



Executive Summary

EC Project No. NMP3-CT-2006-033297

The Project Status at the end of the second year

The objective of this project is to study the growth of complex oxide thin films for electro-optic and piezoelectric applications. The major deposition method pursued in this project is Chemical Beam Epitaxy (CBE) for which hardware and processes are developed to achieve good film uniformities on 100 to 150 mm wafers, to allow for systematic stoichiometric variations in combinatorial research, and to allow for in-situ structured growth by laser assistance. Pulsed laser deposition (PLD) - a technique for small samples only - is used as complimentary method in order to advance faster in materials and characterization knowledge.

The second project year was characterized by major achievements towards the goals of the project. Partner **ABCD** completed and debugged the tool for chemical beam epitaxy (CBE), which was developed in the frame of this project. The tool is now routinely operational up to temperatures of 750 °C, occasionally up to 850 °C. The film uniformity with all segments open was tested at various temperatures and flux intensities, using TiO₂ as model material, deposited from TTIP (Titanium Tetra-IsoPropoxide) precursor gas. Fig. 1 presents a thickness map realized by optical reflectivity measurements across a 6" wafer. From the modeling of flux distribution, a min-max uniformity of +/- 0.5 % was calculated. The measured distribution showed a very satisfying variation of +/- 2% - along one diameter even +/- 0.5 % - for a deposition at 560 °C. Possibly, temperature uniformity, tightness of gas shower head, and precision of wafer alignment must be improved to achieve the predicted values. The showerhead was also tested for creating defined gradients in the thickness distribution of TiO₂ by selectively closing segments. The obtained gradients coincided in a satisfactory manner with the calculated impingement distributions, thus proving that the programmable shower head is useful for **combinatorial** research (fig. 1) .

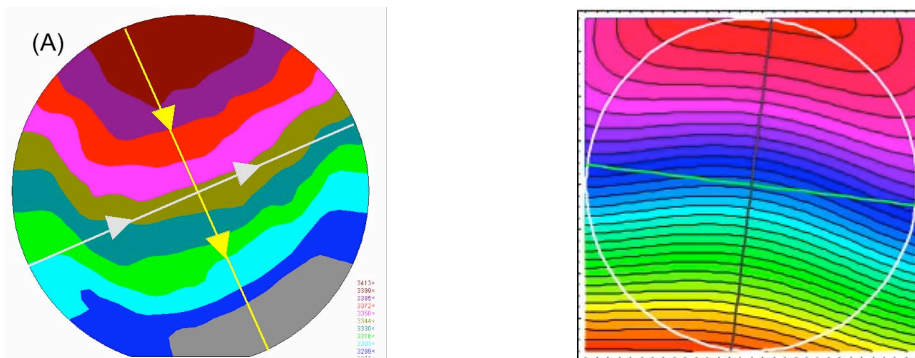
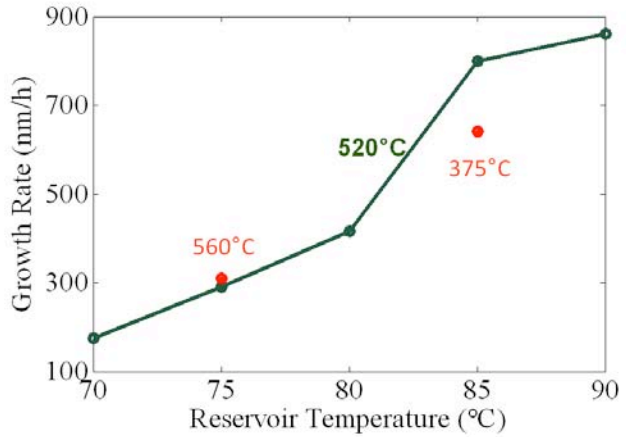


Figure 1: *Optically determined thickness map of a 330 nm thick TiO₂ film on a 150 mm wafer when all segments are open (left), and with selectively closed segments for creating a strong thickness gradient with factor 5 variation (right). The thickness difference between two colors amounts to 0.4 %.*

The **EPFL-APL** partner investigated relevant equipment parameters and processes for LiNbO₃ deposition. In a first step Nb₂O₅ deposition was studied as a function of the reservoir temperature with a new precursor (alkoxide-type) provided by **SAFC** (fig. 2). The increased temperature leads to an increased pressure in the reservoir vapor, and thus to a higher flux to the substrate, leading to the expected rate increase. The transition from mass transport limited to reaction limited regime is found to be at around 520 °C substrate temperature at 75 °C reservoir temperature (corresponding to 0.043 mbar).

Figure 2: Growth rate of Nb_2O_5 at 520 °C as a function of precursor reservoir temperature.



In a second step, the Li precursor pressure was studied as a function of the reservoir temperature, and optimized for a given Nb flux to achieve the desired perovskite phase of $LiNbO_3$. This goal was reached, apart from a small amount of an unknown phase (unattributed peak) was detected (fig. 3). Hence, deposition of an almost pure polycrystalline $LiNbO_3$ has been achieved, and this at much lower temperature than with PLD.

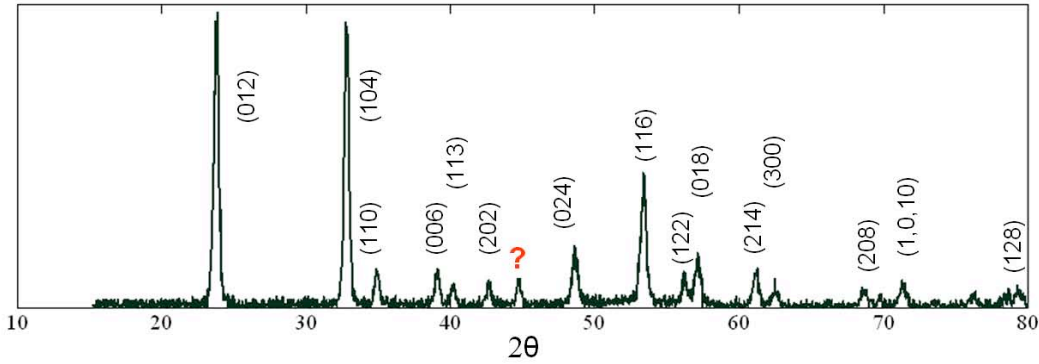


Figure 3: X-ray θ - 2θ diffraction pattern of a 190 nm thick $LiNbO_3$ thin film deposited by CBE at 550 °C.

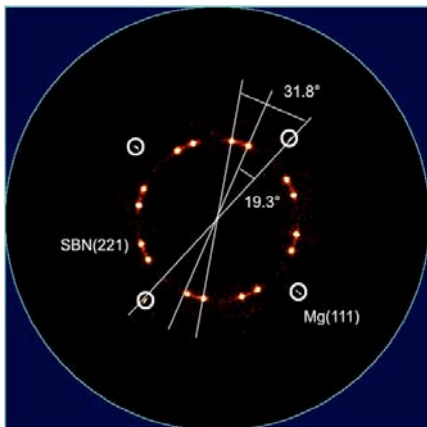


Figure 4: Pole figure for $SBN(221)$ reflections, deposited by PLD, cooled with $10^\circ C/min$ from $650^\circ C$ to room temperature in oxygen RF plasma at 150W.

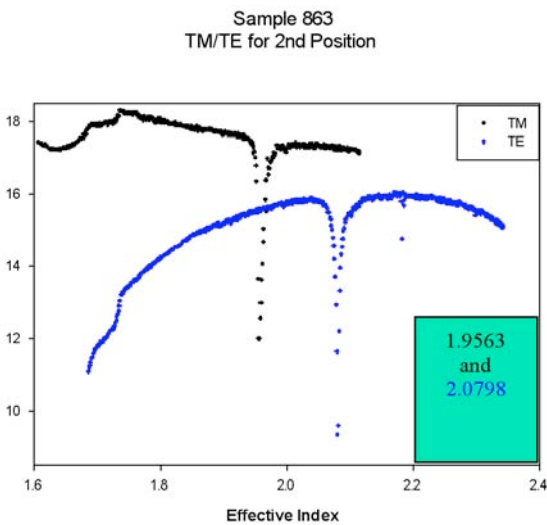


Figure 5: Optical coupling into SBN film on MgO as evaluated by a prism technique (dark mode spectrum).

Partner **NIL** has further advanced in SBN 50/50 thin film synthesis by PLD techniques. Growth on MgO substrates was studied. Very well (001)-oriented, epitaxial films were

obtained. They show growth domains ("twinning") as revealed by pole figure XRD (see fig. 4). The complex (001) plane of SBN allows for two different epitaxial relations. An additional relation can be interpreted as a result of a transitory strontium niobate phase competing with the correct SBN phase during the nucleation process. Partner **UoS** investigated one of the samples by a prism-coupling technique for the determination of the optical refractive index. One of the results is shown in Fig. 5. The effective indices corresponding to the two transmission dips are 1.9563 and 2.0798 for the TM and TE mode, respectively.

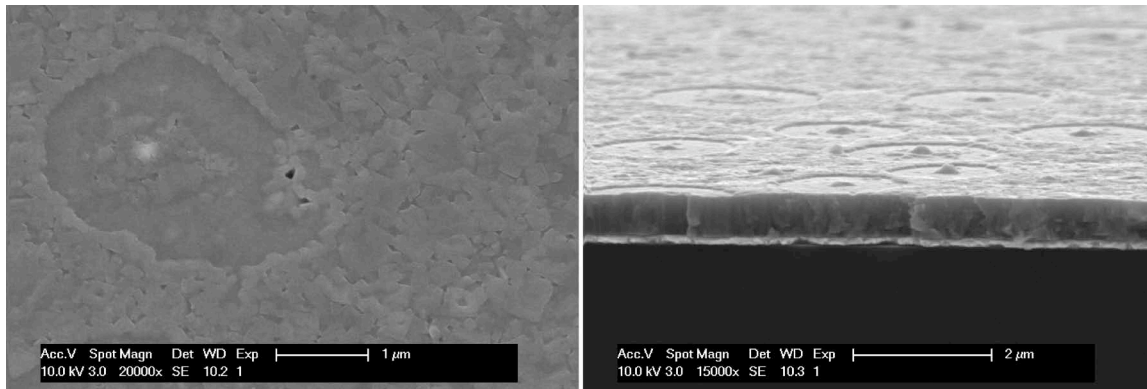
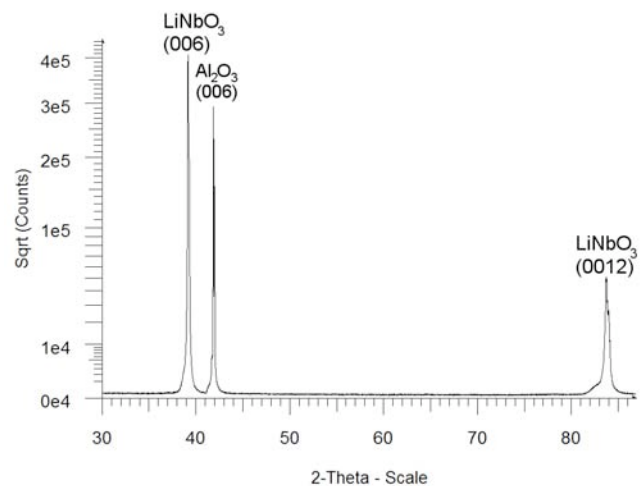


Figure 6. SEM images showing the surface (left) and cross-section (right) of an NKLN-1.5% CaTiO₃ film deposited on Pt/Ti/SiO₂/Si.

Partner **EPFL-LC** continued the work on (Na_{0.475}K_{0.475}Li_{0.05})(Nb_{0.92}Ta_{0.05}Sb_{0.03})O₃ (NKN-based) perovskite materials, exploring routes for improving the film growth by dopants. The resultant films were preferentially (100)-oriented. Their morphology was significantly improved in comparison to earlier depositions. The surface roughness was relatively low, except for occasional hillocks, which may have formed as a result of the post-annealing treatment. The grain structure was dense and non-columnar (Figure 6), which makes this type of film promising for piezoelectric applications.

Figure 7: X-ray θ - 2θ diffraction pattern of PLD film of LiNbO₃ on sapphire (001) substrate.



Shortly before the 18th month meeting the focus of WP4 shifted towards the production of LiNbO₃ films by PLD. This was decided for two reasons. Firstly, the CBE process was still at a relatively early stage of development. Secondly, the production of KNN-based films via PLD was still proving challenging. Therefore, in order to provide samples for the characterization partners to analyze, the decision was taken to attempt the deposition of LiNbO₃ films via PLD. For the sake of optical applications, sapphire and MgO substrates were used. Phase pure and very well (001)-oriented LN films were obtained on sapphire (see fig. 7). Unfortunately, these films are cracked due to thermal mismatch of the two materials. Having a larger thermal expansion, MgO appears to be more adequate for LN deposition. Indeed, no cracks were observed on MgO. Growth on Pt worked as well. Piezo-

sensitive AFM allowed for the conclusion that the film is piezoelectric. Depositions on LN substrates provided by **SAES** are in work.

Partner **CNRS** advanced in micro characterization of optical properties by means of SNOM techniques, and etching of LN. The SNOM was tested at an artificial sub-micron period transparent optical grating with the index variation in the plane. The developed instrument (H-SNOM) allows for simultaneous mapping of amplitude and phase of transmitted or reflected light, and shear forces. This allows to correlated index variations with topographical features. Fig. 8 shows shear force and phase mapping of the same area of an LN/Si sample made by ABCD and EPFL-APL. The difficulty is to differentiate depth variation and index change in the phase change information.

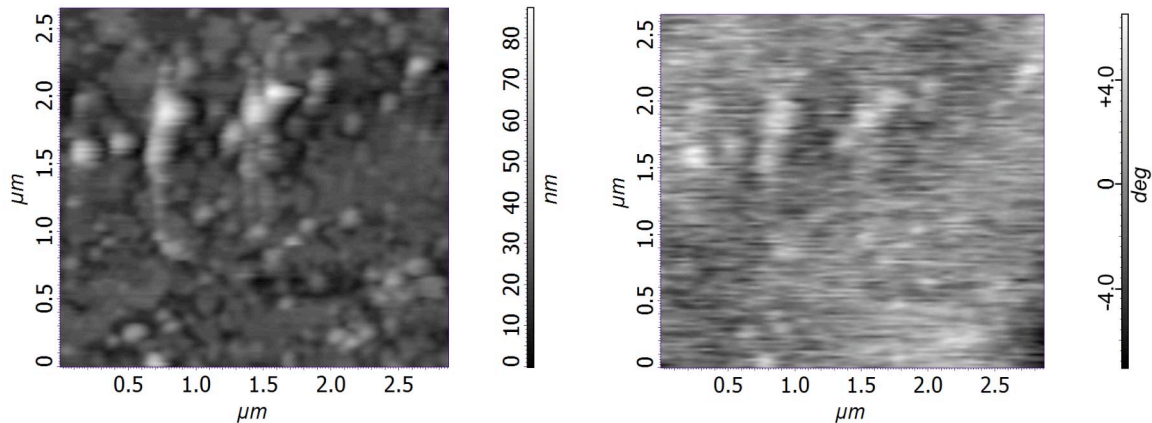


Figure 8: H-SNOM imaging of LN/Si sample: shear force (left) and optical phase (right).

Apart of characterization tasks (see fig. 6), partner **UoS** advances in the structuration technology of LN crystals by the poling inhibition method (fig. 9). It is hoped to apply this method to epitaxial thin films as well, as an alternative to dry etching techniques investigated by partner **CNRS**.

Figure 9: Pyramidal LN feature obtained by the poling inhibition method.

