DUTCH-BELGIAN BEAMLINE
AT ESRF

EUROPEAN
SYNCHROTRON
RADIATION FACILITY

ESRF

Experiment Report Form

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

(next page)

DUBBLE	Experiment title: **Structural evolution of electronic perovskite-type oxide thin films by chemical solution deposition monitored by SAXS**	**Experiment number**: **26-02-463**
Beamline: BM-26B 'Dubble'	**Date(s) of experiment**: From: 16-7-2009 To: 20-7-2009	**Date of report**: 21-7-2009
Shifts: 12	**Local contact(s)**: dr. G. Portale	

Names and affiliations of applicants (* indicates experimentalists):

J.E. ten Elshof*, S. Khan*, S.A. Veldhuis*, T. Stawski*, R. Besselink* (Inorganic Materials Science, Universiteit Twente); H.L. Castricum* (Universiteit van Amsterdam)

Report: (max. 2 pages)

The chemical solution deposition technique is a highly flexible and well-known method for the fabrication of electronic mixed metal oxide films from liquid precursor solutions, nanoparticle dispersions and sol-gels [1]. The technology is thought to hold great promise for future low-cost printable electronics, sensors, and MEMS applications.

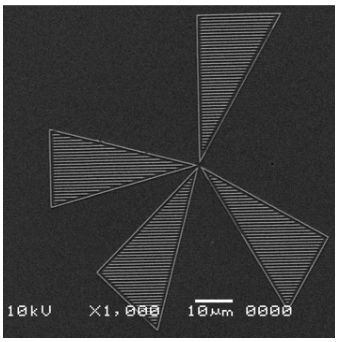

Figure 1. NIL-patterned PZT. Line width is 380 nm.

Recently, we started with a new research program on nanoscale functional ceramics and began to develop new methodologies to make

- Ultrathin (<100 nm) films of the high-k dielectric $BaTiO_3$ (BTO) phase, intended for next generations of miniaturized multi-layer ceramic capacitors (MLCCs) with high capacity.
- Micro- and nanoscale patterns of the piezo- and ferroelectric lead zirconate titanate phases $Pb(Zr,Ti)O_3$ (PZT) by soft lithographic nano-imprint lithography (NIL) [2].

An example of a soft lithographically patterned PZT nanopattern is shown in Figure 1. The resolution of the lines is about 380 nm, higher than similar metal oxide nanopatterns reported till date [3].

The precursor solutions that are used for chemical patterning and thin film formation consist of a mixture of metal organic precursors in the desired proportions, optionally with stabilizing agents and solvents. The solutions are transformed into thin films or nanopatterns after deposition and drying. Depending on the nature of the solution and method of preparation, the precursors and stabilizing agents may associate into small physically and/or chemically bonded aggregates of <10 nm diameter, possibly with a fractalic structure, but this all remains hypothetical and controversial [1]. For instance, Ti and Zr alkoxides (and mixtures of the two in ethanol) are known to form polymeric entities with a fractalic structure [4], but the influence and the location in solution of elements like Ba^{2+} and Pb^{2+} is unknown. Are they built into a fractalic network, or do they stay isolated in solution? Do the sols consist of a mixture of elements, or does the solution contain a mixture of binary oxide sols/precursor solutions? What happens to the sol when the solvent is evaporated in a thin film drying process? In the current experiments that we carried out at Dubble between 16. and 20. July, we investigated these first steps in the sol-gel process of PZT and BTO in more detail, with the aim to

1. Study the influence of processing variables (compositions, concentrations, time, etc.) on size and shape of primary particles in PZT and BTO precursor solutions.

2. In-situ monitor the drying process of BTO and PZT thin films.

We have carried out SAXS measurements at the DUBBLE beamline BM-26B on PZT and BTO sols in various stages of development. We obtained data at short detector distance and studied samples with different chemical compositions. By analyzing the SAXS data and combining them with other techniques, such as dynamic light scattering (DLS), we will be able to obtain a full description of the effect of composition and other preparation parameters on the development of the structure. We varied composition, solvents, nature of stabilizers, preparation procedure and ageing time in the as-prepared sols. Sols were introduced in thin-walled glass (10 micron thick) capillaries, which were stored at low temperature to prevent them from structural evolution. The applied beam energy was 16 keV, and the sample-detector distance 1.5 m.

Thanks to optimized slit settings and focusing on the beam stop and efficient assistance by our local contacts, a high resolution could be obtained, also for capillaries. We experienced a very stable beam delivery throughout the experiment. Excellent reproducibility of the scattering patterns was found, enabling observation of reactant- and catalyst-dependent development of sols, and structural evolution of as-dried films.

A very important but almost unexplored stage in the preparation of a sol-gel derived material the drying step. The most exciting and interesting part of our experiments were the in situ drying experiments, for which a special setup has been developed by Guy Eeckhaut and Wim Bras, which we were kindly allowed to use. We successfully attempted in-situ drying experiments of sols using this setup, at various temperatures. The high intensity of the ESRF synchrotron beam was ideal for studying the rapid structural evolvement during thin film drying, in some cases within 60 seconds. We are actually able to witness the initial nucleation process of titania/zirconia particles, precipitation of Ba- and Pb (hydr)oxides, and determine the conditions under which the highest degree of chemical homogeneity on nanoscale in an as-dried film can be obtained. Although the analysis of our data will require much more work, we can already say that the SAXS experiments we did gave new insights as to what is happening. Under certain conditions we can obtain a completely amorphous, structure-less film, which is probably homogeneous on nanoscale. Under other conditions the Zr/Ti and Ba/Pb (hydr)oxides formed at different moments in the process, and a less homogeneous as-dried precursor remains.

In this way, a deeper understanding of network formation during rapid drying is being acquired, and this will have a broader applicability than in sol-gel derived electroceramic thin films alone. Other examples are e.g. the formation of thin ordered mesoporous materials by ‘evaporation-induced self-assembly’, which is now under very extensive study for a wealth of applications. On the whole, a better understanding of these processes will allow a more rational design of recipes for nanoscale electroceramics, by recognition of the parameters that can be tuned to optimize the structure, and thus the in the end the electrical (dielectric, piezoelectric, ferroelectric) properties.

References

[1] R.W. Schwartz, Chemical solution deposition of perovskite thin films, *Chem. Mater* **9** (1997) 2325.
[2] C.R. Martin and I.A. Aksay, Submicrometer-scale patterning of ceramic films, *J. Electroceram.* **12** (2004) 53.
[3] M.J. Hampton *et al*., The patterning of sub-500 nm inorganic oxide structures, *Adv. Mater*. **20** (2008) 2667.
[4] J. Sekulić, J.E. ten Elshof, and D.H.A. Blank, A microporous titania membrane for nanofiltration and pervaporation, *Adv. Mater*. **16** (2004) 1546.