Nucleation and Crystallisation Kinetics of Chemical Solution Deposited Electroceramic Thin Films

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Electroceramic thin films have been routinely fabricated by chemical solution deposition (CSD) techniques to achieve high performance products at low technical efforts and cost [1]. PZT is an important piezoelectric and ferroelectric material for industrial applications such as micro-electromechanical systems (MEMS), energy harvesting concepts, and non-volatile random access memories. Different CSD routes have been developed to deposit high quality PZT layers [2]. In general, detailed knowledge of the crystallisation pathway and morphology evolution is essential to optimise the whole deposition process. Due to the high rate at which the reactions and transformations occur during the standard rapid thermal annealing of PZT coatings, in situ observations of the nucleation and phase formation have not yet been realised. Recent work shows the capabilities as well as the limitations of in situ laboratory XRD for investigating the nucleation and crystallisation kinetics in PbTiO₃ (PTO) layers [3]. Being the extreme of Ti rich PZT, PTO is considered the dominant component of PZT with respect to the phase formation process. In our study, the heating rate and the minimum film thickness that allowed us to observe the dynamics of the transformations differed significantly from the standard parameters. Yet, it was possible to deduce kinetic values by applying a non-isothermal Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach (see e.g. Ref. [4]) and to correlate these findings with the morphology of ferroelectric PTO layers. However, significant deviations between the measured data and the model were observed in the early stage of the perovskite phase formation below 760 K. At these temperatures, the decomposition of organic residues and the reaction of the precursor layer with the underlying platinum substrate to PtPb and Pt₃Pb [5] take place which obviously follow different kinetic laws. In addition, the phase transition from tetragonal to cubic at ~763 K leads to the merging of split reflections. This made the exact determination of peak areas all the more difficult when the reflections are very weak as in the initial phase of the crystallisation. In summary, the crucial factor to limit the time-resolution of these measurements to the range of several tens of seconds was the low photon flux of the laboratory source.

In order to collect data at the required sub-second time resolution under realistic processing conditions, i.e. during rapid heating of thin coatings, we performed in situ synchrotron x-ray diffraction experiments at Beamline P08. The sample layers were spin-coated onto oxidised and Pt coated Si wafers and dried at 200 °C on a laboratory hot plate for 2 min. Afterwards, the samples were annealed in an Anton Paar domed hot stage that was mounted on the diffractometer. Four modules of MYTHEN type microstrip detectors were installed to record four reflections in parallel at a photon energy of 10.5 keV. In this setup, diffraction patterns were collected within 0.1 s exposure time. Since the heating rate φ of the hot stage was linear only up to rates of a few degrees per second, a constant φ of 2 °C s⁻¹ was chosen for all measurements. The film thickness was varied by applying coating solutions of different concentrations. Annealing conditions were alternated from oxidising to reducing atmosphere by purging the dome with nitrogen to observe the effect of the surrounding gas on the reaction kinetics.

Fig. 1 shows two representative contour plots for the in situ heating experiments of PbTiO₃ films carried out in the different gas compositions. The film thickness of both samples was in the range of 50 nm. It is evident that the nitrogen enriched atmosphere led to a prolonged existence of the intermediate phase (2θ ~ 29°) in comparison to the oxygen rich atmosphere and that the resulting orientation of the films differed. This has already been expected from previous work done on much thicker films [5] but is now confirmed for thin films and in situ heat-treatment as well. Based on the obtained time and temperature resolved data, the kinetic parameters for the formation and decomposition of the lead platinum phase can now be evaluated quantitatively. In summary, the applied in situ synchrotron x-ray diffraction method fulfilled the expectations to observe the pathway of film formation under conditions rather close to the actual process parameters.
Fig. 1: Contour plots and temperature-time relations for the in situ annealing of PbTiO$_3$ thin films in a) oxygen-rich and b) nitrogen-enriched atmosphere.

References