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► **To cite this version:**

Maria Isabel Rua-Taborda, Onuma Santawitee, Angkana Phongphut, Bralee Chayasombat, Chanchana Thanachayanont, et al.. Printed PZT Thick Films Implemented for Functionalized Gas Sensors. Key Engineering Materials, 2018, 777, pp.158-162. 10.4028/www.scientific.net/KEM.777.158 . hal-01911808

**HAL Id: hal-01911808**

**<https://hal.science/hal-01911808>**

Submitted on 8 Feb 2021

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# Printed PZT Thick Films Implemented for Functionalized Gas Sensors

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**Keywords:** PZT, thick film, screen-printing, sacrificial layer, MEMS, sensor, mesoporous silica

**Abstract.** Attractive for MEMS, PZT thick films are often microstructured on Si supporting platforms to span the gap between ceramics and thin film technologies. Printing process might lead to lower cost than ceramic process to open routes for MEMS applications. In this paper processing by screen-printing of Au/PZT/Au thick-films supported on alumina or completely released from the substrate are described. Investigations of the film microstructures nevertheless show lower densification than those of bulk ceramics. Prior to selective coating deposition, routes to improve the reduction of the film's porosity are proposed.

## Introduction

Attractive for microsystems, PZT thick films are often microstructured on silicon (Si) supporting platforms to span the gap between the bulk and the thin film technologies [1]. For some applications, printing process might lead to lower cost than traditional ceramic process for PZT-MEMS manufacturing, because of no needs for slicing and polishing piezoelectric ceramics prior to electrodes deposition. Freestanding thick-films or completely released devices can also be interesting to eliminate the mechanical effect of the substrate on their electromechanical properties [2]. However, compared to those of piezoceramics, the higher brittleness and the lower piezoelectric properties of PZT freestanding structures are mostly related to the high porosity of the piezoelectric layer. Before the deposition of selective coating, processing's study of Au/PZT/Au thick-films partially supported on alumina or completely released from the substrate is necessary. In this paper, the fabrication process thanks to the association of the low-cost screen-printing technology associated with the sacrificial layer method is described. The microstructure of the films and microceramics as well as their electromechanical properties are investigated. Some performances of the fabricated PZT thick films and microceramics dedicated to selective sensors applications are also shown.

## Screen-Printing Process and PZT Paste Preparation

The screen-printing method (Fig.1) is a low-cost alternative process to classical silicon manufacturing. This process requires specific inks, made of powders and organic binder mixed together, to be transferred onto the substrate through open areas of meshes of the patterned screen by a squeegee. The deposited film, in the range of 1-100  $\mu\text{m}$ , is then dried and fired to achieve sintering and adherence of the thick film on the substrate. The most valuable advantages of screen-printing are the low investment costs for equipment, choice of materials including the substrate and

paste and the implementation of complex geometries. Our piezoelectric microsystem consists in a three-dimensional thick-film structure made of a thick PZT layer sandwiched between two gold electrodes. The layers can be supported on a substrate as in the classical process, or they can be free-standing as described in the next paragraph. The software CleWin5 is used to design the electrodes and the piezoelectric layers. Each layer of the design is converted separately into a suitable photo-plotter format that can be translated into a patterned thick-film screen. Piezoelectric thick-film fabrication steps are typically undertaken sequentially, starting from the paste formulation and screen-printing, followed by drying, co-firing and finally polarization [3]. Piezoelectric printed films are required to be dense, crack-free, and reproducible with a uniform thickness, and must exhibit high piezoelectric properties. The commercial gold ink (ESL8836 from ElectroScience Laboratories) is used for the electrode layers whereas the PZT paste is prepared at the laboratory. Previous work shown a better densification and reproducibility of PZT thick films when using a commercial PZT powder mixed with the eutectic phase LBCu instead of borosilicate glasses [4]. The  $\mu\text{m}$  particle size of the different powders ( $<10\mu\text{m}$ ) helps for improving the sintering in liquid phase. The piezoelectric paste is prepared from a commercial piezoelectric PZT powder (PZ26 from Ferroperm) mixed with 3wt% LBCu (25wt%  $\text{Li}_2\text{CO}_3$ , 40wt%  $\text{Bi}_2\text{O}_3$ , 35wt%  $\text{CuO}$ ), blended with an organic vehicle (ESL4000 from ElectroScience Laboratories) [5]. The weight percentage is optimized to have adapted viscosity for printing (Fig. 2).

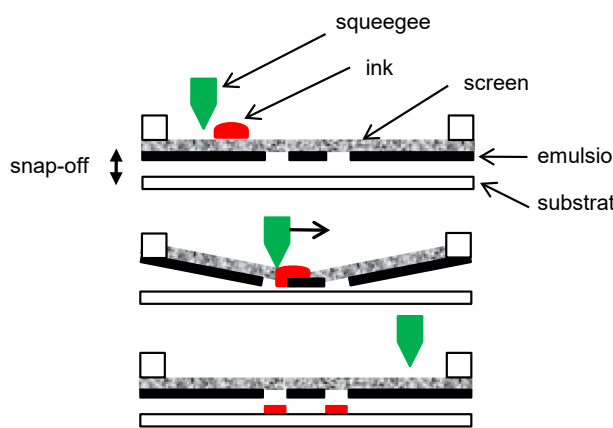


Figure 1: Principle scheme of the screen-printing process

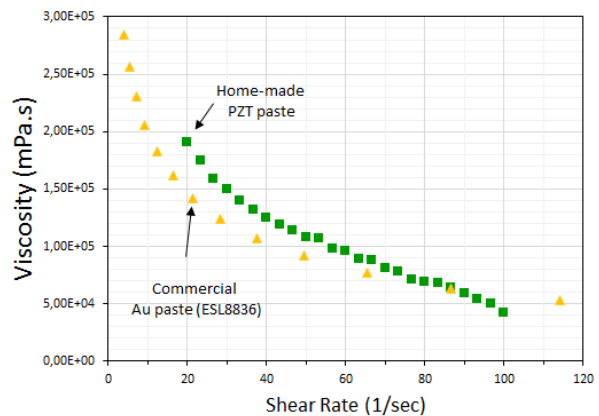


Figure 2: Viscosity of the used pastes

### Partially or Totally Released PZT Thick Films for Sensors Application

As well, free-standing thick-film devices comprising only screen-printed piezoelectric materials and electrodes without the passive platforms can be interesting for MEMS applications. A route developed in our lab [5] for the microstructuration of free-standing thick-films includes the use of a sacrificial layer in the screen-printing process. For this process, a composite  $\text{SrCO}_3$ -epoxy sacrificial layer is first printed and cured at  $150^\circ\text{C}$  prior to the screen-printing and drying of the structural layers. Then, depending on the layer's nature, the samples are fired between  $850^\circ\text{C}$  and  $900^\circ\text{C}$  under dry air and finally immersed in a phosphoric solution. In case of Au/PZT/Au free-standing layers, the pressure step is added before firing as for the fabrication of the EH. Nevertheless, in this process, differential shrinkage associated to the chemical reactions and/or different thermal expansion coefficients of the substrate and the inorganic powders (Au, PZT,  $\text{SrCO}_3$ ) during the firing process still lead to a residual porosity. To reduce the interactions with the sacrificial layer, the  $\text{SrCO}_3$ -epoxy composite layer is replaced by a commercial polyester paste (ESL244T) printed and cured at  $120^\circ\text{C}$ . Besides the improvement of densification as demonstrated in the next paragraph, this sacrificial layer doesn't need any further dissolution after firing, being decomposed during the firing. This process is applied to disk and cantilevers processing in the next paragraph.

**Au/PZT/Au disk microceramics.** The sacrificial layer process using the new polyester based sacrificial layer is applied for the realization of Au/PZT/Au disks (Fig.3). This new sacrificial layer clearly allows a better shrinkage of the PZT microceramics. The higher densification observed on figure 4 is in accordance with the better electromechanical properties measured on the PZT disks after their polarization. The planar vibration modes are studied and electromechanical factor of more than 30% are measured for disks 100 $\mu$ m thick and with diameter of 6 or 8mm (Fig 5). Quality factor of around 100 are also found. A densification of 6g/cm<sup>3</sup> measured by SEM and confirmed by gas pycnometry is evaluated. It corresponds to a porosity of 13%, clearly lower than for supported PZT layers on stainless steel for instance [6]. The obtained properties compare well to those of the ceramics and offer for instance opportunities for vibration-based damage detections [7].

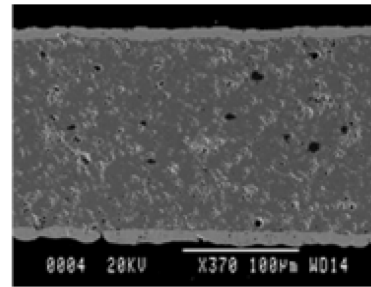
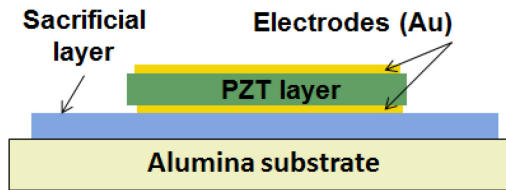


Figure 3: Cross-section of the Au/PZT/Au disk before co-firing

Figure 4: SEM cross section of printed Au/PZT/Au disk fired with the new polyester sacrificial layer

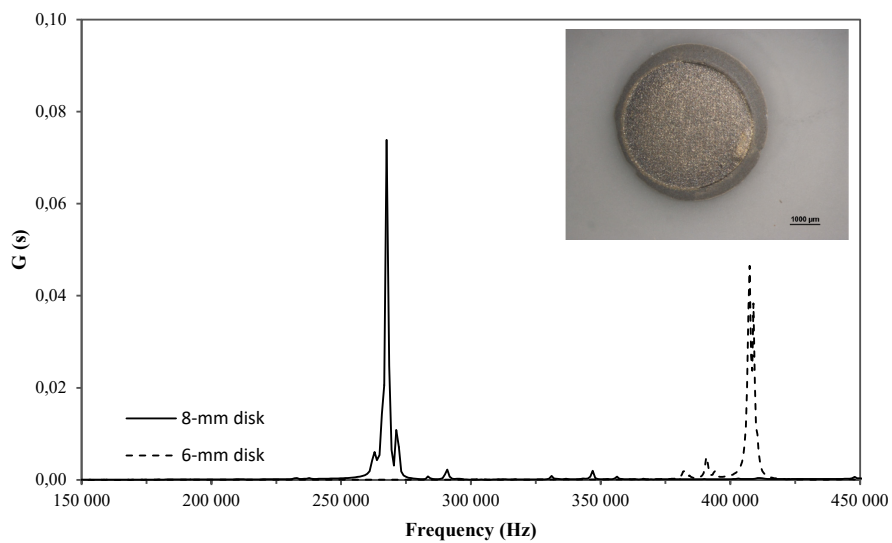


Figure 5: Conductance of Au/PZT/Au disks (planar vibration mode)

**Resonant Au/PZT/Au cantilevers:** The simple design of PZT cantilevers are fabricated with the same process as for the disks (Fig. 6). The printing of the clamping pad is a supplementary step to have partially released electroded cantilever. Different size of cantilever can be shaped, but 2 mm wide and 8 mm are studied (Fig.7). The thickness is approximately 100 $\mu$ m. Again, good densification and high resonance frequency for the in plane 31 vibration mode (>70kHz) are measured. High quality factor (>500) are also observed. These cantilevers presenting high densification and high quality factor can be used as gravimetric sensors for the detection of gas concentration for instance [8].

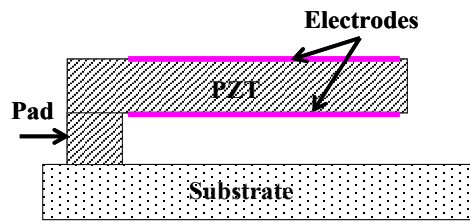


Figure 6: Cross-section of a free-standing cantilever after sacrificial layer releasing



Figure 7: Photograph of printed layers before firing

### Mesoporous Silica Used as Sensitive Coating for Au/PZT/Au Resonant Thick-Films

A chemical gas sensor generally contains two important components which are a receptor and a transducer. Receptors detect and transform chemical information into a form of energy which is measured and transformed into useful analytical signal by transducers. Piezoelectric cantilevers or disks can be fabricated to be transducers in this study (Fig. 8). Organic, inorganic or composite materials can be used as receptors (sensitive coating) for gas sensors [9]. In this work, inorganic mesoporous silica is used as the sensitive coating on cantilever-based volatile organic compounds (VOCs) gas sensors [10]. The most interesting feature of these materials is their regular pore structure with suitable pore dimension to absorb VOCs molecules. Furthermore, they have a large surface area and easily controllable pore sizes by changing synthetic formulations and methods [11-13]. In this study, two different microstructures of mesoporous silica: Mesoporous Cellular Foam (MCF) and Santa Barbara Amorphous-15 (SBA-15) are synthesized by a sol-gel method with different compositions and conditions to deposit on the cantilevers. Their pore characters are characterized by SEM and TEM techniques (Fig. 9). MCF shows interconnected spherical pores network whereas SBA-15 exhibits rod pores with diameter approximately 20 and 7 nm, respectively. The distinct characteristics of sensing layer materials are anticipated that have effects on capacity in VOCs gas detection of the gas sensors.

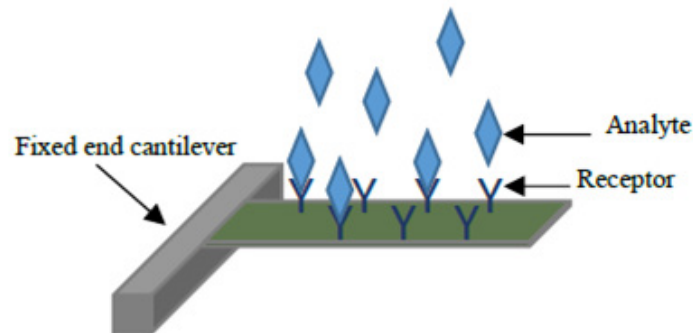


Figure 8: A cantilever-based gas sensor

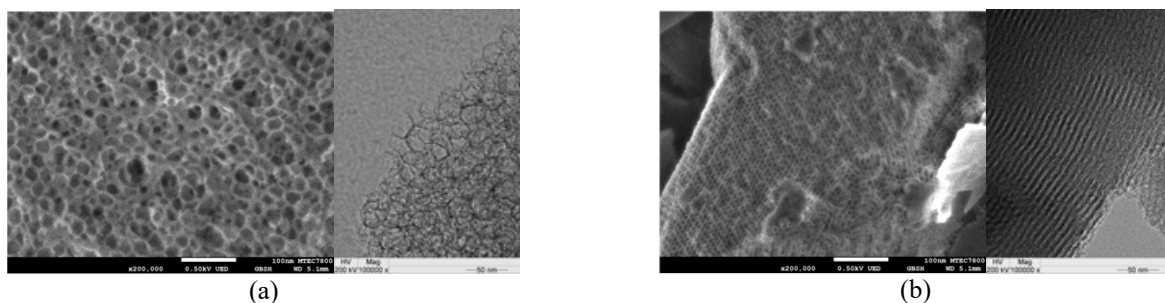


Figure 9: SEM and TEM characterizations of pores structure (Mesoporous Cellular Foam (MCF), magnification 200k (a), and Santa Barbara Amorphous-15 (SBA-15), magnification 100k (b))

## Conclusion

The screen-printing process appears to be attractive for the implementation of PZT MEMS with thickness spanning the gap between ceramics and thin films. Thick-film microstructuring of piezoelectric materials without lead and improvement of densification by SPS techniques avoiding the use of glass or eutectic phases are under progress. On the other side, the PZT cantilevers functionalized with mesoporous sensitive coatings for VOCs detection are under investigation.

## Acknowledgments

The authors thank the SIAM PHC 2017 program (“Detection of formaldehyde and benzene vapor using mesoporous silica-coated piezoelectric cantilevers”).

## References

- [1] Glynn-Jones, SP Beeby, NM White, “Towards a piezoelectric vibration-powered microgenerator”, *Proc.Sci. Meas. Technol.* 148, 68–72 (2001).
- [2] R. Xu, A. Lei, C. Dahl-Petersen, K. Hansen, M. Guizzetti, K. Birkelund, E.V. Thomsen, O. Hansen, “Screen printed PZT/PZT thick film bimorph MEMS cantilever device for vibration energy harvesting”, *Sensors and Actuators A.* 188, 383–388 (2012).
- [3] N. White and JD Turner, “Thick-film sensors: past, present and future”, *Meas. Sci. Technol.* 8, 1-20 (1997).
- [4] R. Lakhmi, H. Debéda, I. Dufour, C. Lucat and M. Maglione, “Study of screen-printed PZT cantilevers both self-actuated and self-read-out”, *International Journal of Applied Ceramic Technology.* 11, 311-320 (2014).
- [5] H. Debéda, P.Clément, E. Llobet and C. Lucat, “One-step firing for electroded PZT thick-films applied to MEMS”, *Smart Mater.* (2015).
- [6] H. Debéda, M-I Rua Taborda, S. Zarabi, D.Nairn, L.Wei, A. Salehian, “Printed MEMS-based self-contained piezoelectric-based monitoring device for smart grids”, *Powermems 2017*, Kanazawa, Japan. (2017)
- [7] H. Debéda, C. Lucat, V. Budinger-Pommier; “Printed piezoelectric materials for vibration-based damage detection”, *Proceedings Engineering /j.proeng.* 11.254 (2016).
- [8] P. Clément E. Perez, O. Gonzalez, R. Calavia, C. Lucat, E. Llobet and H. Debéda, *Sensors and Actuators B: Chemical*, 237, 1056–106 (2016).
- [9] A. Hulanicki, S. Glab and F. Ingman, “Chemical sensors definitions and classification”, *Pure and Applied Chemistry*, 63(9) 1247-1250 (1991).
- [10] Y. Chu, H. Kim, K. Song, Y. Shul, K. Jung, K. Lee and M. Han, “Preparation of mesoporous silica fiber matrix for VOC removal”, *Catalysis Today.*74(3) 249-256 (2002).
- [11] E. Magner, “Immobilisation of enzymes on mesoporous silicate materials”, *Chem. Soc. Rev.*, 2, 6213-6222 (2013).
- [12] N. Zucchetto, M. J. Reber, L. Pestalozzi, R. Schmid, A. Neels, D. Brühwiler, “The structure of mesoporous silica obtained by pseudomorphic transformation of SBA-15 and SBA-16” , *Microporous and mesoporous materials* 257, 232-240 (2018).
- [13] L. Wei, Y. Zhao, Y. Zhang, C. Liu, J. Hong, H. Xiong, J. Li, “Fischer–Tropsch synthesis over a 3D foamed MCF silica support: Toward a more open porous network of cobalt catalysts”, *Journal of Catalysis* 340, 205-218 (2016).