High throughput exploration of ferroelectric thin film materials using both a temperature-gradient method and a compositional spread technique

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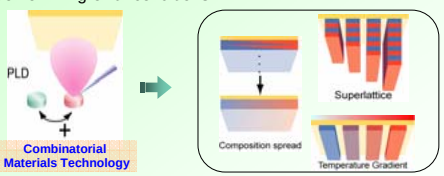
The Emergence of Nanoscale Cooperative Phenomena (ERKCS49)

Motivation :

There have been numerous investigations on transition metal thin films due to their interesting electric and magnetic properties. Obtaining single phase thin films of such complex metal-oxides with excellent crystalline quality by pulsed-laser deposition or other techniques is time-consuming because of the numerous growth parameters to be optimized. A temperature-gradient thin-film growth method allows us to more efficiently determine ideal growth conditions in the exploration of thin films.

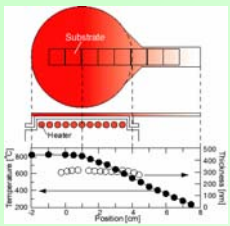
Capability of Combinatorial Thin Film Technology :

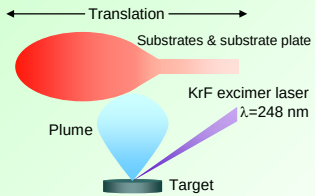
A "*multi-sample*" approach offers a more efficient materials exploration and optimization of film growth conditions.



- Rapid materials exploration with new function
  - Quick and systematic fabrication of binary or ternary phase diagram
  - Non-equilibrium materials (alloys, doped materials, artificial superlattices, etc)
- Quick optimization of epitaxial thin film growth conditions
  - Growth temperature, growth mode, supply rate etc.

Temperature gradient thin film growth method :

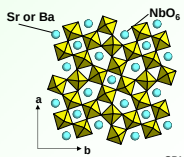




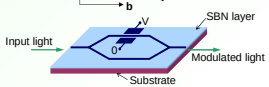
A temperature gradient over the film deposition surface is achieved by placing a specially designed substrate plate in front of a 6.3 cm-diameter radiative heater. This substrate heater unit can be operated above 800 °C in air, and is equipped with motors allowing for precise translation (up to 7 cm) synchronized with the laser firing. For conventional film growth or when operated as part of our PLD-CCS system, a temperature uniformity of ±5 °C is achieved over a 5 cm diameter area. In case of this temperature-gradient film growth, a specially designed substrate holder yields a smooth temperature gradient covering a range of temperatures from 200 °C to 830 °C over a distance of 7.5 cm and in an oxygen background pressure between 100 mTorr and 1×10^{-6} Torr.

$Sr_{1-x}Ba_xNb_2O_6$ (x=0.25~0.75) :

- Tungsten Bronze Type Crystal Structure
- Ferroelectric Materials (Tc=50~200˚C)
- Very High Pockels Coefficient (1400 pm/V : X=0.25, $LiNbO_3$: 31 pm/V) "Super Pockels" Materials



- Optical Switch : Electric-Field Induced Modulation of the Refractive Index



Characterization of thin-film samples:

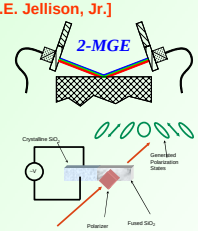
- 2-modulator generalized ellipsometer (2MGE)
- XRD
- Piezo-response force microscopy (PFM)

2MGE and XRD results :

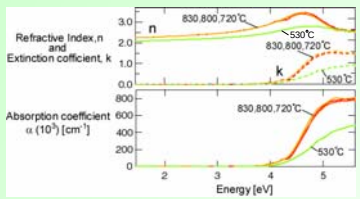
2-modulator generalized ellipsometer (2MGE) **[see poster by G.E. Jellison, Jr.]**

Technique and capabilities:

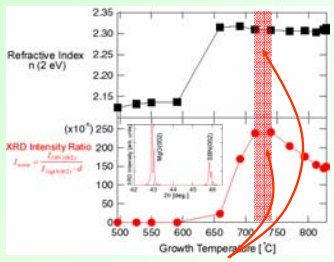
- Two polarizer-photoelastic modulator (PEM) pairs operating at 50.2 and 60.2 kHz
- Wavelength range: 220-880 nm (1.41 to 5.64 eV)
- Determines film thickness, surface roughness, optical characteristics of films such band gap and refractive index
- 2-MGE measures 8 parameters (other ellipsometers usually measure 2) => Anisotropic bulk materials and films



G.E. Jellison Jr, and A. Modine, Appl. Opt. 36, 8184 (1997);36, 8190 (1997).



Spectroscopic values of the refractive index n, the extinction coefficient k, and the absorption coefficient α were obtained for samples grown at various temperatures. A marked difference is observed between the optical properties measured on a sample deposited at 500°C and several samples obtained above 700°C. To illustrate this temperature dependence more clearly, we plot the refractive index at 2.0 eV as a function of the deposition temperature. An almost step-like change is observed between 600°C and 650°C, with no further change at higher temperatures.



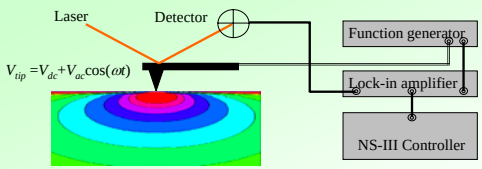
Optimal Growth Temperature around 750 ˚C !

X-ray diffraction (XRD) shows that crystallized SBN films are obtained above 650°C with an SBN[001]//MgO[001] epitaxial relationship. To visualize the dependence of crystallinity as a function of growth temperature, we normalize the intensity of the SBN(002) reflection peak SBN(002) with respect to the intensity of the MgO(002) ($I_{MgO(002)}$) and the slightly varying film thickness *d*.

Strong crystallization occurs at temperatures above 650-700°C, with the strongest values of I_{norm} observed between 700°C and 750°C. At higher substrate temperatures, the x-ray intensity corresponding to this normal orientation decreases.

Since optical properties are a measure of the local coordination in the material, this dependence indicates that crystallization starts to occur around 600°C but full grain growth requires temperatures of at least 700°C.

Piezo-response force microscopy images:
Local measurements of the electro-mechanical properties



$V_{tip} = V_{dc} + V_{ac}\cos(\omega t)$

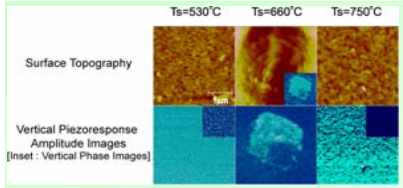
Application of AC bias to the tip

$V_{tip} = V_{dc} + V_{ac}\cos(\omega t)$

results in cantilever deflection

$d = d_0 + A(\omega, V_{dc}, \ldots) V_{ac}\cos(\omega t + \varphi)$

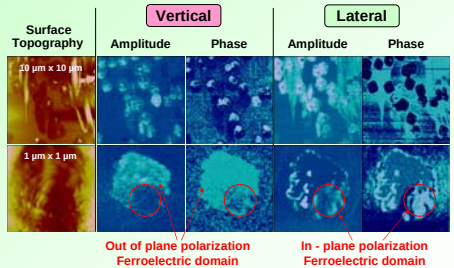
S.V. Kalinin and Dawn A. Bonnell, "Imaging mechanism and Quantification of Scanning Force Microscopy of Ferroelectric Surfaces, in Nanoscale characterization of ferroelectric materials", Eds. M. Alexe and A. Gruverman, in print.



Surface topography and piezo-response images for films deposited at different temperatures are shown in left figures.

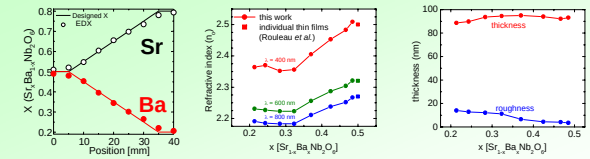
For a deposition temperature of **750 °C**, the surface exhibits well-formed crystallites with an average RMS roughness of 1 – 2 nm. The PFM image shows non-vanishing amplitude and constant phase, indicating that these films are uniformly ferroelectric and have a preferential polarization orientation.

For the low deposition-temperatures (**530 °C**), the film surface is virtually flat with extremely small RMS roughness (0.5 nm). The PFM image is devoid of any observable features, and the PFM phase shows high noise; therefore, we can conclude that this sample is not electromechanically active.
An unusual surface morphology was observed for the sample deposited at **660 °C**. The film forms a number of nearly square features.



The dominant part of each of these "islands" is in a single *c* domain state as evidenced by high vertical response amplitude and uniform phase and the lack of lateral PFM signal. The near-zero PFM amplitude and high phase noise outside of these islands suggest that this portion of the film has extremely weak electromechanical properties.

SBN composition spread thin film : (for technical detail, see the other poster)



After the determination of the optimal growth temperature for epitaxial SBN films, various compositions (Ba:Sr ratios) were explored using a composition-spread approach (described in a separate poster in more detail). The measured stoichiometry was in good agreement with the desired composition for all samples. Ellipsometry was again used to determine the refractive index for each composition. Comparison to the known value of an individual film at 50% Ba shows excellent agreement. Our data show a strong increase of refractive index and decrease of surface roughness with increasing Ba content in the studied range of 20% to 50%.

Summary:

In order to optimize thin-film growth-temperatures more quickly, a temperature-gradient method was developed and applied to the technologically important electro-optical material $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN:50). Combined results from X-ray diffraction, ellipsometry, and piezo-response force microscopy illustrate the mechanisms of crystallization, phase formation, and development of ferroelectric properties. $Sr_{1-x}Ba_xNb_2O_6$ films with compositions ranging from $0.2 \leq x \leq 0.5$ were fabricated in a single "compositional-spread" run at the optimal growth temperature, allowing us to determine the composition-variation of the refractive index.

Significance and impact :

These results demonstrate that a combination of temperature-gradient and composition-spread is very powerful and efficient way for the exploration of transition metal oxide thin films with interesting physical properties. These high-throughput thin-film techniques accelerate the discovery and the optimization of complex materials, and have become an integral part of many of our broader research efforts.
Samples from these studies will now be more carefully characterized by dielectric measurements, and via external collaborations by microwave (George Wash. Univ.) and optical (SUNY Buffalo) methods.