



	Experiment title: <b>Structural evolution of nanostructured oxidic and hybrid organic-inorganic thin films monitored by SAXS</b>	<b>Experiment number:</b> <b>26-02-512</b>
<b>Beamline:</b> BM-26B 'Dubble'	<b>Date(s) of experiment:</b> From: 12-4-2010 To: 16-4-2010	<b>Date of report:</b> 18-4-2010
<b>Shifts: 9</b>	<b>Local contact(s):</b> dr. G. Portale	
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### **Report: (max. 2 pages)**

Wet chemical syntheses, notably sol-gel synthesis and chemical solution deposition, are well-established methods for the fabrication of mixed metal oxide and hybrid organic/inorganic thin films from liquid precursors [1]. They provide great flexibility and hold great promise for nanotechnology applications, including energy-efficient molecular separation membranes [2] and low-cost printable electronics, sensors and MEMS applications. The solutions that are used for patterning and thin film formation consist of a mixture of metal organic or organosilica precursors, stabilizing agents and solvents. The precursors and stabilizing agents associate into small physically and/or chemically bonded fractal aggregates of 1-10 nm diameter, one order of magnitude smaller than the dimensions of the targeted structures. These aggregates transform to thin films and nanopatterns after well-controlled deposition, drying and thermal consolidation. A complex relation exists between the various processing parameters and the obtained nanostructure, and the final structure is determined both by the reaction conditions during synthesis as well as to the conditions applied during the drying procedure. Detailed understanding of both stages is therefore essential to allow effective tailoring of these nanostructured devices.

Three main factors determine network formation during drying: the intrinsic reactivity of the precursors, the concentration increase of the various reactants upon solvent evaporation, and the surface charges in the sol. These surface charges are determined by the colloidal structure and by the presence of additional charged species (e.g. acids and salt ions). In order to understand these processes and allow tailoring of the nanostructure, we need to systematically assess which factors dominate at what stage, and to what extent they influence the structure. For thin layers, structural evolution typically occurs on a second-to-minute scale during drying. The high intensity of a synchrotron beam is ideal for studying the drying behaviour with SAXS. A deeper understanding can thus be acquired of network formation during rapid drying.

We specifically focused on the following systems:

- Hybrid microporous and mesoporous membranes for energy-efficient molecular separation, prepared from organosilane precursors. These membranes combine molecular separation selectivity with exceptional structural stability [2]. We have already used SAXS to tune the structure of the colloidal sols that are used for membrane coating [3]. Acquiring a better understanding of the processes during the drying stage will allow further improvement of the porous nanostructure. This will lead to a broad application window for molecular separation membranes in gas separation and nanofiltration.

- Ultrathin (<100 nm) films of high-*k* dielectric barium titanate BaTiO<sub>3</sub> (BTO) for next generations of miniaturized multi-layer ceramic capacitors (MLCCs) with high capacity.
- Micro- and nanoscale patterns of piezo- and ferroelectric lead zirconate titanate Pb(Zr,Ti)O<sub>3</sub> (PZT) by soft lithographic methods such as micro-transfer molding and soft imprint lithography [4].

The central aim was to study the formation mechanism of nanostructured materials by assessing the influence of processing variables on the development of size and shape of the colloids, as well as the relation between colloidal structure, crystallite formation and porosity. We attempted to distinguishing physically- (solvent evaporation) from chemically- (ageing) induced network formation, and to acquire information on the evolution of crystallinity and porosity in drying films.

Small-angle X-ray scattering (SAXS) measurements were carried out at the DUBBLE beamline BM-26B on (organo)silica sols with various stages of development. We obtained data at short detector distance and studied silica colloidal sols with different bridging groups, sols from metal alkoxydes and combinations thereof. By combining SAXS with other techniques, such as DLS (which determines the hydrodynamic radius of the sol particles), we can obtain a full description of the effect of the organic groups on the development of the structure. We varied independently the precursor concentration, the catalyst concentration, the type of catalyst, the hydrolysis ratio and the concentration of stabilizing agents. The applied beam energy was 16 keV, and the sample-detector distance 1.5 m.

Although we suffered from various beam disruptions and crashes of the new data-acquisition software, we were still able to complete the major part of our measurement program. Thanks to optimized slit settings and focusing on the beam stop and efficient assistance by our local contacts, a high resolution could be obtained. 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.

About half of the time was devoted to in-situ drying experiments, for which a special setup had been developed by Guy Eeckhaut and Wim Bras, which we were kindly allowed to use. We successfully carried out in-situ drying experiments of sols using this setup, at various temperatures. These drying experiments showed that the porosity of a colloidal organosilica sol depends on a combination of the concentration of (acid or base) catalyst during drying, the availability of water and the size of the colloids. No indications were found for a stepwise transition between a mesoporous or microporous material. The temperature seems to be a relevant factor especially at higher hydrolysis ratios. Understanding the development of porosity upon drying is highly relevant for the further development of molecular separation membranes.

The association and crystallization behaviour of BTO and PZT sols was studied both during in-situ synthesis and during drying. We found that the availability of water was a crucial factor in the formation of nanostructures.

The obtained results will allow us to better understand how colloidal networks develop during drying, as well as to relate synthesis conditions to applicability of the various materials.

## References

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