

High-throughput growth temperature optimization of ferroelectric $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ epitaxial thin films using a temperature gradient method

I. Ohkubo,^{a)} H. M. Christen, Sergei V. Kalinin, G. E. Jellison, Jr., C. M. Rouleau, and D. H. Lowndes

Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

(Received 30 October 2003; accepted 3 January 2004)

We have developed a multisample film growth method on a temperature-gradient substrate holder to quickly optimize the film growth temperature in pulsed-laser deposition. A smooth temperature gradient is achieved, covering a range of temperatures from 200 to 830 °C. In a single growth run, the optimal growth temperature for $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ thin films on MgO(001) substrates was determined to be 750 °C, based on results from ellipsometry and piezoresponse force microscopy. Variations in optical properties and ferroelectric domains structures were clearly observed as function of growth temperature, and these physical properties can be related to their different crystalline quality. Piezoresponse force microscopy indicated the formation of uniform ferroelectric film for deposition temperatures above 750 °C. At 660 °C, isolated micron-sized ferroelectric islands were observed, while samples deposited below 550 °C did not exhibit clear piezoelectric contrast. © 2004 American Institute of Physics. [DOI: 10.1063/1.1650916]

There have been numerous investigations on transition metal thin films due to their interesting electric and magnetic properties.¹ Obtaining single phase thin films of such complex metal-oxides with excellent crystalline quality by pulsed laser deposition² or other techniques is time consuming because of the numerous growth parameters to be optimized. To more quickly determine ideal growth conditions in the exploration of thin films, several research groups have implemented “multisample” approaches based on the principles of combinatorial materials technology.^{3,4} In particular, the use of a variable-temperature substrate heater is a powerful tool for the quick optimization of growth temperature and was reported for sputter deposition almost 40 years ago,⁵ but has only recently been applied to complex oxides.^{6,7}

Here we report the technical implementation and performance specifics of a temperature-gradient method based on conventional radiative heating of a metallic substrate holder, using an exposed Pt-based filament. The apparatus is based on—and integrated with—our pulsed-laser deposition based method of continuous compositional-spread (PLD-CCS) as described elsewhere.⁸ The method has successfully been applied to the ferroelectric complex oxide, strontium barium niobate ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) (SBN).

SBN is an attractive ferroelectric material because it exhibits an exceptionally large electro-optic (EO) coefficient, r_{33} , making it a potential material of choice for miniaturized EO modulators, real-time holography applications, and information storage technologies. In particular, r_{33} can be varied by changing compositions ration of Sr and Ba, thus achieving values of r_{33} 10–40 times larger than obtained on congruently grown lithium niobate, the current industry standard.⁹

In our implementation, the temperature gradient over the

film deposition surface is achieved by placing a specially designed substrate plate, as shown in Fig. 1(a), 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). 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. However, intentionally asymmetric radiation loss combined with the limited thermal conduction within the metallic heat plate, lead to significant, but controlled spatial temperature variations. For temperature-gradient film growth, we thus designed a special substrate holder as shown in Fig. 1(a) yielding a smooth

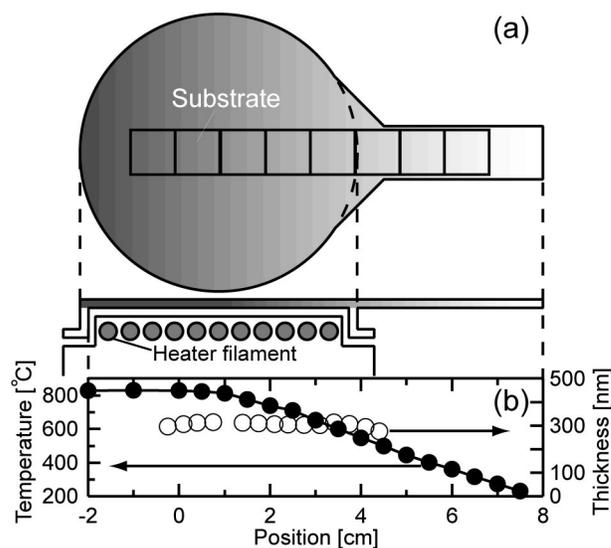


FIG. 1. (a) Schematic representation of the substrate heater with a top plate yielding a smoothly varying temperature profile. (b) Temperature variation across the substrate plate (filled circles, left scale) and obtained film thickness (open circles, right scale), showing satisfactory temperature linearity and thickness uniformity.

^{a)}Electronic mail: okuboi@ornl.gov

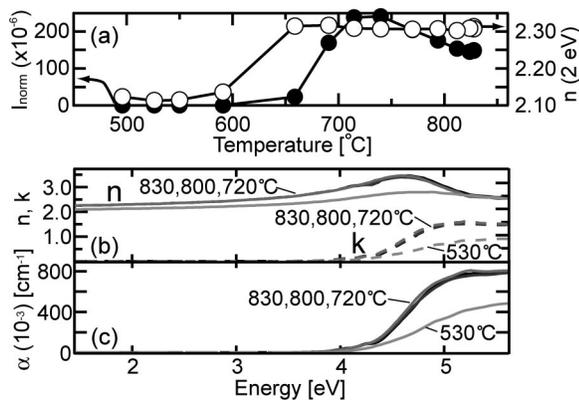


FIG. 2. (a) Normalized XRD intensity of SBN(002) peaks (filled circles, left scale) and refractive index (empty circles, right scale) at 2.0 eV. The XRD intensity is normalized by the MgO(002) substrate peak intensity and the SBN film thickness as determined by 2-MGE. (b) Spectroscopic values of the refractive index n , the extinction coefficient k , and the absorption coefficient α , SBN:50 films grown on MgO(001), determined by 2-MGE.

temperature gradient covering a range of temperatures from 200 to 830 °C over a distance of 7.5 cm [Fig. 1(b)] and in an oxygen background pressure between 100 mTorr and 1×10^{-6} Torr. In initial test runs, the temperature at 18 points on the substrate holder was measured by individual thermocouples and shown to be highly reproducible [in fact, the 18 data points in Fig. 1(b) were obtained on six separate runs]. A two-color pyrometer is then used for minor run-to-run adjustments of the heater power. During film growth onto this temperature-gradient substrate holder, a position-dependent laser repetition rate was used in combination with an oscillatory linear motion of this heater to obtain a uniform thickness distribution of SBN thin films on MgO(001) substrates.¹⁰ These thicknesses were determined by two-modulator generalized ellipsometry (2-MGE)¹¹ measurements; as shown in Fig. 1(b), they vary by less than 15% across the area of interest for this study (500–830 °C).

$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ (SBN:50) films were deposited at an oxygen pressure of 15 mTorr by impinging KrF excimer laser ($\lambda = 248$ nm) pulses at an average repetition rate of 10 Hz and an energy density of 3.8 J/cm² on ceramic SBN:50 targets placed at a distance of 6.5 cm from the MgO(001) substrates.

X-ray diffraction (XRD) shows that crystallized SBN films are obtained above 650 °C with an SBN[001]//MgO[001] epitaxial relationship. Growth occurs via a rotation of the SBN[110] orientation of 18.43° with respect to that of the MgO substrate, as determined from x-ray phi scans, and is consistent with a previous report.¹² To visualize the dependence of crystallinity as a function of growth temperature, we normalize the intensity of the SBN(002) reflection peak $I_{\text{SBN}(002)}$ with respect to the intensity of the MgO(002) ($I_{\text{MgO}(002)}$) and the slightly varying film thickness d , i.e., $I_{\text{norm}} = I_{\text{SBN}(002)} / (I_{\text{MgO}(002)} d)$.

As shown in Fig. 2(a), strong crystallization occurs at temperatures above 650–700 °C, with the strongest values of I_{norm} observed between 700 and 750 °C. At higher substrate temperatures, the x-ray intensity corresponding to this normal orientation decreases.

Figures 2(b) and 2(c) depict spectroscopic values of the refractive index n , the extinction coefficient k , and the ab-

sorption coefficient α . Accurate values of the optical functions are obtained above and below the band edge, and are consistent, within experimental error, with published values.¹³ The 2-MGE is very sensitive to cross-polarization effects, which were not observed, indicating the films were highly c perpendicular, even near the heterointerface. 2-MGE therefore measures only the ordinary optical functions.

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 in Fig. 2(a) the refractive index at 2.0 eV as a function of the deposition temperature. An almost step-like change is observed between 600 and 650 °C, with no further change at higher temperatures. 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. The decrease in x-ray intensity above 750 °C (in a regime where the optical properties and thus the short-range structure do not change) is therefore interpreted in terms of a poorer epitaxial relationship between the substrate and the film, and a broader distribution of grain orientations.

To more clearly visualize and interpret the changes occurring in these films as function of deposition temperature, atomic force microscopy (AFM) and PFM measurements^{14,15} were performed in a configuration based on a commercial AFM (MultiMode, NS IIIA, Digital Instruments). To avoid the capacitive crosstalk, the gold-coated tips ($\lambda \approx 125$ μm , resonant frequency ~ 150 kHz) were mounted in a custom tip holder for direct tip biasing (typically 6 V_{pp}). Phase θ and amplitude A of vertical and lateral PFM signals were recorded sequentially. Topographic images were processed using usual line flattening; PFM phase and amplitude images are unprocessed.

Surface topography and piezoresponse images for films deposited at different temperatures are shown in Fig. 3. For a deposition temperature of 750 °C, the surface exhibits well-formed crystallites with average rms roughness of 1–2 nm [Fig. 3(c)]. The PFM image shows nonvanishing amplitude [Fig. 3(f)] and constant phase [Fig. 3(i)], indicating that these films are uniformly ferroelectric and have a preferential polarization orientation. An unusual surface morphology was observed for the sample deposited at 660 °C [Fig. 3(b)]. 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 [Fig. 3(e)] and uniform phase [Fig. 3(h)] and the lack of lateral PFM signal (not shown). 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. Finally, for the low deposition temperatures (530 °C), the film surface is virtually flat with extremely small rms roughness [0.5 nm, Fig. 3(a)]. The PFM image [Fig. 3(d)] is devoid of any observable features, and the PFM phase [Fig. 3(g)] shows high noise; therefore, we can conclude that this sample is not electromechanically active.

These observations are consistent with the combined ellipsometry and x-ray data, indicating in fact that a uniformly

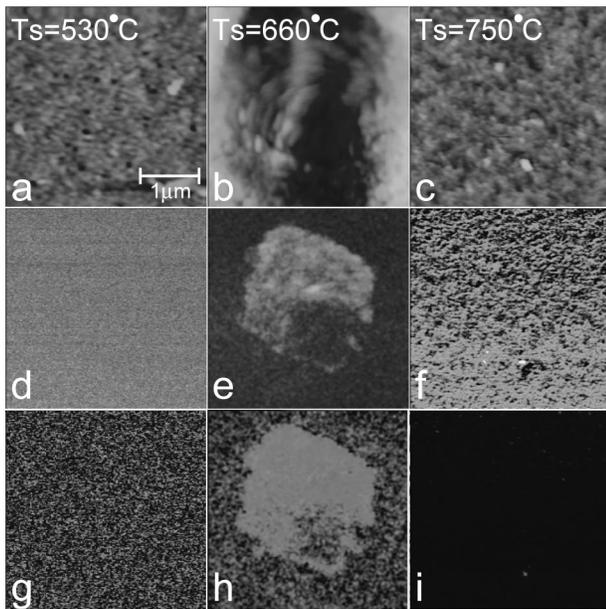


FIG. 3. Surface topography (a),(b),(c) and vertical (d),(e),(f) and lateral (g),(h),(i) piezoresponse amplitude images of SBN surface deposited at 530 °C (a),(d),(g), 660 °C (b),(e),(h), 750 °C (c),(f),(i).

crystallized, electromechanically active film is only formed at higher temperatures. In the intermediate temperature regime, the film consists of separate regions with very different electromechanical properties. Ellipsometry suggests a crystalline-like refractive index for these samples. However, the model-dependent data analysis is based on the assumption of a uniform layer, contrary to the observed microstructure. While this simplification prevents us from making definite statements about the refractive index in this “mixed” region, it is remarkable that the ellipsometry data shows a dominance of the refractive index corresponding to the fully crystallized phase. This appears to indicate that the local properties of the material are already “crystal-like” at the intermediate deposition temperatures, where AFM and x-ray data show incomplete crystallinity.

To summarize, a temperature-gradient apparatus based on radiative substrate heating allows us to simultaneously deposit thin films onto multiple samples at different growth temperatures spanning a range of 500 °C. For a series of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ films on $\text{MgO}(001)$ substrates, variations in optical properties and ferroelectric domain structures were clearly observed as function of growth temperature, and these physical properties can be related to their different crystalline quality. The results indicate a sharp “step” in the refractive index near 650 °C but full crystallization occurring only at a slightly higher temperature.

Research sponsored by the U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

- ¹H. Koinuma, *Mater. Res. Bull.* **19**, 21 (1994).
- ²D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, *Science* **273**, 898 (1996).
- ³X.-D. Xiang, X. Sun, B. Griceno, Y. Lou, K. Wang, H. Chang, W. G. Wallace-Freedman, S. Chen, and P. G. Schultz, *Science* **268**, 1738 (1995).
- ⁴I. Takeuchi, R. B. van Dover, and H. Koinuma, *Mater. Res. Bull.* **27**, 301 (2002).
- ⁵K. Kenndy, Atomic Energy Commission Report UCRL-16393, Sept., 1965.
- ⁶T. Koida, D. Komiyama, H. Koinuma, M. Ohtani, M. Lippmaa, and M. Kawasaki, *Appl. Phys. Lett.* **80**, 565 (2002).
- ⁷J. Nishimura, T. Fukumura, M. Ohtani, Y. Taguchi, M. Kawasaki, I. Ohkubo, H. Koinuma, H. Ohguchi, K. Ono, M. Oshima, and Y. Tokura, *Appl. Phys. Lett.* **82**, 1571 (2003).
- ⁸H. M. Christen, C. M. Rouleau, I. Ohkubo, H. Y. Zhai, H. N. Lee, S. Sathyamurthy, and D. H. Lowndes, *Rev. Sci. Instrum.* **74**, 4058 (2003).
- ⁹T. Mitsui and S. Nomura, *Landolt-Börnstein* **16**, 538 (1981).
- ¹⁰I. Ohkubo, H. M. Christen, G. E. Jellison, Jr., the 204th Meetings of the Electrochemical Society Proceedings (to be published).
- ¹¹G. E. Jellison, Jr., and A. Modine, *Appl. Opt.* **36**, 8184 (1997); **36**, 8190 (1997).
- ¹²J. M. Marx, Z. Tang, O. Eknayan, H. F. Taylor, and R. R. Neurgaonkar, *Appl. Phys. Lett.* **66**, 274 (1995).
- ¹³S. Schwyn Thöny, K. E. Youden, J. S. Harris, Jr., and L. Hesselink, *Appl. Phys. Lett.* **65**, 2018 (1994).
- ¹⁴S. V. Kalinin and D. A. Bonnell, in *Nanoscale Characterization of Ferroelectric Materials*, edited by M. Alexe and A. Gruverman (in press).
- ¹⁵S. V. Kalinin and D. A. Bonnell, *Phys. Rev. B* **65**, 125408 (2002).