Ferroelectric thin film fabrication by direct UV-lithography

M. Benkler[1] and T. Hanemann[1,2]

[1]Department of Microsystems Engineering, Laboratory for Materials Processing, University Freiburg

[2]Institute for Applied Materials - Material Process Technology, Material and Process Development, Karlsruhe Institute of Technology

manuel.benkler@imtek.uni-freiburg.de, +49 761/203-7555

Ferroelectric films with high values of ferroelectricity, piezoelectricity and dielectricity, like lead-zirconate-titanate films (PZT, $PbZr_{0.52}Ti_{0.48}O_3$) with perovskite structure, are widely used in the fields of sensors, energy harvesting, capacitors and FERAMs [1,2,3]. In this paper a novel, very easy way to produce micro patterned lead-zirconate-titanate ceramic thin films on silicon substrates by direct UV-lithography is shown.

Therefore a sol based on methacrylic acid was developed to generate photosensitive metal organic PZT precursor gel films. This sol was spincoated on silicon wafers and dried afterwards to obtain photosensitive gel films. These PZT xerogel films were patterned using conventional UV-lithography equipment and developed afterwards with organic solvents. The resulting patterned gel films were pyrolized and crystallized in air via rapid thermal annealing (RTA) in order to obtain crystalline ceramic PZT thin films. The samples were analyzed by XRD technique and SEM-images. Micro patterned, crack free, crystalline PZT thin films were obtained by this method.

The presented process has several advantages over other methods using photopolymerizable monomers for directly UV-photopatternable PZT films [4,5,6]. The sol synthesis is much more simple. No sophisticated techniques, like the use of inert gas atmosphere, are needed. Also higher resolutions in the lower µm-range and crack free ceramic thin films were achieved.

Figure 1 shows schematically the synthesis of the developed sol for direct UV-lithography. Methacrylic acid was used as photopolymerizable monomer, which is able to dissolve the needed metal precursors lead acetate, zirconium and titanate alkoxides. As UV-photoinitiator a diphenyl-benzoylphosphine oxide was added. This basic sol was then diluted with 2-methoxyethanol as it lowers the viscosity of the sol, which makes it well processible by spin-coating, and secondly stabilizes the sol. This sol is used to produce photosensitive gel films and these films can be patterned by UV-lithography.

An overview of the film deposition and patterning process is shown in figure 2. After the litho-graphic steps the resulting preceramic xerogel films (see figure 3) were pyrolized and crystallized by rapid thermal annealing. Figure 4 shows SEM-images of the ceramic microstructured thin PZT films. The films are polycrystalline, fine grained, crack free and 50-60 nm thick. Phase transition to the desired perovskite phase during thermal annealing of the PZT film was investigated by XRD measurements (see figure 5). The desired polycrystalline perovskite structure is formed at temperatures around 650 °C; below this temperature the phase transition from the pyrochlore phase to the desired perovskite phase was not completed.

This simple method unifies deposition and patterning steps. The needed metal organic sol can be used like a normal photoresist and hence this method can be easily used with existing cleanroom infrastructure. This method is an interesting alternative to today's mostly used patterning processes like photoresist lift-off or etching. The expansion of this method to mostly all oxide ceramics should be possible as the proof of concept was demonstrated by patterning PZT.

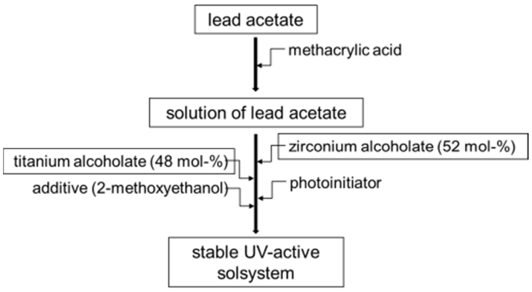

Figure 1: Schematic representation of the sol synthesis

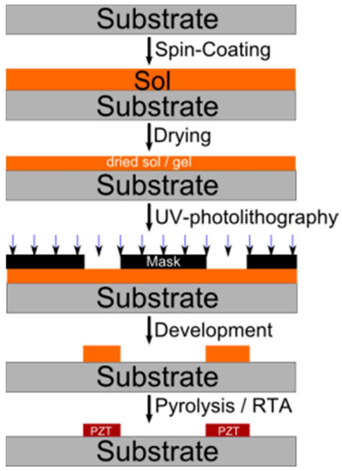

Figure 2: Scheme of the process chain

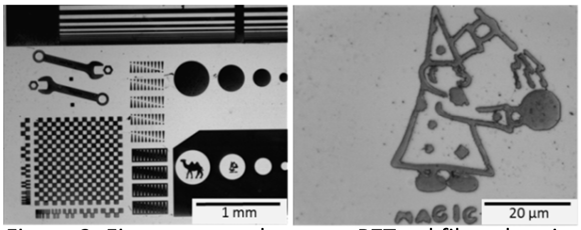

Figure 3: Fine patterned organo-PZT gel film, showing the high resolution of the process

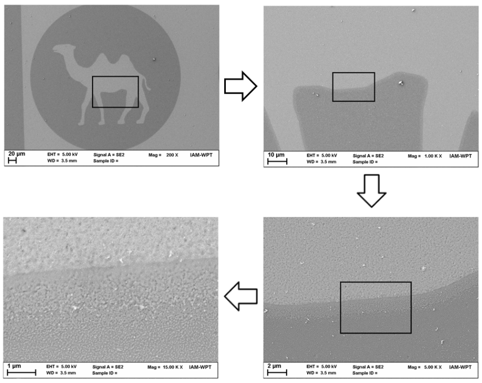
Figure 4: SEM-images showing the surface morphology of the pyrolized film

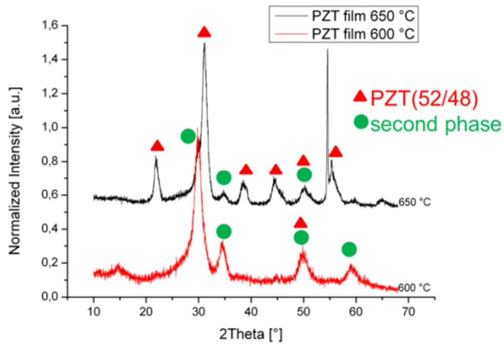

Figure 5: XRD patterns for PZT-films deposited on silicon substrates

Acknowledgement

The authors thank the state of Baden-Württemberg, "Ministerium für Wissenschaft, Forschung und Kunst", for financial support within the graduate school "Generierungsmechanismen von Mikrostrukturen" (GenMik).

References

[1] P. Muralt; Ferroelectric thin films for micro-sensors and actuators: a review; *Journal of Micromechanics and Microengineering*; **2000**, *10*; pp. 136-146,

[2] S.R. Anton, H.A. Sodano; A review of power harvesting using piezoelectric materials (2003-2006); *Smart Materials and Structures*; **2007**, *16*; pp. R1-R21,

[3] G.H. Haertling; Ferroelectric Ceramics: History and Technology; *Journal of the American Ceramic Society*; **1999**, *82*; pp. 797-818,

[4] Marson, S.; Dorey, R.; Zhang, Q. & Whatmore, R.: Thick PZT micro-features obtained by direct patterning of photosensitive precursor solution; *Integrated Ferroelectrics, TAYLOR & FRANCIS LTD,* **2003***, 54*, pp. 585-593,

[5] Marson, S.; Dorey, R. A.; Zhang, Q.; Whatmore, R. W.; Hardy, A. & Mullens, J.: Direct patterning of photosensitive chemical solution deposition PZT layers; *Journal of the European Ceramic Society,* **2004***, 24*, pp. 1925-1928,

[6] Kololuoma, T.; Hiltunen, J.; Tuomikoski, M.; Lappalainen, J. & Rantala, J. Sidorin, Y. & Tervonen, A. (Eds.): Directly UV-photopatternable PLZT thin films prepared with the sol-gel technique; *Integrated Optics: Devices, Materials, and Technologies VIII,* **2004***, 5355*, pp. 33-39.