temperature on the uncoated cantilever behavior. This experiment is done with a constant relative humidity of 50%.

• Humidity effect

The changes of the relative humidity from 40% to 90% are generated by the climate EXCAL in order to study the effect of (high) humidity on the uncoated and coated cantilever behaviors. This experiment is done at a stable temperature of 25° C.

B. Studying water vapor and VOCs effects

The effects of low humidity level of water vapor (< 15% relative humidity, rH) and VOCs in ppmv levels on the PZT sensor are observed at room temperature ($21\pm1^{\circ}$ C). However, the vapor generation is done by heating the target solution at different temperatures. They are set at around 20-30°C lower their boiling point (Table 4.4). Each concentration is generated and monitored for 30 min. An initial mass and a calculation of an initial vapor concentration for each vapor are illustrated in Appendix B-4.

	Benzene Toluene		Ethanol	Deionized water
General characteristic				
Grade	HPLC, 99.9%	HPLC, 99.9%	HPLC	-
Manufacture	Sigma-	Aldrich	Merck	
Boiling point (°C)	80	110	78	100
Vapor pressure at 20°C (mmHg)	74.6	22	44.3	17.5
Experiment condition				
I. Generated vapor temperature (°C)	50	80	60	80
- Initial concentration (ppmv)	2947	2945	8006	15097
- Vapor concentration range (ppmv)	8-1487	8-1472	21-4003	38-7548
II. Generated vapor temperature (°C)	60	-	-	-
- Initial concentration (ppmv)	4081	-	-	-
- Vapor concentration range (ppmv)	11-2023	-	-	-

Table 4.4 Organic solvents and set temperature for generating the target vapors by PUL110

C. Recording

For all sensing systems, the acquisition data (conductance, G as a function of the frequency) is measured with the Agilent E5063B network analyzer for the in-plane axial longitudinal vibration mode at an actuation power of -15 dBm in order to decrease noise in spectrum (explained in Appendix B-5). One spectrum measurement takes 16 s. Then, the obtained data is recorded by Labview program (Figure 4.20) and are extracted using a polynomial fit with Matlab. The electrical model and significant equations for calculation of the polynomial fit are reported in Appendix B-2. Examples of the polynomial fit used for decreasing noise is shown in Figure 4.21 [13].



Figure 4.20 Labview program for recording of : (a) temperature and humidity (%rH) detected and analyzed by the thermometer/hygrometer and Arduino card, respectively and (b) G(B) data detected and analyzed by the PZT sensor and the network analyzer, respectively.



Figure 4.21 Examples of the polynomial fit used for decreasing noise in (a) the conductance peak, (b) zoom on the conductance peak (c) the resonant frequency spectra [13].

4.4 Loading HMDS functionalized MCF-Si on the PZT cantilever transducer

4.4.1 Loading procedure

A. Optimized concentration of sensitive material

In order to drop HMDS functionalized MCF-Si powder (in HMDS:MCF-Si ratio of 0.15) at the free-end of the PZT cantilevers, the powder of sensitive material needs to be dispersed in media with an appropriate concentration. Deionized (DI) water is used as the media in this procedure because it does not have interaction with this powder. Two different concentrations (50 mg/mL and 100 mg/mL) of HMDS functionalized MCF-Si suspension in DI water are prepared and dispersed by an ultra-sonic machine. Then, for first attempts, 2 μ L of each suspension is dropped on a broken cantilever (in the length×width of 4×2×0.1 mm³) obtained from Grall's work [13] by a micropipette (Gilson, model of MICROMAN M10E) with a ≈ 2 mm distance between the micropipette and the free-end cantilever. After drying in the oven at 80°C for 1 h, the distribution of powder onto cantilevers are observed by optical microscope, as shown in Figure 4.22. The suspension with 100 mg/mL looks smoother and with higher homogeneity. Therefore, this concentration is chosen for preparing the cantilever sensor in the next section.



Figure 4.22 Optical images of the HMDS functionalized MCF-Si drop coating on the $4 \times 2 \times 0.1 \text{ mm}^3$ Au/PZT/Au cantilever (a) 50 mg/mL and (b) 100 mL/min.

B. Drop casting on the real cantilevers

According to Chapter 3, the screen printed cantilever with the length×width×thickness of $3\times2\times0.1$ mm³ is selected to be exploited as a transducer in this work. Then, 100 mg of the HDMS functionalized MCF-Si powder is dispersed in 1 mL of the deionized water by the ultra-sonic machine. However, the used cantilever ($3\times2\times0.1$ mm³) is shorter than the trial cantilever ($4\times2\times0.1$ mm³). Thus, instead of 2 µL, only 1 µL of the suspension is dropped onto the $3\times2\times0.1$ mm³-cantilever. Finally, the droplet is dried in an oven at 80°C for 1 h. The cantilever transducer with HMDS functionalized MCF-Si is ready to be used as VOCs sensor. The mass of HMDS functionalized MCF-Si on the cantilever is measured by the microbalance after drying. Its value is around 50 µg. Photographs of the cantilever before and after coating with HMDS functionalized MCF-Si drop casting is revealed in Figure 4.23(a-c). SEM image of HMDS functionalized MCF-Si drop casting is revealed in Figure 4.23(e).



Figure 4.23 Images of (a) uncoated cantilever, (b) HMDS functionalized MCF-Si coated cantilever, (c) optical image of HMDS functionalized MCF-Si coated cantilever, and (d) SEM image of dropped HMDS functionalized MCF-Si on cantilever, (e) 3D thickness between anchor and coating areas.

4.4.2 Electrical characteristics of the uncoated and coated PZT sensor

A. Conductance measurements

This section focuses on comparing uncoated and coated cantilever sensors (in size of $3 \times 2 \times 0.1 \text{ mm}^3$). Each cantilever is placed in the open cell and is connected to the Agilent E5063B network analyzer at room temperature ($\approx 25^{\circ}$ C), as shown in Figure 4.11. For the longitudinal vibration mode, the conductance (*G*) is measured before and after loading of sensing material (HMDS functionalized MCF-Si). As can be seen in Figure 4.24(a), the additional mass of the sensing material leads to the decrease of the resonant frequency from 257050 Hz to 255719 Hz ($\Delta f_0 \approx 1331$ Hz). Moreover, the quality factor (*Q*) of the PZT cantilever sensor downshifts by ≈ 157 . However, the obtained conductance spectrum after loading the sensing material is still enough to be used as the cantilever sensor with $Q \approx 210$. These behaviours were found with a longer cantilever with PEUT coating in previous work of our team (Figure 4.24(b)) [14].



Figure 4.24 Effect of sensitive coating deposit on conductance response of PZT sensors (a) the $3 \times 2 \times 0.1 \text{ mm}^3$ cantilevers measured with electrical power of -15 dBm (this work), and (b) the $8 \times 2 \times 0.1 \text{ mm}^3$ cantilevers of previous work at IMS laboratory [14].

B. Gravimetric sensitivity

The gravimetrically experimental and theoretical sensitivity values of the cantilever sensors are defined with the eq. 4.1 and 4.2 [13], where *m* is the cantilever mass, Δm is the additional mass deposited uniformly on the cantilever, f_0 is the resonant frequency of uncoated cantilever, and Δf_0 is the resonant frequency shift after loading the sensing material.

$$S_{ex} = \Delta f_0 / \Delta m$$
 eq. 4.1
 $S_{th} = -f_{0,\text{uncoated cantilever}} / 2 m$ eq. 4.2

The experimental sensitivity can be directly obtained from a change of the resonant frequency and after loading sensing material (
$$\Delta f_0 \approx 1331 \text{ Hz}$$
), and the additional mass is the mass of the sensing material ($\Delta m \approx 50 \mu g$). For the theoretical sensitivity, $f_{0,uncoated cantilever}$ is the experimental value of the uncoated cantilever (257050±1 Hz) and *m* is the calculated value of the uncoated cantilever (257050±1 Hz) and *m* is the calculated from eq. 4.4 [15]. Table 4.5 presents factors used in calculation. The calculated mass of the cantilever is around 5.45 mg. Table 4.6 sums up the experimental and theoretical values of mass sensitivity (*S*) and the limit of detection (*LOD*) of the PZT cantilever. Slight differences are obtained probably due to errors in practical measurements of mass and frequency. Moreover, the sensing material is not covered on all of free-end area of cantilever (Figure 4.23).

$$m_{total} = m_{PZT} + m_{Au} = \rho_{PZT} V_{PZT} + \rho_{Au} V_{Au}$$
eq. 4.3

where ρ is density, and V is volume.

$$LOD = 3\sigma/S$$
 eq. 4.4

where σ is the standard deviation of the resonant frequency.

Constituting layer's cantilever	ρ (kg/m ³)	L (µm)	W (μm)	t _{total} (µm)	V (m ³)	<i>m</i> (mg)
PZT	7200	2506	1707	102	4.36×10 ⁻¹⁰	3.14
Au	18500	2393	1449	36	1.25×10 ⁻¹⁰	2.34
Calculated cantilever mass						5.45

Table 4.5 The physical characteristics of the coated PZT cantilever

Remark: Density (ρ) of PZT and Au are from [13].

Table 4.6 The gravimetric sensitivity of the PZT cantilever

Contilouor turo	Experime	ntal value	Theoretical value	
Canthever type	Sex (Hz/µg)	LOD _{ex} (ng)	S_{th} (Hz/µg)	LOD _{th} (ng)
PZT cantilever ($L \times W \times t$: $3 \times 2 \times 0.1 \text{ mm}^3$)	27	110	24	125
	1 4 4 15			

Remark: The resonant frequencies are measured at -15 dBm.

4.5 Effect of environment on the PZT sensor

In real workplace conditions, the environmental factors possibly affect the operation of cantilever transducers. According to previous experiments [15], [16], the uncoated PZT screen-printed cantilevers were sensitive to temperature and humidity. In practice, one more cantilever sensor should be in parallel connection to VOCs sensors for monitoring environmental effect during VOCs detection. For this experiment, the responses of PZT cantilever sensors to temperature and humidity are observed in order to receive their compensated values for analyzing VOCs detection in Section 4.6.

4.5.1 Temperature effect

A. Results

The responses of the uncoated PZT cantilever sensor under different temperatures are investigated at a fixed relative humidity. Figure 4.25(a) illustrates the response of the PZT cantilever sensor in the range of 20-40°C at the relative humidity of 50%. The results show that increasing the ambient temperature decreases the resonant frequency. A linear decrease is obtained from plotting the resonant frequency shifts as a function of the temperature. Its slope is the temperature sensitivity of the cantilever ($\approx -23\pm5$ Hz/°C), as shown in Figure 4.25(b).



Figure 4.25 The $3 \times 2 \times 0.1$ mm³ cantilever transducer's response under different temperatures at relative humidity of 50% (a) the resonant frequency at different temperatures, and (b) the resonant frequency shifts as a function of temperature (test with the Climate EXCAL as mentioned in Section 4.3.1).

B. Discussion

These resonant frequency changes are due to temperature dependence of cantilever material's properties. Theoretically, the resonant frequency of the cantilever sensor depends upon values of Young's modulus of elasticity (*E*), length (*L*), thickness (*h*), and density (ρ) of cantilever's constituting layers as represented in eq. 4.5-4.6 [15]. As a result, the resonant frequency varies with the temperature because of the thermal expansion and Young's modulus variation (eq. 4.7) [17]. The increase of ambient temperature contributes to stiffness dropping [18] and expansion of the cantilever sensor. However, influence of the thermal expansion is very low compared to the Young's modulus effect. The values of coefficient of thermal expansion (α) and temperature coefficient of Young's modulus (α_E) of the PZT material are approximately 6 ppmv/°C and -200 ppmv/K, respectively [19], [20], [21]. Thus, the thermal expansion effect can be neglected [15].

$$f_{0,31}^{(n)} = \frac{(2n-1)}{4L} \sqrt{\frac{E}{\rho}}$$
eq. 4.5

$$f_{0,31}^{(n)} = \frac{(2n-1)}{4L} \sqrt{\frac{E_p h_p + E_{Au}(h_{top Au} + h_{bottom Au})}{\rho_p h_p + \rho_{top Au}(h_{top Au} + h_{bottom Au})}}$$
eq. 4.6

where $f_{0,31}^{(n)}$ is the resonant frequency, p is the PZT layer and Au is the gold electrode layer.

$$\frac{\delta f_0}{f_0} = \frac{\alpha + \alpha_E}{2} \,\delta T \tag{eq. 4.7}$$

Instead of using the absolute temperature sensitivity, calculation of the relative temperature sensitivity $S_{ppmv^{C}}$ can be done by eq. 4.8 in order to compare with previous works.

$$S_{ppm/^{\circ}C} = (S_{Hz/^{\circ}C}/f_{0,ref}) \times 10^{6}$$
 eq. 4.8

where $S_{ppmv/^{\circ}C}$ is the relative temperature sensitivity in ppmv/^{\circ}C unit, $S_{Hz/^{\circ}C}$ is the absolute temperature sensitivity in Hz/°C, and $f_{0,ref}$ is the resonant frequency at lowest temperature used in the experiment (20°C)

According to Table 4.7, the different geometries of the PZT thick film sensors present almost similar values of the temperature sensitivity with film's fabrication onto the same kind of sacrificial layer material (polyester) [16]. A PZT film bound on the alumina substrate as in Ferrari's work gave also similar sensitivity [22]. However, in comparison with the PZT thick film sensors of Lakhmi [15], the observed difference may be due to the differences in experimental conditions and material properties (with higher porosity).

Geometry	Resonant frequency	Temperature sensitivity Hz/°C ppmv/°C		Experimental cor	Source	
(L×W×t) mm ³	(KIIZ)			Temperature (°C)	rH (%)	
PZT cantilever sensors sandwiched between Au electrodes (free-standing on alumina substrate)						
1×1×0.1	660	-47	-71	25-45	60	[16]
3×2×0.1	257	-23±5	-90±19	20-40	50	This work
8×2×0.1	70	-9	-130	19-25	None	[15]
PZT thick film resonant pressure sensor in disk form (bound on alumina substrate)						
None	58	None	-70	None	None	[22]

Table 4.7 The absolute temperature sensitivity of the uncoated PZT cantilever sensors

Remark: rH is the relative humidity.

In addition, the temperature dependence of resonant sensors can be removed from raw results of the resonant frequencies counted the temperature effect ($f_{31,c}$) by eq. 4.9. [15].

$$f_{31,nc}(t) = f_{31,c}(t) - S_t T(t)$$
 eq. 4.9

where $f_{3l,nc}$ is the resonant frequencies after removing the temperature effect, S_t is temperature sensitivity (-23 Hz/°C for the 3×2×0.1 mm³ PZT cantilever sensor in this work), *T* is temperature, and *t* is time.

4.5.2 Water vapor effect

A. Results

• Low humidity level (ppmv level)

The responses of the uncoated and coated PZT cantilever sensors under the different concentrations of water vapor after removing the temperature effect are shown in Figure 4.26. With HMDS functionalized MCF-Si, the resonant shifts due to the adsorbed water molecules of the coated sensor are observed at \approx 500 ppmv. Whereas, the equivalent shifts of uncoated sensor appear at higher concentration (\approx 2500 ppmv). The sensitivities to humidity of both sensors are presented in Figure 4.27. The coated sensor has higher sensitivity compared to the uncoated sensor.



Figure 4.26 Response of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under concentration sequences of water vapor: (a) uncoated sensor, and (b) HMDS functionalized MCF-Si coated sensor (the sensing system is connected to PUL110 as mentioned in Section 4.3.2.).



Figure 4.27 Resonant frequency as a function of vapor concentration of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the water vapor.

• *High humidity level (40-90%rH)*

The responses of the uncoated sensor under a concentration sequence of water vapor are investigated at 25°C (Figure 4.28). The increase of relative humidity from 40% to 70% moderately decreases the resonant frequency shifts due to water adsorption of the cantilever. For higher humidity conditions of 80% and 90%, the resonant frequency plummets by \approx 300 Hz and 1900 Hz, respectively.



Figure 4.28 Responses of the uncoated PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the relative humidity in the range of 40-90 %rH (a) the resonant frequency changes as a function of time, and (b) the resonant frequency shift as a function of the relative humidity (the sensing system is connected to Climate EXCAL mentioned in Section 4.3.1.).

In order to get the linear decrease of the resonant frequency shift for calculation of the humidity sensitivity, the uncoated and coated sensors are studied under the relative humidity range of 40-70%, as shown in Figure 4.29. The resonant frequency shift as a function of the relative humidity of both sensors are shown in Figure 4.30. The sensor with HMDS functionalized MCF-Si coating still presents higher sensitivity compared to the uncoated sensor.



Figure 4.29 Response of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the relative humidity in the range of 40-70 %rH (a) uncoated sensor, and (b) HMDS functionalized MCF-Si coated sensor (the sensing system is connected to Climate EXCAL mentioned in Section 4.3.1.).



Figure 4.30 Resonant frequency as a function of relative humidity (in the range of 40-70% rH) of the uncoated and coated PZT cantilever sensor ($3 \times 2 \times 0.1 \text{ mm}^3$ in size).

B. Discussion

Effects of water vapor on mesoporous materials as well as on resonant frequency of cantilever sensors are quite complicate phenomena. They depend on the humidity level and on the stages of sorption and desorption in materials used as sensing layer or cantilever. During water exposure, density of porous materials will be modified because of mass increase, and dimensions (particularly thickness) will also be modified. Stiffness (Young's modulus) of transducers could also be changed, decreasing or increaseing depending on the humidity level.

Blanc's work [23] illustrated the behavior of mesoporous titanium oxide (TiO_2) coated Love sensors under different humidity. It was shown that with combined resonant frequency measurements of ellipsometry and modelling, the resonant frequency could be changed because of the following reasons:

- Adsorption and desorption in micro/meso-porous materials during water exposure: these are well known phenomena called mass effect.
- Strong modification of stiffness (which is linked with the Young's modulus) of sensors: this effect has two alternatives of stiffness decreasing and stiffness increasing behaviours, as represented in Figure 4.31.



Figure 4.31 (a) Schematic diagram of a Love wave platform with a TiO₂ mesoporous sensitive coating, (b) shear modulus (C_{44}) variation of the TiO₂ thin film versus the relative humidity level at 18°C (To be noticed that $C_{44} = E/[2(1+\nu)]$, C_{44} is the shear modulus, *E* is the Young's modulus, and ν is the Poisson's ratio.), and (c) capillary contraction phenomena with re-increasing of the shear modulus in the condensation zone (the initial values used in these simulations are 2.9 GPa and 7.5 GPa for C_{44} and *E*, respectively) [23].

In the case of cantilever sensors, stiffness transitions in presence of some analytes were found in previous research [24], [25], [26]. Thundat *et al.* [24] reported that the coating materials had an influence on the resonant behaviors of the silicon cantilevers. These cantilevers could overcome negative or positive resonant frequency shifts with phosphoric acid or gelatin coating, respectively. Hans *et al.* [25] presented that gold coating usually had a low wettability towards water and higher affinity to alcohol. Finally, Huber *et al.* [26] found that with uncoated silicon cantilever, positive
stiffness effect was dominant under ppmv level of humidity (<1000 ppmv). Besides, they also studied cantilevers covered with zeolite or silica and proposed a more precise model for resonant frequency shifts, where Young's modulus of the porous materials had to be considered. Indeed, it depended not only on temperature, but also on occupancy of sorption sites, as shown in eq.4.10 [26]. However, this equation was applyied to the frequency changes in flexural mode.

$$\Delta f_0(t) = f_0 \left[-\frac{1}{2m_{tot}} + \frac{1}{2E_{tot}} \frac{\alpha_E}{m_{NP}} \frac{h_{NP}}{(h_{NP} + h_{Si})} \right] \Delta m_{water}(t)$$
 eq. 4.10

where f_0 is the resonant frequency, *m* is mass, tot is total, *E* is Young's modulus, α_E is sorbate dependency of Young's modulus per mass of sorbent, *NP* is nano particles coating, *Si* is silicon cantilever, *h* is thickness.

In this work, the linear decreases (due to negative shifts in resonant frequency) in the humidity sensitivities of the uncoated and coated sensors are presented under humidity 0-90%rH. The coated sensor shows higher humidity sensitivity compared to the uncoated sensor because a lot of pores of HMDS functionalized MCF-Si activate water adsorption of the coated sensor. Table 4.8 compares these obtained results, and presents outcomes in previous literatures.

Cantilever characteristic	Humidity range	Sensitivity (negative responses)		*Mass uptake for	
		(Hz/%rH)	(Hz/ppmv)	500 ppmv (µg)	
PZT cantilever (3×2×0.1 mm ³ in	n size) fabricated in this v	vork			
Uncoated cantilever	0-5000 ppmv	0.624±0.125	0.002±0.001	0.037 ± 0.007	
	(0-16%rH)			(M)	
	12480-21840 ppmv	3.221±0.001	0.010 ± 0.001	0.190 ± 0.001	
	(40-70%rH)			(M+S)	
HMDS functionalized MCF-	0-5000 ppmv	4.680±0.094	0.015 ± 0.001	0.278 ± 0.006	
Si coated cantilever	(0-16%rH)			(M)	
	12480-21840 ppmv	4.361±0.170	0.014±0.001	0.261±0.012	
	(40-70%rH)			(M)	
PZT cantilever of previous resea	arch				
$8 \times 2 \times 0.1 \text{ mm}^3$ [15]	10-60%rH	1-1.5	-	-	
$1 \times 1 \times 0.1 \text{ mm}^3$ [16]	<70%rH	7.5	-	-	
Silicone cantilever of previous r	research				
-COOH functionalized Zeolite	< 1000 ppmv	-	1-2	-	
coated cantilever [27]					
Hexafluoro-2-propanol-	100 ppmv	-	≈0.025	-	
functionalized SBA-15					
mesoporous silica coated					
cantilever [28]					

Table 4.8 The responses to humidity (0-70%rH) of the uncoated and coated PZT cantilever sensors in this work and the responses to humidity of cantilever sensors in previous research

Remarks:

1. * is when the experimental sensitivity is 27 Hz/ μ g.

2. 1000 ppmv of water vapor is equal to 740 mg/m³.

3. M is mass effect and S is stiffness or Young's modulus effect.

Considering the responses of cantilever sensor under various relative humidity (0-90%rH), the mechanism of water formation onto the sensor surface can be classified into two forms by the different ranges of relative humidity, as shown in Figure 4.32 [18]. The adsorbed water forms isles acting as additional mass on the sensor surface at low humidity (0-70%rH), but water layers can be formed at high humidity (80-90%rH). Thus, this discussion part will be explained according to the humidity level.



Figure 4.32 Schemes of water formation on sensors under different ranges of the relative humidity (adapted from [18]). To be noticed that low level of humidity is < 80% rH.

• At low relative humidity (0-70%rH)

For uncoated sensor with Au electrodes, the difference in sensor behaviors under various humidity levels are clearly observed. Although the residual porosity in the PZT cantilever transducer is quite low (6.2%), a little sensitivity to humidity (≈ 0.002 Hz/ppmv) is still presented with humidity exposure in ppmv level (0-5000 ppmv or 0-16%rH). However, it shows a five times increase in humidity sensitivity under higher humidity condition (40-70%rH) with the humidity sensitivity of ≈ 0.01 Hz/ppmv. This can be explained by the fact that the amount of adsorbed water molecules in sensor is enough to induce a decrease in stiffness (Young's modulus) of the cantilever sensor. Moreover, the adsorbed water forms the water isles on the cantilever acting as additional mass on the sensor surface. Thus, the risen humidity sensitivity (at 40-70%rH) of the uncoated sensor is correlated to both stiffness and mass effects.

For coated cantilever sensor, its humidity sensitivity is still stable (≈ 0.015 Hz/ppmv) under ppmv level (0-16%rH) and 40-70%rH of water vapor. This implies that the mass effect due to adsorbed water molecules by the HMDS functionalized MCF-Si adsorbent (sensitive coating) mainly takes place under these humidity ranges.

• At (extra) high relative humidity (80-90%rH)

This condition is tested only with the uncoated sensor. Beyond the critical humidity of 80%, the water isles join and there is formation of water layers on the cantilever surface (Figure 4.32) [18]. This may cause a lot of additional mass on the sensor surface and the decrease in cantilever stiffness. Both factors probably induce the sharp fall of the resonant frequency as shown in Figure 4.28.

After increasing humidity to 90% rH, the uncoated sensor is re-tested by decreasing humidity from 90 to 40% rH. We can observe that the resonant frequency cannot reach the same value at 40% rH (Figure 4.28). This is because the absorbed water molecules cannot move from pores in the cantilever by decreasing humidity at 25°C.

In comparison with some sensors in previous literatures (Table 4.8), the uncoated and coated sensors prepared in this work have lower humidity sensitivity. Consequently, they are interesting candidates for VOCs detection.

4.5.3 Conclusions of environmental effects on the PZT cantilever sensor

The increases of temperature and humidity decrease the resonant frequency of the PZT cantilever sensor. The temperature changes have a strong effect on the cantilever behavior ($\approx -23\pm5$ Hz/°C), but compensation with a temperature sensor could be done. While the maximum sensitivity to humidity of the uncoated and coated sensors (0-70%rH) are around \approx -0.010 Hz/ppmv and

 \approx -0.015Hz/ppmv, respectively. However, both sensors shows lower humidity sensitivity compared to previous PZT sensors of our team. As a result, they are possible to use for VOCs detection.

4.6 VOCs detection by PZT cantilever sensor

With the sensing system connecting with the PUL110 mentioned in 4.3.2, the responses of the uncoated and the HMDS functionalized MCF-Si coated PZT cantilever sensor under VOCs are investigated at room temperature in this section. As mentioned in section 4.5.1, even if the room is under air conditioner, the temperature effect is removed from the raw results by eq. 4.9 before plotting relations between the resonant frequency and time under concentration sequences of target vapors. To be noticed that with nitrogen gas flow in this sensing system, the relative humidity in the target vapor (HPLC grade) is very low and stable. Thus, the humidity factor is not considered in calculation of this part.

4.6.1 Benzene detection

Firstly, the responses to benzene vapor are observed for the uncoated cantilever sensor. The obtained results have no distinctive shifts for concentration sequences lower 871 ppmv. However, the slightly positive shifts (<10 Hz) are investigated between concentrations of 871 ppmv and 2023 ppmv as shown in Figure 4.33.



Figure 4.33 Response of the uncoated PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the benzene vapor with concentration sequence between 11 ppmv and 2023 ppmv.

Figure 4.34 illustrates the responses of the coated sensor under two concentration sequences. For low concentration values (8 ppmv to 138 ppmv), the positive shifts are observed. However, at 252 ppmv the resonant frequency begins to decrease (Figure 4.34(a)). Thus, higher concentration values are introduced by increasing chamber's temperature of PUL110 for generating vapor from 50°C to 60°C. Figure 4.34(b) presents a slow decrease of the resonant frequency. Saturation of the response seems also to appear for a benzene concentration higher than 1000 ppmv. However, the calculated sensitivity to benzene vapor obtained from the slope of plotting the resonant frequency shift as a function of vapor concentration (Figure 4.35) is very low.



Figure 4.34 Responses of the HMDS functionalized MCF-Si coated PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the benzene vapor in two concentration sequences (a) 8-252 ppmv, and (b) 11-2023 ppmv.



Figure 4.35 Resonant frequency as a function of vapor concentration of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the benzene vapor.

4.6.2 Toluene and ethanol detection

As can be seen from Figure 4.36(a) and (b), the resonant frequency shifts of the uncoated sensor under toluene vapor are positive with small values, while the coated sensor expresses a steadily decrease of the resonant frequency. Furthermore, the responses under ethanol vapor of the uncoated and coated sensors have similar tendency, but different amplitude shifts, as shown in Figure 4.36(c) and (d).



Figure 4.36 Responses of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the toluene vapor in a concentration sequence (a) uncoated sensor and (b) HMDS functionalized MCF-Si coated sensor, under the ethanol vapor in a concentration sequence (c) uncoated sensor, and (d) HMDS functionalized MCF-Si coated sensor.

Figure 4.37 compares the sensitivity of the uncoated and coated sensors under benzene, toluene, and ethanol vapor. As it was expected, the uncoated PZT sensor hardly shows sensitivity to VOCs compared to the coated PZT sensor. However, the coated PZT sensor reveals the different degree of sensitivity for different VOCs. With selectivity behavior of the sensing material, the largest sensitivity is investigated for toluene adsorption (-238 mHz/ppmv). While, there is no sensitivity to benzene molecules.



Figure 4.37 Resonant frequency as a function of vapor concentration of the PZT cantilever sensor $(3 \times 2 \times 0.1 \text{ mm}^3 \text{ in size})$ under the toluene, ethanol, and benzene vapors (a) uncoated sensor, and (b) HMDS functionalized MCF-Si coated sensor.

4.6.3 Discussion

In general, most of the coated cantilever sensors present decreases in resonant frequency after analyte adsorption with stable stiffness. However, in some cases, the sensor stiffness changes are responsible of resonant frequency changes (eq. 4.11). As explained in Section 4.5.2B, the sensor stiffness could be increased or decreased due to various reasons, for instance, some phenomena between analyte and sensor [23], interaction between analyte and sensing material [24], and analyte concentration [26]. For the PZT cantilever sensor, stiffness increasing was found in uncoated sensor under toluene vapor (concentration of 790 ppmv and 1318 ppmv) [15] and oxygen plasma treated multi-wall carbon nanotubes (O-MWCNTs) coated sensor under benzene vapor (concentration is in the range of 50 ppb -1940 ppmv) [29], respectively. These positive responses were caused by the predominant stiffness effect.

$$\Delta f_{0,31} = \frac{f_{0,31}}{2} \left[\frac{\Delta k}{k} - \frac{\Delta m}{m} \right] \qquad \text{eq. 4.11}$$

where $\Delta f_{0,31}$ is the resonant frequency variation, $f_{0,31}$ is the resonant frequency, k and m are stiffness and mass of the uncoated cantilever, and Δm is the mass of sensitive coating deposition.

In this work, uncoated PZT cantilever sensor with Au electrodes has no obvious responses to VOCs. It expresses positive shifts in resonant frequency under each vapor of benzene, toluene, or ethanol. These results could be interpreted that the positive stiffness changes are the main cause of increasing in the resonant frequencies.

Considering HMDS functionalized MCF-Si coated PZT cantilever sensor (Table 4.9), the unexpected results with very low sensitivity to benzene vapor are found. According to Baimpos *et al.* [30], the expected adsorbed mass in mesoporous silica may have the order of magnitude of 7.95 μ g at 500 ppmv of benzene vapor with Langmuir adsorption loading. Furthermore, if this adsorption leads to mass effect in the sensor using the experimental sensitivity of 27 Hz/µg, a negative resonant frequency shift of 214 Hz should be obtained. However, in practice, the response of coated sensor at 500 ppmv of benzene vapor contributes to a negative resonant frequency shift of only ≈2.5 Hz. It is possible to assume that there is a competition between increasing stiffness and mass effects with a major effect of the stiffness.

More precisely, the responses of this coated sensor under different concentrations of benzene vapor are classified into 2 ranges which are the following:

• At benzene concentrations lower than 200 ppmv: the positive stiffness effect prevails the mass effect.

• At benzene concentrations higher than 400 ppmv: mass effect wins the positive stiffness effect. Nevertheless, the frequency shift seems to reach a plateau with increasing benzene vapor from 1490 ppmv to 2023 ppmv. This is believed that the mesoporous silica has reached a saturating state. These results are similar to those observed in the literature with printed PZT cantilevers and high specific area sensitive MWCNTs coatings [31]. Baimpos et *al.* [30] also noticed that vapor sorption in porous zeolite material covering Si cantilevers could also affect Young's Modulus. Also, from 500 ppmv to 2000 ppmv of benzene, loadings in FAU zeolite were constant.

However, our coated sensor shows negative resonant shifts of response to toluene vapor with high sensitivity of -238 mHz/ppmv, response time values lower than 2 minutes, and the limit of detection (LOD) \approx 25 ppmv. Besides, a moderately negative response to ethanol vapor is observed with sensitivity of -42 mHz/ppmv and LOD \approx 71 ppmv. These negative shifts can be presented due to predominant mass effect.

Considering the chemical properties of the analyzes (Table 4.9), although benzene and toluene have close values of molecular diameter and polarity index, their vapor pressure and chemical structure are different. These parameters could be used to explain the difference in bezene or toluene selectivity of the coated sensor. Higher vapor pressure of benzene is possibly correlated to develop sensor stiffness. The methyl group (-CH₃) of toluene may be in favour with adsorbent containing the methyl group of HMDS. In comparison with toluene response, the moderate sensitivity to ethanol vapor is possibly caused by the polarity effect on sorption.

		-	-			
	Benzene	Toluene	Ethanol	Deionized water		
General characteristic						
Formula	C_6H_6	C_7H_8	C_2H_6O	H ₂ O		
Molecular weight (g/mol)	78.11	92.14	46.07	18.02		
Molecular diameter (Å)	5.26	5.68	4.50	2.80		
Polarity index	2.7	2.4	4.3	10.2		
Boiling point (°C)	80	110	78	100		
Vapor pressure at 20°C (mmHg)	74.6	22.0	44.3	17.5		
Experimental values						
Sensitivity (mHz/ppmv)						
- Uncoated sensor	(+) 3.0±0.1	(+) 6.3±0.6	(+) 8.0±1.4	(-) 2.0±0.4		
- Coated sensor	(-) 6.0±0.1	(-) 238.0±5.2	(-) 42.0±1.8	(-) 15.0±0.3		
(50 µg of sensing material)						
Real gravimetric sensitivity (mHz/(mg/m ³))						
- Uncoated sensor	(+) 0.9±0.1	(+) 1.7±0.2	(+) 4.3±0.4	(-) 2.7±0.1		
- Coated sensor (50 µg of sensing material)	(-) 1.9±0.1	(-) 63.2±1.4	(-) 22.3±0.6	(-) 20.3±0.1		
Calculated values from theory (Assumed that the gravimetric sensitivity, $S = 27 \text{ Hz/}\mu\text{g}$)						
Mass uptake for 500 ppmv (µg)						
- Coated sensor (50 µg of sensing material)	0.115±0.001	4.400±0.096	0.778±0.033	0.278±0.006		

 Table 4.9 Characteristics of target solvents and the sensitivities to target vapors of sensors [32], [33]

Remarks:

1. Real gravimetric sensitivity $(Hz/(mg/m^3)) = Sensitivity (Hz/ppmv)/X$

X is analyte concentration of 1 ppmv in mg/m³ unit. X values of benzene, toluene, ethanol, and water are 3.19, 3.76, 1.88, and 0.74 mg/m³, respectively.

3. (+) is the positive shifts and (-) is the negative shifts.

In comparison with other works from IMS team (Table 4.10), it is distinct that the HMDS functionalized MCF-Si sensitive layer coated PZT sensor gives improved toluene sensitivity compared to the PEUT coated PZT cantilever (with the same kind of sintering aid). Moreover, its efficiency is similar to silicon cantilevers with zeolite coating. Based on the developed silicon cantilever of other teams, the coated PZT sensor in this subject is likely to have higher toluene sensitivity.

Cantilanan tama	Vibration	Sensing layer		Tanget yonen Sensitivity		Def/Vaca
Cantilever type	mode	Туре	Mass	Target vapor	(Hz/ppmv)	Kei/Year
Developed cantilever	sensors obtained from	m IMS Laboratory and co-w	orkers in Spa	in and Thailand		
PZT cantilever						
 3×2×0.1 mm³ 	In plane	None	None	Water	(-) 0.002	
	longitudinal			Benzene	(+) 0.003	
	mode			Toluene	(+) 0.006	
				Ethanol	(+) 0.008	This work
		HMDS functionalized	50 µg	Water	(-) 0.015	THIS WOLK
		MCF-Si		Benzene	(-) 0.006	
				Toluene	(-) 0.238	
				Ethanol	(-) 0.042	
 8×2×0.1 mm³ 		PEUT	-	Toluene	(-) 0.015	[14]/2013
		O-MWCNTs	-	Benzene	(-) 0.001	[29]/2016
		Zeolite (DAY structure)	807 µg	Benzene	(-) 0.306	[34]/2014
			227 µg	Benzene	(-) 0.064	
Silicon cantilever		•	-			
• 5×0.4×0.06	Out-of-plane	PEUT	-	Toluene	(-) 0.001	[14]/2013
mm ²	nexural mode					
Developed cantilever sensors obtained from others						
Silicon cantilever						
 0.2×0.1×0.003 	Out-of-plane	-COOH functionalized	10 mg	Benzene	(-) 0.100	[27]/2018
mm ³	flexural mode	mesoporous silica	-	Toluene	(-) 0.180	
	nanoparticles		Ethanol	(-) 0.200	1	
		Hexafluoro-2-propanol-	1	Ethanol	(-) 0.040	[28]/2011
		functionalized SBA-15		Water	(-) 0.025	
		mesoporous silica			() 01020	
					1	

 Table 4.10 Response of the resonant sensors under various kinds of target vapors

Remarks: (+) is the positive shifts and (-) is the negative shifts.

4.6.4 Conclusions of using the PZT cantilever sensor for VOCs detection

This study illustrates that the HMDS functionalized MCF-Si coated PZT cantilever sensor (in length× width×thickness of $3\times2\times0.1$ mm³) is benefit to use in the field of toluene detection at room temperature with low response to humidity. Its response to toluene gives the sensitivity and LOD values of \approx 240 mHz/ppmv and \approx 25 ppmv, respectively. These values are improved compared to PEUT coated PZT and silicon cantilever sensors in previous work of our team.

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General Conclusion

This thesis work consists of the first highlighted exploitation of printing technique for fabrication of piezoelectric resonant transducer application, with disk or cantilever shape. The screen-printing thick film technology has been chosen for these transducer's process because it is an inexpensive and flexible technology for fabricating free-standing specimens in a micro-scale with the sacrificial layer technique. In particular, during this PhD's work, microstructure and electromechanical properties of screen-printed piezoelectric ceramic transducers have first been optimized and secondly, resonant cantilevers gas sensors based on PZT in a sandwich with electrodes and coated with a mesoporous sensitive coating have been successfully applied for toluene detection.

In the first chapter, after considerations on properties and effects on health of volatile organic compounds (VOCs) and on chemical sensors, a focus on resonant cantilever gas sensors and the possible sensitive coatings deposited on it has been made. A survey on gravimetric sensors, including cantilever sensors studied at IMS has also been proposed in order to help the understanding of the contribution of this PhD's work.

In the second chapter, tools, procedure and materials selected for the processing have been thoroughly detailed. These elements are necessary for the comprehension of the next chapter where optimization of the materials used in the PZT formulation has been first studied, by varying the sintering aid LBCu proportion and the PZT particle sizes. The PZT powder is a commercial hard type from Ferroperm (Pz26). The firing conditions with a stable time of 2 hours at 900°C, and the sacrificial layer nature based on polyester have been here kept constant. A disk shape has been preferred for easier microstructural analysis (SEM and Optical microscope), dielectric and electromechanical characterizations (following IEEE standards). The best results have been obtained with 3 wt.% LBCu, in a ratio of 26.7/40.0/33.3 with a density of \approx 7.4 g/cm³ with attritor or planetary milled PZT powder (particle size, $D_{0.5} < 1 \ \mu$ m). The reference density value for the bulk PZT ceramic is 7.7 g/cm³.

Then, two types of sacrificial layers (polyester and corn-starch based) and electrodes (Au and Ag/Pd), have been shown to influence the final properties. Regarding the sacrificial layer nature, with the corn-starch based sacrificial layer, the printed disk shows 3.8% lower porosity compared to that of the disk printed on the polyester sacrificial layer. This is due to a difference in the thermal decomposition of these two new sacrificial layers. However, the surface roughness of the corn starch based paste is quite high. This could contribute to discontinuity in the bottom electrode and dropping of electrical properties. Thus, the polyester has been kept as the sacrificial layer in the further studies. Studies of the effect of electrode nature, paste's solvent compatibility and coefficient of thermal expansion have shown to be critical for quality of the top electrode and of the PZT/electrode interface. The printed disks with Ag/Pd electrodes (diameter 7.5 mm, thickness 140 μ m) have given the best electromechanical factor with a value of $k_p \approx 0.47$ for the planar vibration mode, and the highest phase angle ($\approx 88\%$). Additionally, the relative dielectric permittivity (ε_r = 1300 and $k_p = 0.57$).

Referring to the VOCs detection application, the optimized PZT paste has been fabricated into various cantilever geometries (from 6×2×0.1 mm³ to 3×1×0.1 mm³) with the polyester sacrificial laver. However, only the cantilevers in dimension of 3×1×0.1 mm³ with Au electrodes have been shown to be adapted for gas sensing and for further drop casting of the sensitive material on its the surface free-end area. Its gravimetric sensitivity has been evaluated to ≈ 27 Hz/µg, the quality factor higher than 300 and noise ≈ 1 Hz. One type of inorganic mesoporous silica, mesocellular foam (MCF-Si), has been synthesized by sol-gel method by using P123 as a template and 1,3,5trimethylbenzene (TMB) as a pore expander. Interconnected spherical pore structure has been observed by TEM analysis. Hexamethyldisilazane (HMDS) functionalization has been done to decreas hydrophilic behavior and the optimum ratio of HDMS:MCF-Si has been found to be 0.15. Surface area and pore size of \approx 500 m²/g and \approx 6 nm, respectively have been measured for MCF-Si :0.15HMDS. Among three kinds of VOCs (benzene, toluene, and ethanol), our sensor with 50 µg of functionalized MCF-Si and working with the in plane longitudinal mode at ≈240 kHz can show the greatest response to toluene vapor (sensitivity ≈ 240 mHz/ppmv) compared with other VOCs vapors and humidity. This sensitivity has been mainly attributed to mass effect in the sensitive coating, as for ethanol tests or high humidity levels. Stiffness effect with an increase of the resonance frequency could be observed with uncoated cantilevers whatever the kind of vapor. Considering benzene tests, competition between stiffness and mass effects could be observed with coated sensors, leading to very low sensitivity to benzene (<10 mHz/ppmv). The low sensitivity under benzene compared to toluene could make it possible discrimination between these two highly toxic pollutants. In comparison with previous using resonant cantilever, silicon cantilever $(5 \times 0.4 \times 0.06 \text{ mm}^3)$ coated with a polymer PEUT sensing layer showed toluene sensitivity of ≈ 1 mHz/ppmv at 3 kHz (out of plane mode), and with the same PEUT coating, printed PZT cantilever of IMS of size $8 \times 2 \times 0.08$ mm³ gave toluene sensitivity of 15 mHz/ppmv at 70 kHz (in plane vibration mode). Therefore, our shorter cantilever coated with functionalized MCF-Si offers higher potential of toluene detection.

Some perspectives of this thesis work are as the following:

• Improvement of screen-printed film densification

Exactly, there are still many alternatives that can be introduced for increasing densification of the printed films and impeding defects (such as cracks, warpage, or inhomogeneity in the layers), for instance,

- (1) In addition to optimization of the PZT particles size, the influence of the sintering aid powder size could be studied as well as its homogeneity. A pre-melting of the LBCu sintering aid followed by its milling before its incorporation in the paste is an option which should give a more reproducible microstructure (avoid CuO cluster for instance).
- (2) Changes of method in mixing ceramic powders such as mixing PZT powder and LBCu sintering aid with attritor or planetary mills instead of using the three dimensional shaker should be tried.
- (3) Optimization of sintering dwell temperature, sintering dwell time, and heating rate is another interesting pathway.

- Improvement of electrical connection
 - (1) In the case of disks, the wires and glue sizes can affect the mechanical vibration of the resonator. Different options of electrical connections improvement can be thought: (i) spring contact pins (ii) thin Au (< 20μ m) wires bonded by thermosonic energy, (iii) thin printed tapes. Options (i) and (ii) would require flat disks; in the third option, the tapes would be free-standing thanks to the sacrificial layer process.
 - (2) For disk or cantilevers, Au electrodes paste formulation could be improved to adjust its CTE to that of the PZT while keeping good electrical properties. The MgTiO₃ oxide additive could be added as for Ag/Pd electrode.
- Applications
 - (1) Based on the good properties achieved with the disks, applications such as actuation, mechanical energy harvesting or structural health monitoring could be envisaged. In all cases, the disks should be further glued. Gas detection using the planar or thickness vibration mode could be also attempted with or without sensitive coating
 - (2) For the cantilever based gas sensor, a better understanding of the competition between stiffness and mass effects are the perspectives of this work with comparison with other gravimetric sensors coated with the same MCF-Si sensitive coating but operating with other vibration modes (cantilever with flexural vibration mode or QCM). Complementary adsorption/desorption isotherms of PZT and mesoporous silica with other gases could be helpful.
- Use of non-lead piezoelectric ceramics instead of PZT

As European Community started RoHS (Restrictions on the use of certain Hazardous Substances), which restricts using of lead (Pb) in electronic equipment, non-lead piezoelectric ceramics are considered replacing PZT. During this thesis work, potassium sodium niobate ($K_{0.5}Na_{0.5}$)NbO₃, KNN, obtained from LUSAC were mixed with organic vehicle paste to form KNN pastes. Then, they were fabricated in the disk form. Unfortunately, sintered KNN disks completely cracked after firing at 900°C for the first experiment. Thus, the appropriate processing conditions and sintering aid should be surveyed in the future work.

Appendix

Appendix A: For Chapter 2

Appendix A-1: Datasheets of concerned materials

1. Ferroperm TM Piezoelectric Pz26 (Navy I) Hard type



Ferroperm[™] Piezoelectric Pz26 (Navy I) Hard relaxor type PZT



Microstructure of Pz26 (Navy I) at a magnification of 5000 times

A hard PZT with low ageing rates and low loss

Pz26 is an all-round hard PZT material with good coupling factors, high Curie temperature, high mechanical quality factor, low dielectric loss and very good stability over time. Pz26 can be used as a direct replacement for all other Navy I materials. Benefits include strongly improved ageing rates, and extremely stable performance from orders ranging over several years.

Repeatable performance

The main focus through our entire production process is to provide materials and components with the highest possible reproducibility of properties and parameters and to obtain the lowest aging rates in the industry.

Our materials have a variation of ±5% for all parameters. This reduces the requirements for impedance matching, frequency tuning and dimensioning of the housing meaning fewer rejects and lower costs.

Customised solutions

We have more than 60 years of experience in the production of advanced piezoelectric ceramics. Our team has extensive expertise in customising designs to match the customer's needs.

Please contact us to discuss your requirements in further detail.

Meggitt A/S

Our product competencies and services: Piezoelectric ceramics | Multilayer | Thick-film | InSensor® | PiezoPaint®



Key benefits

- Lowest batch to batch variation in the industry
- Stable material with consistent performance
- Customised or standard designs

Key features

- High Curle temperature
- Low dielectric loss
- Good stability over time

Applications

- High-power underwater transducers
- Medical therapeutic transducers
- Dental cleaners
- Hydrophones
- Level sensors

Contact

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Porthusvej 4, DK-3490 Kvistgaard Denmark Tel: +45 49 12 71 00 e-mail:pz@ferroperm.net

www.meggittlerroperm.com







Ferroperm[™] Piezoelectric

Pz26 (Navy I) Hard relaxor type PZT

Material properties		
Electrical	Symbol	Pz26
Relative dielectric permittivity at 1 kHz	K ₃	1300
Dielectric dissipation factor at 1 kHz	tan ö	3 x 10-3
Curie temperature	T _o >	330 °C
Recommended working range	<	230 °C
Electromechanical		
Coupling factors	k _p	0.56
	k,	0.47
Piezoelectric charge coefficient	d ₂₀	300 pC/N
Mechanical		
Mechanical Quality Factor	Q _m t	>1000
Density	P	7.70 g/cm ^a

Note: Due to continuous process improvement, specifications are subject to change without notice. Please be aware that extreme dimensions and geometries can lead to exaggeration in tolerances in all materials.



Free detectric sonatest of Picifit standard discs produced for approval of easy new betch. Rech. point represents a new batch of 20 – 150 kg. The illustrated time-periodic form 1996 to how 2001. Schemely amail variations over time is observed, and escellent stability can therefore





Pleaselectric coupling constants for POSI standard disco produced for approvel of every new batch. Buch point represents a new batch of 20 – 158 kg. The Hustmited time-period is from 1996 to Nov 2007. Sporeney analyzeriations over time is observed, and excellent stability can



Meggitt A/S

Our product competencies and services: Piezoelectric ceramics | Multilayer | Thick-film | InSensor® | PiezoPaint® WBB/CR28,201111



2. Ferroperm TM Piezoelectric ceramics (TF2100 all-round hard PZT)



Ferroperm[™] Piezoelectric ceramics TF2100 all-round hard PZT



SEM picture of TF2100

PZT thick film based on Ferroperm Pz26

Pz26 is an all-round hard PZT material with good coupling factors, high Curie temperature, high mechanical quality factor, low dielectric loss and very good stability over time. Pz26 can be used as a direct replacement for all other Navy I materials. Benefits include strongly improved ageing rates, and extremely stable performance from orders ranging over several years.

The material is compatible with thick film technology and the properties are almost fully conserved in the change from bulk to thick film. The change in properties is mainly attributed to increased porosity in the thick film compared to the bulk material.

Repeatable performance

The main focus through our entire production process is to provide materials and components with the highest possible reproducibility of properties and parameters and to obtain the lowest aging rates in the industry.

Our materials have a variation of ±5% for all parameters. This reduces the requirements for impedance matching, frequency tuning and dimensioning of the housing meaning fewer rejects and lower costs.

Customised solutions

We have more than 60 years of experience in the production of advanced piezoelectric ceramics. Our team has extensive expertise in customising designs to match the customer's needs.

Please contact us to discuss your requirements in further detail.

Meggitt A/S

Our product competencies and services: Piezoelectric ceramics | Multilayer | Thick-film | InSensor® | PiezoPaint®



Key benefits

- Lowest batch to batch variation in the industry
- Stable material with consistent performance
- Customised or standard designs

Key features

- High Curie temperature
- Low dielectric loss
- Good stability over time

Applications

- High frequency medical imaging
- Miniaturised accelerometers
- Integrated miniaturised phased array ultrasound scanners

Contact

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Ferroperm[™] Piezoelectric ceramics TF2100 all-round hard PZT

Material properties

Electrical	Symbol	TF2100
Relative dielectric constant at 1 kHz	K ₂₀ T	520
Dielectric dissipation factor at 1 kHz	tan ô	8 x 10 ⁻³
Electromechanical		
Coupling coefficients	k _p	29
	k,	49
Piezoelectric charge coefficient	d	200 pC/N
	d _{ar}	-50
Piezoelectric voltage coefficient	9	50 x 10 ⁻³ Vm/N
	9 ₃₁	-10
fechanical		
Acoustic impedance	Z,	–15 MRayl
Mechanical quality factor	Q _m r	100

Note: Due to continuous process improvement, specifications are subject to change without notice. Please be aware that extreme dimensions and geometries can lead to exaggeration in tolerances in all materials.

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Our product competencies and services: Piezoelectric ceramics | Multilayer | Thick-film | InSensor® | PiezoPaint" 2010;JSGK,17108



3. Polymer Silver Conductor (ESL 1901-S) used for screen fiducials and connecting between printed resonators and wires



416 EAST CHURCH ROAD KING OF PRUSSIA, PA 19406-2625, U.S.A T: 610-272-8000 F: 610-272-6759

www.electroscience.com

POLYMER SILVER CONDUCTOR

1901-S

RoHS Compliant*

Polymer Silver For Low Temperature Substrates

ESL 1901-S is a silver-filled, flexible resin material designed for use as a conductor on lowtemperature substrates. This silver conductor may be used in the manufacture of four and five wire analogue resistive touch panels, for printed antennas in RFID applications and as conductors in flexible solar cells. After screen-printing and curing the silver film remains reasonably flexible and the resistance of the conductor remains constant over time. This versatile polymer has also been successfully used on other substrates such as cloth.

PASTE DATA

Rheology:	Thixotropic, screen-printable paste
Viscosity: (Brookfield RVT, 1 rpm, No. 6 spindle, 25.5 ± 0.5 °C)	170 ± 10 Pa.s
Shelf Life (at 5 - 25 °C):	6 months

PROCESSING

Screen Mesh, Emulsion: Curing Schedule: Substrate for Calibration: Thinner:

200 or 325 S/S, 25 µm 125°C / 10 min PVC plastic card ESL 659

ESL Europe 1901-S 0706-F

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See Caution and Disclaimer on other side.

TYPICAL PROPERTIES

Cured Thickness: (measured on a 100 mm x 0.25 mm conductor track)	25 - 35 μm
Approximate Coverage:	100 cm ² /g
Resistivity: (measured on a 100 mm x 0.25 mm conductor track)	< 20 mΩ/⊡
Printing Resolution: (line/space)	0.25 mm / 0.25 mm

"None of the six substances referred to in the RoHS Directive (2002/95/EC) are used in the formulation of this product.

ESL Europe 1901-S 0706-F

CAUTION: Proper industrial safety precautions should be exercised in using these products. Use with adequate ventilation. Avoid prolonged contact with skin or inhalation of any vapours emitted during use or heating of these compositions. The use of safety eye goggles, gloves or hand protection creams is recommended. Wash hands or skin thoroughly with sosp and water after using these products. Do not eat or smoke in areas where these materials are used. Refer to appropriate MSDS sheet.

DISCLAMER: The product information and recommendations contained herein are based on data obtained by tests we believe to be accurate, but the accuracy and completaness thereof is not guaranteed. No warranty is expressed or implied regarding the accuracy of these data, the results obtained from the use hereof, or that any such use will not infinge any patent. BectroScience assumes no liability for any injury, loss, or damage, direct or correspuential, arising out of its use by others. This information is furnished upon the condition that the person receiving its hall make his own tests to determine the subtability thereof for his particular use, before using it. User essumes all risk and liability whatsoever in connection with his intended use. BectroScience's only obligation shall be to replace such quantity of the product proved defective.

4. (ESL 4924) used for fiducials on alumina substrates



INSULATING COMPOSITION

4924

HOS Heaters on Steel® . COS Circuits on Steel® . TFOS Thick Film on Steel®

Cadmium, Lead, Nickel and Barium-Free*

ESL 4924 is a dielectric composition designed to insulate unabraded, unoxidized, ferritic steels. The 4924 is non-porous and its TCE closely matches that of BS970/1449 Type 430-S17 or AISI Type 430 stainless steel. Three separately fired layers of 4924, having a total minimum thickness of 80 micrometers, provide excellent breakdown voltage between top conductive prints and the stainless steel base. It is essential that the stainless steel is only handled using protective gloves and that all printing is carried out in clean room conditions. With ESL 9695 or 9501-CH terminations and 29XXX Series resistors used as heating elements 4924 is recommended as an 850°C firing overglaze. These materials are also useful in other TFOS (Thick Film on Steel)[®] applications.

PASTE DATA

RHEOLOGY:	Thixotropic, screen printable paste
VISCOSITY: (Brookfield RVT, ABZ Spindle, 10 rpm, 25.5°C ± 0.5°C)	120 ± 20 Pa-s
COLOR:	Dark blue
SHELF LIFE: (25 °C)	6 months
PROCESSING	
SCREEN MESH/EMULSION:	165 S/S, 0.0 μm
LEVELING TIME:	5-10 minutes
DRYING AT 125 °C: (Depending upon substrate volume)	> 15 minutes
FIRING TEMPERATURE:	850 °C to 930 °C
OPTIMUM:	850 °C
TIME AT PEAK:	10 minutes

4924 0412-C

ESL Affiliates

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SUBSTRATE FOR CALIBRATIC	ON:	Unabraded, unoxidized 430 S17 s	tainless steel
		122.5 mm diame	eter x 1.2 mm
THINNER:			ESL 401
TYPICAL PROPERTIES			
FIRED THICKNESS: (At least 3 layers between 9695 a measured using an Elcometer 34	and 430 S 17 stainless st I5 thickness gauge)	teel,	> 80 µm
BREAKDOWN VOLTAGE: (Measured on an 88 mm diameter 108 mm diameter area of dielect using a standard Clare Flash Tes	er 9695 print on a ric at 25 °C in air, ster)		>1800 VAC
APPROXIMATE COVERAGE: (8	80 μm thickness)		40 cm ² /g
INSULATION RESISTANCE: (Measured on an 88 mm diameter diameter area of dielectric using	er 9695 print on a 108 mr 500 VDC at 25 °C in air)	n	
	After storage at 93 % ± 2	% RH, 25 °C ± 2 °C for 48 hours	> 10 ⁹ Ω
	At 300 °C		> 10 ⁹ Ω

A wide range of ESL materials are compatible with 4924 permitting the fabrication of other COS (Circuits on Steel) [®].

4924 0412-C

* Complies with RoHS, ELV, WEEE and CHIP 3 EC directives

CAUTION: Proper industrial safety precautions should be exercised in using these products. Use with adequate ventilation. Avoid prolonged contact with skin or inhalation of any vepors emitted during use or heating of these compositions. The use of safety eye poggles, glowes or hand protection creams is recommended. Wash hands or skin thoroughly with scape and water after using these products. Do not est or anote in arraws where these matching have some where the matching have and water after using these products. Do not est or anote in arraws where these matching have some matching have.

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5. Cermet Gold Conductor (ESL-8836) used for fiducials on aluminum nitride substrates and electrodes



CERMET GOLD CONDUCTOR

8836 8836-A

ESL 8836 and 8836-A mixed bonded thick film gold pastes are specially designed for thin printing. They produce a very smooth, dense film of 6 to 9 micrometers fired thickness. ESL 8836 is particularly well suited for automatic thermosonic wirebonding. While they have a wide firing range, a peak firing temperature of 850°C gives the best properties.

ESL 8836-A is an alloyed version of 8836. Its properties are similar to 8836, but it is designed for ultrasonic wire bonding using 25 micrometers diameter aluminum wire.

PASTE DATA

Thixotropic, screen printable paste
250±25 Pa-s
Mixed
6 months

PROCESSING

SCREEN MESH/	EMULSION:	325/25 µm
LEVELING TIME	: (25°C)	5-10 minutes
DRYING AT 125°	°C:	10-15 minutes
FIRING TEMPER	ATURE RANGE:	850°C-930°C
	OPTIMUM:	850°C
	TIME AT PEAK:	10-12 minutes
RATE OF ASCEN	IT/DESCENT:	60°C-100°C/minute
SUBSTRATE OF	CALIBRATION:	96% alumina
THINNER:		ESL 413

8836/A 9711-E

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China: Shanghai Agmet Electro-Solence Laboratory Ltd. + Second Floor Bidg. 12A1 + #223 North Fe Te Road + Walgacojao Free Trade Zone + Shanghai, China Tet: (011-96)-21-5866-0497 + ShanghaiSales@ShanghaiESL.com

Europe: Agmet, Ltd. + 8 Commercial Road + Reading, Berkshire, England R02 002 + Tel: (011-44)-119-987-3139 + Fax: (011-44)-118-986-7331 + Sales();ESLEurope.co.uk

TYPICAL PROPERTIES

FIRED THICKNESS:		6-9 µm	
RESISTIVITY:	8836	≤ 6 mΩ/square	
	8836-A	≤ 10 mΩ/square	
PRINTING RESOLUTION: (Line/Space)		125 µm x 125 µm	
APPROXIMATE COVERAGE:		80-85 cm ² /gram	
ADHESION: (90° pull, 2.0 mm x 2.0 mm pads, 80 Au/20	Sn solder)		
Initial pull strength:		30-40 N	
Aged 48 hours at 150°C:		≥ 20 N	
THERMOSONIC WIRE BONDING: (125°C bonding temperature)			
(25 µm Au)	8836	6-9 grams	
	8836-A	5-8 grams	
(50 µm Au)	8836	20-26 grams	
	8836-A	19-25 grams	
ULTRASONIC AI WIRE BOND: (25 µm, 1% Si, Al wire)			
Initial pull strength:	8836	7-9 grams	
	8836-A	6-10 grams	
Aged 48 hours at 150°C:	8836	4-7 grams	
	8836-A	5-6 grams	
Aged 200 hours at 150°C:	8836	3-4 grams	
CONTACT RESISTANCE: (Change in contact resistance of Al bonds, 1000 hours at 150°C)			
	8836-A	Insignificant	
EUTECTIC DIE BONDING:		Excellent	
COMPATIBILITY:	ESL 3900, 39	80, R-300-A and D-R-300-B	
	E	SL 4905-C, 4905-CH, 4911	

8836/A 9711-E

CAUTION: Proper industrial safety precautions should be exercised in using these products. Use with adequate ventilation. Avoid prolonged contact with skin or inhelation of any vapors emilied during use or heating of these compositions. The use of safety eye goggles, gloves or hand protection creams is recommended. Wash hands or skin throughly with scap and water after using these products. Do not eat or arroke in areas where these makerias are used. Refer to appropriate MDDS sheet.

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6. (ESL 400) used for organic vehicle in PZT pastes



VEHICLE

400

RoHS Compliant*

ESL 400 Vehicle is used as an additive to ESL pastes in order to reduce viscosity without losing paste performance.

PRODUCT DATA

Rheology:

Syrup-like consistency

Viscous liquid

Appearance:

PROCESSING

Addition to paste:

stirred in as required to lower viscosity

(usually up to 2% is used, however more may be used if the final product suits the application)

	ESL Europe 400 Vehicle 1211-A
ESL Affiliates	
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	See Caution and Dischaimer on next page.

7. Protective polymer coating (ESL 244-T) used for polyester sacrificial layer



PROTECTIVE POLYMER COATING

244-T

RoHS Compliant*

ESL 244-T is a screen-printable resin coating. This coating may be used to protect silver polymer on glass substrates.

PASTE DATA

Rheology:	Thixotropic, screen-printable paste
Viscosity: (Brookfield RVT, 10 rpm No. 7 spindle, 25.5 ± 0.5 °C)	100 ± 20 Pa.s
Shelf Life (20 - 25 °C):	6 months
PROCESSING	
Screen Mesh, Emulsion:	200 S/S, 38 μm
Curing Schodulou	125°C / 5 15 min
curring schedules.	125 67 5 - 15 1111
Substrate for Calibration:	Glass
Thinner:	ESL 110

ESL Europe 244-T 0705-A

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See Caution and Disclaimer on other side.

TYPICAL PROPERTIES

Cured Thickness: (1 layer measured on glass)

Approximate Coverage:

10 - 15 μm 120 cm²/g

ESL Europe 244-T 0705-A

*None of the six substances referred to in the RoHS Directive (2002/95/EC) are used in the formulation of this product.

CAUTION: Proper industrial safety precautions should be exercised in using these products. Use with adequate ventilation. Avoid prolonged contact with skin or inhalation of any vapours emitted during use or heating of these compositions. The use of safety eye goggles, gives or hand protection creams is recommended. Wash hands or skin thoroughly with scep and water after using these products. Do not eat or smoke in areas where these materials are used. Refer to appropriate MSDS sheet.

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8. Epoxy (ESL CV 59) used for mixing in corn starch/epoxy based paste sacrificial layer



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FICHE DE DONNÉES DE SÉCURITÉ Nº 375

RÈGLEMENT: RÉVISION: DATE DE REDACTION: DATE D'IMPRESSION:

CE No. 1907/2006, Article 31 2 01.06.2015 02.03.2018

SECTION 1: IDENTIFICATION DE LA SUBSTANCE/DU MÉLANGE ET DE LA SOCIÉTÉ/L'ENTREPRISE

1.1 Identificateurs de produit

Liant CV59

1.2 Utilisations identifiées pertinentes de la substance ou du mélange et utilisations déconseillées

Solvant

1.3 Renseignements concernant le fournisseur de la fiche de données de sécurité

ESL Europe (Agmet Ltd) 8 Commercial Road Reading Berkshire RG2 0QZ Royaume-Uni.

Adresse e-mail: sds@esleurope.co.uk

1.4 Numéro d'appel d'urgence

UK: 0118 918 2400 International: +44 118 918 2400

Lundi - vendredi 8h00 à 16h30 (heure anglaise) Langue anglaise

SECTION 2: IDENTIFICATION DES DANGERS

2.1 Classification de la substance ou du mélange

Classification en accord avec la réglementation (EC) No 1272/2008

Cette substance n'est pas classée comme dangereuse selon la législation de l'Union européenne.

Agmet Ltd commerçant en tant que ESL Europe Domiciliation: 8 Commercial Road, Reading, Berkshire. RG2 0QZ. Royaume-Uni, No. 1494424

2.2 Contenue d'étiquette

Etiquetage en accord avec la réglementation (CE) No 1272/2008

N'est pas une substance dangereuse selon le SGH.

2.3 Autres dangers

L'évaporation des solvants durant les étapes de sérigraphie et de séchage

SECTION 3: COMPOSITION/INFORMATIONS SUR LES COMPOSANTS

Nature chimique: Résine époxy dispersée dans un solvant organique

3.1 Substance

Sans objet

3.2 Mélange

Réglementation (CE) No 1272/2008

CAS	NOM CHIMIQUE	%	CLASSIFICATION
N/D	Résine époxy	15 - 40	N/D
124-17-4	Acétate de Butyle diglycol	60 - 85	N/D

SECTION 4: PREMIERS SECOURS

4.1 Description des premiers secours

INHALATION	Déplacer la personne à l'air frais.
INGESTION	Rincer abondamment la bouche avec de l'eau. Solliciter des soins médicaux.
CONTACT AVEC LA PEAU	Laver les régions affectées avec de l'eau. Retirer les vêtements et chaussures contaminés.
CONTACT AVEC LES YEUX	Laver les régions affectées avec de l'eau. Oter les lentilles de contact. Solliciter des soins médicaux.

4.2 Principaux symptômes et effets, aigus et différés

INHALATION	Irritation des voies respiratoires.
INGESTION	Problèmes gastriques tels que vomissements, diarrhées ou
	douleurs abdominales.
CONTACT AVEC LA PEAU	Irritation de la peau.
CONTACT AVEC LES YEUX	Irritation des veux.

4.3 Indication des éventuels soins médicaux immédiats et traitements particuliers nécessaires

Aucun

SECTION 5: MESURES DE LUTTE CONTRE L'INCENDIE

5.1 Moyens d'extinction

Dioxyde de carbone (CO2), mousse, poudre sèche.

5.2 Dangers particuliers résultant de la substance ou du mélange

Aucun

5.3 Conseils aux pompiers

Aucun

SECTION 6: MESURES À PRENDRE EN CAS DE DISPERSION ACCIDENTELLE

6.1 Précautions individuelles, équipement de protection et procédures d'urgence

S'équiper de gants et vêtements de protection. Eviter de respirer les vapeurs. .

6.2 Précautions pour la protection de l'environnement

Eviter la pénétration dans les égouts et les eaux potables.

6.3 Méthodes et matériel de confinement et de nettoyage

Nettoyer dès que possible tout épandage, en le récoltant au moyen d'un produit absorbant. Eliminer le produit conformément aux réglementations locales. Utiliser des conteneurs de rejet adéquats.

6.4 Référence à d'autres sections

Section 13 - Considérations relatives à l'élimination

SECTION 7: MANIPULATION ET STOCKAGE

7.1 Précautions à prendre pour une manipulation sans danger

Utiliser dans un environnement bien ventilé et éviter de respirer les vapeurs. S'équiper de vêtements de protection et de gants en caoutchouc et éviter tout contact avec la peau ou les yeux. Conserver à l'abri de toute source de chaleur. Ne pas manger, boire, fumer ou se maquiller durant l'utilisation de ce produit. Se laver les mains après utilisation. Les vêtements de travail doivent être lavés et rangés séparément des vêtements personnels. Ne pas respirer les vapeurs lors du séchage / cuisson.

7.2 Conditions d'un stockage sûr, y compris d'éventuelles incompatibilités

Conserver dans un récipient hermétiquement fermé. Garder au sec. Entreposer à la température ambiante

7.3 Utilisation(s) finale(s) particulière(s)

Uniquement pour celle détaillée Section 1.2

SECTION 8: CONTRÔLES DE L'EXPOSITION/PROTECTION INDIVIDUELLE

8.1 Paramètres de contrôle

Aucun

8.2 Contrôles de l'exposition

A manipuler conformément aux normes d'hygiène industrielle et aux consignes de sécurité. Le produit ne doit être utilisé que dans des endroits bien ventilés avec aspiration vers l'extérieur. Toujours se laver les mains soigneusement après utilisation.

Protection des yeux et du visage: Lunettes anti-éclaboussures ou des lunettes de sécurité conformes EN 166

Protection de la peau: Porter des gants de protection pour éviter tout contact de la peau.

Protection du corps :

Se vêtir de vêtements de travail afin d'éviter toute souillure des effets personnels. Ces vêtements de travail doivent être lavés et rangés séparément des vêtements personnels.

Protection respiratoire: En cas de ventilation insuffisante, porter un appareil respiratoire approprié.

SECTION 9: PROPRIÉTÉS PHYSIQUES ET CHIMIQUES

9.1 Informations sur les propriétés physiques et chimiques essentielles

a) Aspect	Uniforme, pâte visqueuse
b) Odeur	Très douce
c) Seuil olfactif	donnée non disponible
d) pH	donnée non disponible
e) Point de fusion/point de congélation	donnée non disponible
f) Point initial d'ébullition et intervalle d'ébullition	246 °C (du solvant pur contenu dans la pâte.)
g) Point d'éclair	115 °C - (Cleveland en vase ouvert - du solvant pur contenu dans la pâte)
 h) Taux d'évaporation donnée non disponible 	donnée non disponible

Nom du produit: Llant CV59

i) Inflammabilité (solide, gaz)	donnée non disponible
 j) Limites supérieure/inférieure d'inflammabilité ou d'explosivité 	donnée non disponible
k) Pression de vapeur	donnée non disponible
I) Densité de vapeur	donnée non disponible
m) Densité relative	donnée non disponible
n) Hydrosolubilité	donnée non disponible
 o) Coefficient de partage: n-octanol/eau 	donnée non disponible
 p) Température d'autoinflammabilité 	donnée non disponible
 q) Température de décomposition 	donnée non disponible
r) Viscosité	donnée non disponible
s) Propriétés explosives	donnée non disponible
t) Propriétés comburantes	donnée non disponible

9.2 Autres informations concernant la sécurité

Aucun

SECTION 10: STABILITÉ ET RÉACTIVITÉ

10.1 Réactivité Présente peu ou pas de réactivité avec les acides, bases ou agents oxydants.

10.2 Stabilité chimique

Stable dans les conditions de stockage recommandées.

10.3 Possibilité de réactions dangereuses Donnée non disponible

10.4 Conditions à éviter Donnée non disponible

10.5 Matières incompatibles Donnée non disponible

10.6 Produits de décomposition dangereux Donnée non disponible

SECTION 11: INFORMATIONS TOXICOLOGIQUES

11.1 Informations sur les effets toxicologiques

Toxicité spécifique pour certains organes cibles: exposition unique exposition répétée

donnée non disponible donnée non disponible
Danger par aspiration

donnée non disponible

SECTION 12: INFORMATIONS ÉCOLOGIQUES

12.1 Toxicité Donnée non disponible

12.2 Persistance et dégradabilité Donnée non disponible

12.3 Potentiel de bioaccumulation Donnée non disponible

12.4 Mobilité dans le sol Donnée non disponible

12.5 Résultats des évaluations PBT et VPVB Donnée non disponible

12.6 Autres effets néfastes Donnée non disponible

SECTION 13: CONSIDÉRATIONS RELATIVES À L'ÉLIMINATION

13.1 Méthodes de traitement des déchets

Produit / Emballages

Eliminer ce produit et son récipient dans un centre de collecte des déchets dangereux ou spéciaux. Détruire conformément aux règlements de sécurité locaux/nationaux en vigueur. Ce produit chimique peut être brulé dans un incinérateur chimique équipé d'un système de postcombustion et d'épuration. Eliminer les emballages en tant que produit non utilisé.

SECTION 14: INFORMATIONS RELATIVES AU TRANSPORT

14.1 Numéro ONU

ADR/RID, IMDG & IATA: Classé non dangereux au sens des réglementations de transport.

14.2 Nom d'expédition des Nations unies

ADR/RID:	Marchandise non dangereuse
IMDG:	Marchandise non dangereuse
IATA:	Marchandise non dangereuse

14.3 Classe(s) de danger pour le transport

ADR/RID, IMDG & IATA: Classé non dangereux au sens des réglementations de transport.

14.4 Groupe d'emballage

ADR/RID, IMDG & IATA: Classé non dangereux au sens des réglementations de transport maritime et aérien. 14.5 Dangers pour l'environnement ADR/RID: non IMDG Marine pollutant: non IATA: non

14.6 Précautions particulières à prendre par l'utilisateur Donnée non disponible

SECTION 15: INFORMATIONS RÉGLEMENTAIRES

Cette fiche de données de sécurité est conforme aux exigences du Règlement (CE) n ° 1907/2006.

15.1 Réglementations/législation particulières à la substance ou au mélange en matière de sécurité, de santé et d'environnement Donnée non disponible

15.2 Évaluation de la sécurité chimique Donnée non disponible

SECTION 16: AUTRES INFORMATIONS

Formation

Les utilisateurs doivent être formés à la manipulation du produit et de tous les produits ou équipements associés.

Information supplémentaire

La fiche technique de ce produit est disponible.

Les informations présentes dans ce document sont extraites des ouvrages REACH et de l'expérience acquise par ESL Europe sur le produit.

Appendix A-2: Particle sizes of powders



1. Pz26 (Ferropern)

Raw material, D (0.5) \approx 11 µm (tested at ICMCB).



Milled powder with Planetary mill, D (0.5) \approx 0.4 µm with agglomeration, and milled powder with Attritor mill, D (0.5) \approx 0.6 µm with dispersion (tested at LUCAC).

2. Li₂CO₃ (Sigma Aldrich)



Raw material, D (0.5) \approx 7.5 µm (tested at MTEC).



Milled powder with Planetary mill, D (0.5) \approx 4.6 µm (tested at MTEC).

3. Bi₂O₃ (Sigma Aldrich)



Raw material, D (0.5) \approx 8.4 µm (tested at MTEC).



Milled powder with Planetary mill, D (0.5) \approx 2.5 µm (tested at MTEC).

4. Planetary Milled CuO (Sigma Aldrich)







Appendix A-3: Rheology of some used pastes

The flow behaviors of the homemade PZT pastes and some commercial pastes are observed by a rheometer (ANTON PAAR MCR302) with a PP25 parallel-plate measuring system at 23°C (Figure I). All pastes exhibit decreasing viscosity with increasing shear rates as shown in Figure II. This flow behavior is called pseudo-plastic or shear-thinning which is a typical behavior of the screen-printing pastes. For fabrication of the cantilever transducers, two PZT pastes with the same compositions, but different viscosity (due to different organic vehicle contents) need to be prepared for fabrication of movable and anchor parts. This is because both parts are printed with different screen kinds. The movable part needs smoother surface and thicker thickness compared to the anchor part.



Figure I (a) The rheometer (ANTON PAAR MCR302) of Elorprintec, Pessac and (b) its structure according to information from the manufacture.



Figure II Viscosity of some pastes used in this work (Measurement at 25°C with PP-25 rheometer).

Appendix A-4: Screen-printing conditions

The screen-printing conditions for deposition each layer structure by DEK machine are presented in Table I-II.

Printed layer	Fidmoial	Sacrificial	Bottom	Piezoelect	Тор	
Parameter	Flauciai	layer	electrode	Paste A Paste B and C		electrode
Screen type	М	М	М	S	S	М
Squeegee type	U	U	U	Stain	Stainless steel	
Shim thickness (µm)	250	250	300	300	300	400
Board thickness (mm)	3.1	3.1	3.2	2.6	2.6	3.3
Print gap (mm)	0.7	0.7	0.7	0	0	0.7
Front speed (mm/s)	20	20	20	20	60	20
Front pressure (kg)	2	2	2	2	3	2
Separation speed (mm/s)	1	1	1	1	20	1
Flood height (mm)	0.3	0.3	0.3	5	5	0.3

Table I Printing parameters of the disk structure

Remarks: (1) M is mesh screen. (2) S is stencil screen. (3) U is a polyurethane squeegee (angle of 60°). (4) An angle of stainless steel and polyurethane squeegees are 45° each.

 Table II Printing parameters of the cantilever structures (the PZT pastes are prepared from milled PZT powders)

Printed layer Parameter	Fiducial	Piezoelectric anchor	Sacrificial layer	Bottom electrode	Piezoelectric layer (cantilever)	Top electrode
Screen type	М	М	М	М	S	М
Squeegee type	U	U	U	U	Stainless steel	U
Shim thickness (µm)	250	250	250	300	300	400
Board thickness (mm)	3.1	3.1	3.1	3.2	2.6	3.3
Print gap (mm)	0.7	0.7	0.7	0.7	0	0.7
Front speed (mm/s)	20	20	20	20	60	20
Front pressure (kg)	2	2	2	2	3	2
Separation speed (mm/s)	1	1	1	1	20	1
Flood height (mm)	0.3	0.3	0.3	0.3	0.3	0.3

Remarks: (1) M is mesh screen. (2) S is stencil screen. (3) U is a polyurethane squeegee. (4) An angle of stainless steel and polyurethane squeegees are 45° each.

Appendix B: For Chapter 3 and 4

Appendix B-1: Electrical connection for printed resonators

The electrical connection with Ag-epoxy (ESL1901) based paste (glue) and wires may affect piezoelectric properties of the resonators. Thus, before choosing the type of electrical connections, we did experiments to check their impacts on the electromechanical properties. Commercial disks from PI ceramic company (PRYY+1113) have been chosen for this study because their size are close to our printed disk resonators. The electrical connections are prepared for three alternatives as presented in Table III. In each case, the wire position is in the center of the electrode. The results are shown in Table IV and Figure III-IV.

Table II	Table III Case study for studying effects of electrical connections on prezoelectric properties								
Case	Wire material	Wire diameter (µm)	Glue size	Glue position					
Ι	Ag	100	< 1 mm (a drop, small size)	Middle					
II	Pt	50	< 1 mm (a drop, small size)	Middle					
III	Pt	50	> 1 mm (two drops, big size)	Middle					

Table III Case study for studying effects of electrical connections on piezoelectric properties

able iv Effects of connection of electrical properties of F1 connectal disk (FK11+1115)								
Case	Qm	Resonant frequency (kHz)	k _{eff} (%)	k _p (%)	Distance between the Y axis and the left hand of the admittance circle, $1/R_{\theta}$ (µS)	Cp (nF)		
Ι	186	228	48	54	6.5	3		
II	156	227	47	53	8.0	2		
III	157	229	46	52	22.0	3		
Datasheet (referent values)		227*	-	56*	-	-		

Table IV Effects of connection on electrical properties of DL commercial disk (DDVV+1112)

Remarks

1. Outer diameter of PI disk = 10 mm, thickness of PI disk = 0.2 mm.

2. *The actual value can deviate by ± 5 % (below 2000 kHz) or ± 10 % (from 2000 kHz).

1. Study on effect of the wires nature and size (comparison between Case I and Case II)

The wider diameter of Ag wires gives the larger admittance circle and lower dielectric loss compared to Pt wires with smaller diameter. This means that both diameter and nature of the wires (the Pt wire is stiffer than the Ag wire) affect the final measurement. However, piezoelectric properties of this connection is still in the range of the referent values and other connections.

2. Study on effect of the glue drop size (comparison between Case II and Case III)

Slight changes in Q_m , f_r , and k_p values are observed when depositing a bigger glue drop (differences < 2%). For the small drop size of glue, f_r and k_p values are similar and slightly lower than reference values reported in the datasheet. For bigger drop value, a small effect on the resonator behavior is shown. These results comfort us on the choice of these connections for the characterizations of our printed disks. To conclude, no significant impact on the mechanical damping results indeed from the connection with the small drop and the 50-µm-Pt wire.



Figure III Impedance spectrum of PI commercial disks with different diameter of wire and glue paste compared to Samples in this work.



Figure IV Admittance circles of PI commercial disks with different diameter of wires and glue paste.

Appendix B-2: Electrical model and polynomial fit

When a piezoelectric resonator is electrically operated at its resonant frequency, the output mechanical and the energy conversion efficiency reach the maximum value. Near the resonant frequency, the piezoelectric resonator can be represented by an electrical equivalent circuit, as shown in Figure V(a). This circuit can be divided into two parts: one is the electric part, and the other is mechanical branch (the part surrounded by red dotted lines). R_0 , and C_0 are the dielectric loss resistance and the clamped capacitance of the piezoelectric transducer, respectively. While R_1 , L_1 , and C_1 are the equivalent mechanical resistance, inductor, and capacitance arising from the mechanical vibration, respectively. R_1 is composed of two parts: one is internal mechanical loss of the transducer and the other is the load mechanical resistance [1]. This circuit is related to the admittance Y (via $2\pi f = \omega$), as shown in Figure V(b).



Figure V Diagrams for (a) the equivalent circuit of piezoelectric resonator (Adapted from [2]), and (b) the admittance circle of piezoelectric resonator (Adapted from [3] and noted that f_0 is the maximum frequency of G, f_1 and f_2 are the frequencies of the half G, f_r is the resonant frequency, and f_a is the antiresonant frequency.), and the admittance circle of series LCR in mechanical branch (Adapted from [4] and noted that in this case f_0 reaches to f_r .).

$$Y = \frac{1}{R_1 + jL_1\omega + \frac{1}{jC_1\omega}} + \frac{1}{R_0} + jC_0\omega$$
 eq. I

where Y is the total admittance of the model, ω is the angular frequency.

The conductance (G) which is a real part of Y is defined in eq. II-III.

$$G = \frac{R_1}{R_1^2 + \left(L_1\omega - \frac{1}{C_1\omega}\right)^2} + \frac{1}{R_0} = \frac{R\omega^2}{\left(R_1^2 - \frac{L_1}{C_1}\right)\omega^2 + L_1^2\omega^4 + \frac{1}{C_1^2}} + \frac{1}{R_0}$$
eq. II

$$G = \frac{\frac{C_1 \omega^2}{Q \omega_1}}{\left(\frac{1}{Q^2} - 2\right) \frac{\omega^2}{\omega_1^2} + \frac{\omega^4}{\omega_1^4} + 1} + \frac{1}{R_0}$$
eq. III

where the quality factor is $Q = \frac{1}{R_1} \sqrt{\frac{L_1}{C_1}}$ and the angular pulsation is $\omega_1 = \frac{1}{\sqrt{L_1 C_1}}$.

The susceptance (B) which is imaginary part of Y is defined in eq. IV.

$$B = \frac{C_1 \omega \left(1 - \frac{\omega^2}{\omega_1^2}\right)}{\left(1 - \frac{\omega^2}{\omega_1^2}\right)^2 + \frac{\omega^2}{Q^2 \omega_1^2}} + C_0 \omega \qquad \text{eq. IV}$$

If the complete electrical circuit is considered, the position of the circle is shifted according to the values of R_0 and C_0 , as shown in Figure V(b).

The quality factor (Q) corresponding to the resonant frequency is defined in eq. V., when f_1 and f_2 are the frequencies of the half of conductance, G.

$$Q = \frac{f_0}{|f_1 - f_2|}$$
 eq. V

In the case of $1/R_0$ reaches to zero (dielectric losses is very small) related to Figure V(c), the conductance *G* as a function of the frequency (*f*) can be determined as in eq. VI, where the mechanical resonant frequency f_0 and the quality facror *Q* are defined respectively by $f_0 = 1/2\pi\sqrt{L_1C_1}$ and $Q = 2\pi f_0 R_1/L_1$. In order to extract the resonant frequency, a Taylor expansion is used in eq.VI that gives the eq. VII. A parabolic polynomial fit is used on the raw data at the vicinity of the resonance. The fitting coefficients a_G , b_G , and c_G are identified to the members of eq. VIII to find f_0 for more than one order of magnitude by eq. VIII [5]. Examples of the polynomial fit (f_0 , f_{it}) is slightly higher than this value of the raw result (f_0) [5]. The noise (standard deviation, σ) has been reduced.

$$G(f) = \frac{\frac{2\pi C_1 \omega f^2}{Qf_0}}{1 + \left(\frac{1}{Q^2} - 2\right)\frac{f^2}{f_0^2} + \frac{f^4}{f_0^4}}$$
eq. VI

where ω/ω_1 associated with $2\pi f = \omega$ is considered.

$$G(f)_{f \to f_0} \approx 2\pi C_1 Q f_0 \left(1 - 4Q^2 + 8Q^2 \frac{f}{f_0} - 4Q^2 \frac{f^2}{f_0^2} \right) + \cdots$$
 eq. VII

$$G(f)_{f \to f_0} \approx a_G + b_G f + c_G f^2 + \cdots$$
 eq. VIII



Figure VI Examples of the polynomial fit used for decreasing noise in (a) the conductance peak, (b) zoom on the conductance peak (c) the resonant frequency spectra [5].

Appendix B-3: Commercial sensor and calibration vapor generator

1. Datasheet of the commercial Fifaro gas sensor



PRODUCT INFORMATION

TGS 2602 - for the detection of Air Contaminants

Features:

- * High sensitivity to VOCs and odorous gases
- * Low power consumption
- * High sensitivity to gaseous air
- contaminants
- * Long life
- * Uses simple electrical circuit
- * Small size

The sensing element is comprised of a metal oxide semiconductor layer formed on the alumina substrate of a sensing chip together with an integrated heater. In the presence of detectable gas, sensor conductivity increases depending on gas concentration in the air. A simple electrical circuit can convert the change in conductivity to an output signal which corresponds to the gas concentration.

The TGS 2602 has high sensitivity to low concentrations of odorous gases such as ammonia and H2S generated from waste materials in office and home environments. The sensor also has high sensitivity to low concentrations of VOCs such as toluene emitted from wood finishing and construction products.

Due to miniaturization of the sensing chip, TGS 2602 requires a heater current of only 58mA and the device is housed in a standard TO-5 package.

The figure below represents typical sensitivity characteristics, all data having been gathered at standard test conditions (see reverse side of this sheet). The Y-axis is indicated as sensor resistance ratio (Rs/Ro) which is defined as follows:

Rs = Sensor resistance in displayed gases at various concentrations Ro = Sensor resistance in fresh air Applications: * Air cleaners

- * Ventilation control
- * Air quality monitors
- * VOC monitors
- * Odor monitors



The figure below represents typical temperature and humidity dependency characteristics. Again, the Y-axis is indicated as sensor resistance ratio (Rs/Ro), defined as follows:

Rs = Sensor resistance in fresh air at various temperatures/humidities Ro = Sensor resistance in fresh air at 20°C and 65% R.H.

Sensitivity Characteristics:

Temperature/Humidity Dependency:



IMPORTANT NOTE: OPERATING CONDITIONS IN WHICH FIGARO SENSORS ARE USED WILL VARY WITH EACH CUSTOMER'S SPECIFIC APPLICATIONS. FIGARO STRONGLY RECOMMENDS CONSULTING OUR TECHNICAL STAFF BEFORE DEPLOYING FIGARO SENSORS IN YOUR APPLICATION AND, IN PARTICULAR, WHEN CUSTOMER'S TARGET GASES ARE NOT LISTED HEREIN, FIGARO CANNOT ASSUME ANY RESPONSIBILITY FOR ANY USE OF ITS SENSORS IN A PRODUCT OR APPLICATION FOR WHICH SENSOR HAS NOT BEEN SPECIFICALLY TESTED BY FIGARO.

187

85% R.H. 65% R.H.

60

Basic Measuring Circuit:

The sensor requires two voltage inputs: heater voltage (VH) and circuit voltage (Vc). The heater voltage (VH) is applied to the integrated heater in order to maintain the sensing element at a specific temperature which is optimal for sensing. Circuit voltage (Vc) is applied to allow measurement of voltage (VOUT) across a load resistor (RL) which is connected in series with the sensor. DC voltage is required for the circuit

voltage since the sensor has a polarity. A common power supply circuit can be used for both Vc and VH to fulfill the sensor's electrical requirements. The value of the load resistor (RL) should be chosen to optimize the alarm threshold value, keeping power consumption (Ps) of the semiconductor below a limit of 15mW. Power consumption (Ps) will be highest when the value of Rs is equal to RLon exposure to gas.



Structure and Dimensions:

Specifications:

Mode	l number	TGS2602-B00			
Sensin	g principle		MOS type		
Standar	rd package		TO-5	metal can	
Targe	et gases	Air co (VOCs, am	ntaminants monia, HzS, etc.)		
Typical de	tection range		1 ~ 30p	opm of EtOH	
Standard circuit conditions	Heater voltage	νн	5.0±0	2V AC/DC	
	Circuit voltage	Vc	5.0±0.2V DC	Ps≤15mW	
	Load resistance	RL	variable	0.45kΩ min.	
	Heater resistance	Rн	approx 59Ω at room temp. (typical)		
Flashing	Heater current	Ін	56±5mA		
characteristics under standard test	Heater power consumption	Рн	280mW (typical)		
conditions	Sensor resistance	Rs	10kΩ ~	100kΩ in air	
	Sensitivity (change ratio of Rs)		0.08~0.5	Rs (10ppm of EtOH) Rs air	
	Test gas conditions		normal air at 20±2°C, 65±5%RH		
Standard test conditions	Circuit conditions		Vc = 5.0±0.01V DC VH = 5.0±0.05V DC		
	Conditioning period before test		7 days		

The value of power consumption (Ps) can Sensor resistance (Rs) is calculated with be calculated by utilizing the following formula:

a measured value of VOUT by using the following formula:

$$P_{S} = \frac{(V_{C} - V_{RL})^{2}}{R_{S}} \qquad \qquad R_{S} = (\frac{V_{C}}{V_{RL}} - 1) \times R_{L}$$

For information on warranty, please refer to Standard Terms and Conditions of Sale of Figaro USA Inc. All sensor characteristics shown in this brochure represent typical characteristics. Actual characteristics vary from sensor to sensor. The only characteristics warranted are those in the Specification table above. REV: 06/15



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2. Datasheet of Figaro SR-D1A electronic card

FIGARO

SPECIFICATION FOR SR-D1A

1. Function of SR-D1A Test Unit

The SR-D1A Test Unit is designed to perform the testing and evaluation of both TGS Gas Sensors and Figaro Gas Sensor Modules. By connecting this unit to a 100~240V (AC) power supply, a sensor output signal (VRL) can be obtained which corresponds to a concentration of test gas in ambient air. From this output voltage, sensor resistance (Rs) can be calculated. In addition, by setting a reference voltage (Vref), an H-L level signal can be output. By using an H-L output signal, this unit can be used to control an external apparatus.

2. Dimensions

The dimensions of SR-D1A can be seen in Figure 1.

3. Specifications

Item	SR-D1A			
Product Name	Test unit			
Power	100~240VAC			
Power consumption	Sensors : approx 1.6W Modules: approx. 1.6W			
Power output	Internal: 5V±5% 300mA			
RL	Variable			
Reference Voltage (VREF)	1.0~4.5V DC			
Operating temperature	-10°~+50°C			
Dimensions	125 x 74 x 32mm			
Weight	Main unit: approx 76g AC adaptor: approx 70m			

Table 1 - Specifications of SR-D1A

NOTE: Please specify plug type when ordering: A-type - North America, Japan C-type - Europe





Fig. 1 - Dimensions of SR-D1A (u/m = mm)

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FIGARO

SPECIFICATION FOR SR-D1A

4. Dip Switch (SW1) Settings

According to the type of item to be tested, dip switches (SW1) should be set according to Table 2:

Text Sample	Sachat Din Switch Sattings		T1							
Test Sample	Socket	n Dip Switch Settings		2	3	4	5	RL+	RL-	
TGS8xx	SK1	1 = OFF		Ver		Vere		Comm	act Dr	
TGS26xx	SK2	2,3,4 = ON		VILL	H-L	VALP		Com	BUIKL	
LPM2610, NGM2611	CNI	1 = ON 2,3,4 = OFF	+5V	Vour	VREF	VH (GND)	GND			
Other modules*	CN1 1,2,3,4 = OFF		Refe	r to spec o module	of each		No RL co	onnection		
AMSxxxx	CN2			VOUT	NC	NC				

Table 2 - Dip switch (SW1) settings for SR-D1A

5. Circuit Diagram

The circuit diagram of SR-D1A is sown in Figure 2.



Fig. 2 - Circuit Diagram of SR-D1A

6. Operating Instructions

- 5-1) Prepration
- Step 1 Connect AC power plug to socket JK-1
- Step 2 Set dip switches according to Table 2
- Step 3 Insert test sample into the proper socket as indicated in Table 2 (Note: multiple test samples cannot be measured at the same time)
- Step 4 For TGS8xx and TGS26xx, connect a load resistor (RL) between terminals RL+ and RL- of T1. The nearest resistance value to sensor resistance in target gas concentration

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is recommended for selecting RL. Step 5 - Connect AC plug to AC power

5-2) VRL measurement

After AC power is on, the green LED on the test unit will light and the test sample will be powered. Connect voltage measuring equipment (such as a digital multi-meter) between No. 2 (VRL) and No. 5 of Terminal 1.

Note: The pre-heating period before stabilization is different according to the test sample. For the required pre-heating period, please refer to each sensor's product information.

2

FIGARO

5-3 Adjustment of reference voltage (VREF)

Check that VREF fails within the range of 1.0~4.5V DC. If VREF<1.0V, choose a larger RL value. If VREF>4.5V, choose a smaller RL value.

Once VREF has been checked, connect voltage measuring equipment (such as a digital multi-meter) between No. 4 and No. 5 of Terminal 1. The adjust the VREF to the target thresghold by rotating an adjustable load resistor VR1 (VREF will increase as VR1 is rotated clockwise).

5-4 H-L signal

Connect a fixed $1M\Omega$ resistor between No. 3 and No. 4 of Terminal 1 to avoid chattering. Then, connect voltage measuring equipment (such as a digital multimeter) between No. 3 and No. 5 of Terminal 1. Once this is done, TTL signal of "H" or "L" will be output. If VRL<VREF, 'H" will be output. If VRL>VREF, then "L" will be output.

The H-L signal can be used as a control signal by connecting circuits such as those shown in Figs. 3a-3d to No. 1, No.3, and No. 5 of Terminal 1. In these cases, the control signal will initiate action by each of the circuit components to indicate an "H" signal (e.g. when using an LED, the LED will light up when an "H" signal is output...when using a buzzer, the buzzer will sound when "H" is output).

5-5 Calculation of sensor resistance (Rs) The following formula can be used to calculate Rs:

$$Rs = \frac{Vc - VRL}{VRL} \times RL$$

In the test unit, it is designed that Vc should be 5.0V±5 DC when AC100-240V is applied. For actual Vc measurement, connect measuring equipment to No.1 and No.5 of Terminal 1.



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3

SPECIFICATION FOR SR-D1A

3. Figaro sensor connection



Figure VII Figaro sensor in its closed cell.



Figure VIII Figaro sensor and thermometer/hygrometer connected with Arduino programmed by codes to display resistance, temperature, humidity, and time. To be noticed that these parameters are recorded by Labview program.

4. Example of responses of commercial sensors under VOCs



Figure IX Responses of the Figaro sensor (measured resistance) and Thermometer (measured temperature) under a concentration sequence of toluene vapor. Figaro tests are led under nitrogen flow. However, as the semiconductor oxide used in the Figaro sensor needs to be operated under air, the changes in resistance amplitude are not reliable. These changes are just an indicator on concentration changes.

Appendix B-4: Vapor generator (Calibrage, PUL110)

1. Calculation of permeation rate

Steps used in calculation

- 1. Measuring initial mass of a target (in a liquid state) before and after heating with constancy of temperature, nitrogen flow rate, and nitrogen dilution flow
- 2. Calculating the mass difference (ng) for a heated period (min)
- 3. Calculating the permeation rate (ng/min), and vapor concentration (mg/m³)
- 4. Converting the vapor concentration unit from mg/m³ into ppmv

Used equations

$$Permeation \ rate = \frac{\Delta w}{\Delta t}$$
eq. X

where Δw is mass difference (ng) and Δt is time difference (min)

$$Vapor \ concentration \ = \ \frac{Permeation \ rate}{Nitrogen \ flow}$$
eq. XI

$$Concentration_{ppmv} = Concentration_{\frac{mg}{m^3}} \times K$$
eq. XII

where K = 24.46/Molecular weight of target vapor

Dor	Total mass	∆w	∆t	Permeation rate	Nitrogen flow	Vapor con	centration
Day	(g)	(g)	(min)	(ng/min)	(mL/min)	(mg/m^3)	(ppmv)
1	914.16	-	-	-	100	-	-
2	912.40	1.76	1440	1222222	100	12222	3245
3	910.72	1.68	1440	1166667	100	11667	3097
4	909.12	1.60	1442	1109570	100	11096	2946
5	907.50	1.62	1437	1127349	100	11273	2993
6	905.82	1.68	1438	1168290	100	11683	3101
7	904.20	1.62	1446	1120332	100	11203	2974
8	902.06	1.60	1437	1113431	100	11134	2956
9	901.08	1.52	1436	1058495	100	10585	2810
10	899.62	1.46	1440	1011080	100	10111	2684
						Average	2978

2. Example of information for calculation of toluene permeation rate

Remarks:

1. Total mass is summation of target mass (in the liquid state), a permeation tube, and a permeation cover.

2. Molecular weight of toluene is 92.14 g/mol.

3. The average of vapor concentration (ppmv) is the initial vapor concentration for PUL110 setting.

4. These results are obtained from generation vapor at 80°C.

VOCs	Temperature for vapor generation (°C)	Nitrogen flow (mL/min)	Initial mass (g)	Initial vapor concentration (ppmv)
Water	80	100	922.02	15508
Ethanol	60	100	913.78	7278
Benzene	50	100	913.74	2956
	60	100	912.06	4081
Toluene	80	100	914.16	2978

3.	Set	parameters	for	generating	V(C	s in	this	worl	k
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Remark: Initial mass is summation of initial mass of target (in the liquid state), permeation tube, and permeation cover.

Appendix B-5: The electrical power's influence on noise in conductance spectra



Figure X Conductance spectra of the $6 \times 1 \times 0.1 \text{ mm}^3$ cantilever resonator measured by the Agilent E5063B network analyzer for the in-plane axial longitudinal vibration mode. To be noticed that this printed resonator is connected to platinum wires and measured by the network analyzer directly. One spectrum measurement takes 16 s.

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Academic outcomes

□ Article publications

Santawitee, O., Grall, S., Chayasombat, B., Thanachayanont, C., Hochart, X., Bernard, J., Debéda, H. (2020). Processing of printed piezoelectric microdisks: effect of PZT particle sizes and electrodes on electromechanical properties. *Journal of Electroceramics*, 44(1), 41-51.

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Rua Taborda, M.I., Elissalde, C., Chung, U.C., Maglione, M., Fernandes, E., Salehian, A., Santawitee, O., Debéda, H. (2020). Key features in the development of unimorph Stainless Steel cantilever with screen-printed PZT dedicated to energy harvesting applications. *International Journal of Applied Ceramic Technology*, 1-12, doi.org/10.1111/ijac.13588.

Debéda, H., Rua Taborda, M.I., Santawitee, O., Grall, S., Maglione, M., Chung, U.C., Elissalde, C. (2020), Role of sacrificial and/or protective layers to improve sintering of electroactive ceramics: Application to piezoelectric PZT printed thick films for MEMS. *Ceramics*, 3(4), 453-475.

□ Article Conferences

Chayasombat, B., Muensri, P., Klinthongchai, Y., Inpor, K., Santawitee, O., Debéda, H., Thanachayanont, C. and Prichanont, S. (2020). Characterization of Mesoporous Silica and its Application as an Adsorbent for Benzene Sensing. *In Solid State Phenomena* (Vol. 302, pp. 107-113).

Rua-Taborda, M.I., Santawitee, O., Phongphut, A., Chayasombat, B., Thanachayanont, C., Prichanont, S., Elissalde, C., Bernard, J. and Debeda, H. (2018). Printed PZT Thick Films Implemented for Functionalized Gas Sensors. *In Key Engineering Materials* (Vol. 777, pp. 158-162).

International Conferences (Oral presentation)

Debéda, H., Santawitee, O., Klinthongchai, Y., Phongphut, A., Inpor, K., Chayasombat, B., Thanachayanont, C. and Prichanon, S. (2020). BTEX Detection Using Piezoelectric Cantilever with Mesocellular Foam Silica Functionalized with Hexamethyldisilazane Sensitive Coating. *In 237th ECS Meeting with the 18th International Meeting on Chemical Sensors (IMCS 2020), Montreal,* (May 10-14).

Santawitee, O., Grall, S., Thanachayanont, C., Dufour, I., Debéda, H. (2019). High densified freestanding printed PZT disks or cantilevers for MEMS applications, *In International Workshop on Piezoelectric Materials and Applications in Actuators 2019 (IWPMA2019), Lyon, (October 1-4).*

D National and Bilateral Workshops (Poster presentation)

Santawitee, O., Thanachayanont, C., Bernard, J., Debéda, H. (2019). Processing and characterization of printed AgPd/PZT/AgPd microdisks for piezoelectric vibration energy harvesters, *In 9th National Days on Energy Harvesting and Storage (JNRSE)*, *Blois, (May 23-24)*.

Santawitee, O., Chayasombat, B., Prichanont, S., Thanachayanont, C., Debéda, H. (2018). A microstructural investigation of mesoporous silica used as sensitive coating for cantilever-based VOCs gas sensors, *In IX Franco-Spanish Workshop IBERNAM-CMC2, the Rovira I Virgili University, Tarragona (Spain), (October 4-5).* (Best poster award)

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Résumé Français

La sérigraphie associée à la technique de la couche sacrificielle est un procédé bas coût permettant la préparation de microsystèmes piézoélectriques à base de couches épaisses. Les choix des matériaux et les conditions de traitement peuvent affecter la microstructure et par suite les propriétés électromécaniques des films épais imprimés. Au cours de ce travail, des disques de PZT (PbZrTiO₃) très denses ont tout d'abord été fabriqués à partir d'une encre contenant une poudre de PZT nanométrique et un ajout de frittage. Ces disques, imprimés sur une couche sacrificielle en polyester, ont montré des propriétés proches de celles des échantillons commerciaux. Dans la deuxième partie de ce travail, l'encre optimisée est utilisée pour la fabrication d'un capteur de COVs à base de micro-poutre ($3x2x0,1 mm^3$). La détection est basée sur la mesure de la fréquence de résonance de la micro-poutre. Avec une couche sensible de silice mésoporeuse de grande surface spécifique, une sensibilité de $\approx 0,24 Hz/ppmv$ sous toluène a été obtenue à température ambiante, due à la sorption du gaz dans la silice. Avec ces performances, ce capteur serait bénéfique pour le monitoring de l'environnement.

English summary

Screen-printing associated with the sacrificial layer technique is a low cost process allowing preparation of piezoelectric thick films microsystems. However, material choices and process conditions could affect microstructure and consequently electromechanical properties of printed thick films. In this work, high densified PZT (PbZrTiO₃) disks have been firstly fabricated from a screen-printing paste containing nano-metric PZT powder and sintering aid. These disks, printed on a polyester sacrificial layer showed properties approaching those of commercial samples. In the second part of this work, the optimized paste has been used for processing of a micro-cantilever used for Volatile Organic Compounds (VOCs) sensing. The detection is based on the resonant frequency shift of the vibrating micro-cantilever. By drop casting of a high surface area meso-cellular foam silica onto cantilever in size of $3 \times 2 \times 0.1 \text{ mm}^3$, a sensitivity of $\approx 0.24 \text{ Hz/ppmv}$ under toluene vapor has been obtained at room temperature due to gas sorption in the mesoporous silica. With these performances, this sensor would be benefit to environmental monitoring field.