Self-Assembled Monolayer-Assisted Inkjet Printing of PZT Films on Platinized Silicon

<u>N. Godard¹</u>, D. Sette¹, S. Glinsek¹, and E. Defay^{1,*} Luxembourg Institute of Science and Technology (LIST) Rue du Brill 41, L-4422 Belvaux, Luxembourg *Emmanuel Defay: emmanuel.defay@list.lu

The fabrication costs of integrated piezoelectric devices are mainly determined by the manufacturing process itself. Inkjet printing recently emerged as an efficient lithography-free technique. Patterned structures can be printed on various substrates under ambient atmospheric conditions using only minimal amounts of precursors, thus significantly reducing economic and ecological footprints. In the present contribution we will describe a strategy for printing a sol-gel-based lead zirconate titanate (PZT) ink on platinized silicon.

The employed PZT ink has near-morphotropic-phase-boundary composition (MPB). A mixture of dehydrated lead(II) acetate, zirconium(IV) butoxide and titanium(IV) isopropoxide in 2-methoxyethanol with 10% excess lead is heated at reflux during two hours to ensure homogenization and stabilization of alkoxide species via ligand exchange.¹ The resulting PZT sol is then diluted to 0.3 M with ethylene glycol and bis(2-ethoxyethyl) ether to adjust ink viscosity and surface tension for efficient droplet ejection using Dimatix cartridges.

Platinum has very high surface energy (~ $1 \text{ J} \cdot \text{m}^{-2}$),² which makes direct printing of organic solvent-based inks difficult because of extreme wetting. Alkanethiol self-assembled monolayers (SAMs) can be used to modify the platinum surface and constrain ink spreading. We implemented a two-step printing process to fabricate 2×2 mm² PZT squares (Figure 1a): (1) definition of the pattern borders by printing an alkanethiol ink (1 mM dodecanethiol solution in ethanol/glycerol mixture ³) and (2) filling the defined areas with PZT ink. After drying, pyrolysis is performed at 350 °C and crystallization at 700 °C. The obtained 100 nm-thick structures show a typical Raman signature of PZT in MPB composition ⁴ (Figure 1b) and exhibit ferroelectric switching. This work unveils a fully inkjet printed strategy to pattern PZT thin films, compared to other works were SAMs were patterned by microcontact printing or lithography.^{5,6} We will describe in detail the optimization of inkjet printing from ink formulation to deposition and the influence of the processing parameters on microstructure and functional behavior of the PZT films.



Figure 1 – (a) Optical micrograph of the $2 \times 2 \text{ mm}^2$ crystallized PZT structures. (b) Raman spectrum of the 100 nm-thick crystallized PZT structure (532 nm laser wavelength). Symmetry modes were assigned based on Buixaderas et al.⁴

- 1. Brennecka et al., J. Am. Ceram. Soc. 93, 2010, 3935-3953.
- 2. Vitos et al., Surf. Sci. 411, 1998, 186-202.
- 3. Rianasari et al., *Langmuir* 24, 2008, 9110–9117.
- 4. Buixaderas et al., Phys. Rev. B 91, 2015, 014104.
- 5. Lee et al., MTL Ann. Res. Rep., 2009, MS15.
- 6. Machida et al., Jpn. J. Appl. Phys. 51, 2012, 09LA11.