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Crystallization of amorphous (Ba, Sr)TiO_3/MgO(001) thin films

D. Y. Noh[a] and H. H. Lee
Department of Materials Science and Engineering and Center for Electronic Materials Research, Kwangju Institute of Science and Technology, Kwangju, 506-712, Korea

T. S. Kang and J. H. Je
Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

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The crystallization of amorphous $Ba_xSr_{1-x}TiO_3$ (BST) thin films was studied in a synchrotron x-ray scattering experiment. In a 550 Å thick film, the crystallization to perovskite phase was occurred at around 700 °C, while a 5500 Å thick film became crystalline at 500 °C. The thickness dependence of the crystallization was attributed to the observed intermediate phase nucleated near 600 °C at the interface. In thin films, high annealing temperature was required due to the energy barrier between the perovskite phase and the intermediate phase. In the thick film, the perovskite phase was nucleated directly from the amorphous phase in the bulk of the film concurrent to the nucleation of the intermediate phase at the interface. © *1998 American Institute of Physics.*
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$Ba_xSr_{1-x}TiO_3$ (BST) has been extensively studied due to its excellent dielectric properties required in microelectronic devices like nonvolatile ferroelectric memories.[1,2] Many growth techniques, such as radio-frequency (rf) magnetron sputtering, pulsed laser ablation, and plasma-enhanced metalorganic chemical vapor deposition have been applied to obtain BST films of high quality.[3–5] Crystalline BST films are usually obtained at relatively high substrate temperature. During the film growth, however, interlayers and specific grain structures are developed which cause serious problems of low dielectric constant and the leakage current.[6–8] An alternative approach is to grow amorphous BST films at low temperature and to crystallize them in a post-annealing process. Improvement of the dielectric constant and the leakage currents has been reported on post-annealed amorphous BST films.[9,10]

In this letter, we present a real-time synchrotron x-ray scattering study of the structural evolution of amorphous BST thin films during the post annealing process. Our study reveals that an intermediate metastable phase nucleated near the interface plays an important role in the crystallization to the stable perovskite phase in thin films. In thin BST films (<500 Å) the whole film first transformed to the intermediate phase, and the stable perovskite phase was achieved at higher annealing temperature. On the other hand, in a 5500 Å thick film, the perovskite phase was nucleated in the bulk of the film at relatively low temperature together with the nucleation of the metastable phase at the interface.

The amorphous BST films were grown on single-crystal MgO(001) substrates by rf magnetron sputtering of a sintered BST target at room temperature. As the carrier gas, a mixture of O_2 and Ar was used. The MgO(100) substrates were selected, since MgO single crystals have smooth and stable surface morphology, and relatively small lattice mismatch with BST. All the films studied were grown in a sputter deposition chamber simultaneously to minimize systematic errors. The thicknesses of the BST films studied in this experiment, determined by x-ray reflectivity measurement, were 300, 550, 1150, and 5500 Å. We estimated that the composition of the films used was about $(Ba_{0.5}Sr_{0.5})TiO_3$ from the measured lattice constant of a thick film.

The x-ray scattering measurements were performed at the beamline 3C2 at Pohang Light Source (PLS) in Korea. The incident x rays were focused vertically and horizontally by a toroidal mirror, and monochromatized to the wavelength of 1.74 Å by a double bounce Si(111) crystals. Two pairs of slits in front of the detector provided an appropriate detector resolution. The experiment was carried out by measuring the conventional x-ray powder diffraction profile and the x-ray reflectivity curve at several temperatures during the annealing. The amorphous BST films were annealed in a heating stage that was designed to raise the sample temperature to 800 °C. The annealing was performed in air to avoid oxygen deficiency during annealing. The heating stage was set on a four-circle x-ray diffractometer for the real-time x-ray measurements. The temperature was increased step by step and kept constant during the x-ray measurement.

Figure 1 shows the powder diffraction profiles of (a) a 550 Å, and (b) a 5500 Å thick BST films measured at several temperatures during the annealing process. A broad hump, indicated by the arrows in the figure, appeared at around 3.07 $Å^{-1}$ close to the substrate MgO(002) Bragg peak in all the samples in the temperature ranging from 500 to 600 °C. The broad peak appeared out of the tail of the MgO(002) peak which was enhanced due to the interface truncation effect. We suspect that the broad peak represents the formation of an intermediate metastable phase.

In the inset of Fig. 1(a), the diffraction profile of the intermediate phase measured at 700 °C was illustrated. The intense substrate peak was subtracted to emphasize the x-ray diffraction pattern of the intermediate phase. The peak was at 3.07 $Å^{-1}$ with the full width at half maximum of about

a)Corresponding author. Electronic mail: dynoh@matla.kjist.ac.kr

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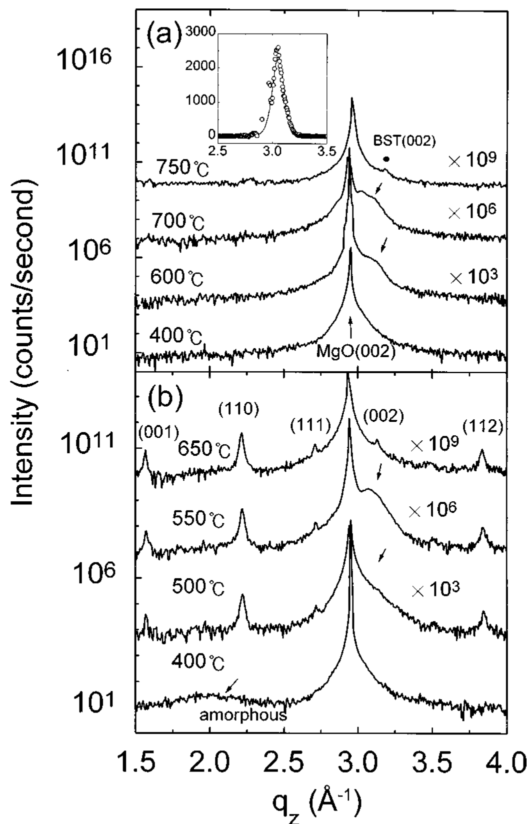

FIG. 1. The x-ray powder diffraction profiles of (a) a 550 Å thick BST film and (b) a 5500 Å thick BST film measured during real-time annealing. Note that logarithmic scale was used in y axis to signify the weak scattering feature of the intermediate phase. The inset of (a) represents the diffraction profile of the intermediate phase. To emphasize the peak, we used linear scale in y axis. The line is best fit to Lorentzian to deduce the width of the peak.

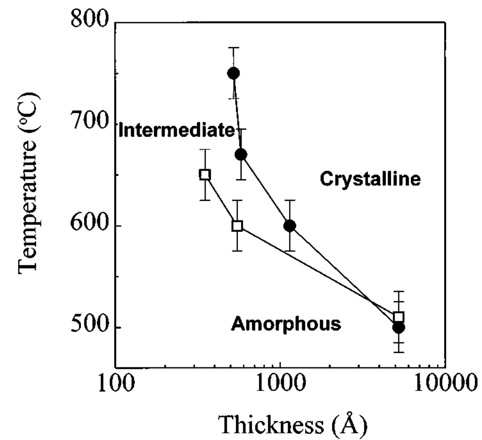

FIG. 2. The annealing temperatures to the perovskite phase (filled circles) and to the intermediate phase (open squares) as a function of film thickness.

$0.12\ \text{Å}^{-1}$. The crystal domain size of the intermediate phase deduced using Scherrer's formula[11] was about 40 Å in all the films, which indicates that the intermediate phase was a nanocrystalline phase. The nanocrystallinity of the intermediate phase was similar to the nature of the metastable pyrochlore phase observed in PZT films.[12] On the other hand, the intermediate phase shows different peak position from the reported metastable pyrochlore phase in BST.[13,14] We also believe that the composition of the film was not changed during the formation of the intermediate phase since the transformation was mainly structural in nature. Detailed atomic configuration of the intermediate phase is to be determined in future.

The nucleation of the stable crystalline perovskite phase was quite sensitive to the film thickness. In the thin 550 Å film a small but sharp perovskite Bragg peak indicated by BST(002) in Fig. 1(a), appeared upon annealing to 700 °C as the broad peak from the intermediate phase disappeared. The thinnest 300 Å sample was not even transformed to perovskite phase up to 750 °C (data not shown) which was the highest temperature studied in this work. In the meanwhile, in the thick 5500 Å film the perovskite Bragg peaks started to show up at as low as 500 °C. The diffraction profile at 500 °C shown in Fig. 1(b) demonstrates clearly the perovskite Bragg peaks as well as the precursor of the intermediate phase. This indicated that the perovskite phase was nucleated as the intermediate phase was formed. The peak from the intermediate phase became distinct at 550 °C and disappeared upon further annealing to 650 °C.

Figure 2 summarizes the annealing temperatures to the intermediate phase and to the perovskite phase as a function of the film thickness. It is clear that the thin films undergoes two stage transformations to reach the crystalline perovskite phase, while the thick film transforms directly from the amorphous to the crystalline phase. In thin films, the amorphous phase first transforms to the intermediate metastable phase. Since the energy barrier from the metastable phase to the perovskite phase is probably higher than that from the amorphous to the perovskite phase, the crystallization temperature in the thin films is higher as shown in the figure. In the thick films or in bulk BST, the amorphous phase transforms directly to the perovskite phase at relatively low annealing temperature.

The observed thickness dependence of the crystallization in BST might be related to the film-substrate interfacial behavior during the crystallization. To study the interfacial behavior, we performed an x-ray reflectivity measurement that is one of the powerful methods to study morphological properties of buried interfaces.[15] The x-ray reflectivity represents the interference pattern of the reflected x rays from the surface and the interface, which is described by[16]

$$S_{\text{spec}}(\mathbf{q}) = \frac{A}{q_z^2}\left[\rho_1^2 e^{-q_z^2\sigma_1^2} + (\rho_2-\rho_1)^2 e^{-q_z^2\sigma_2^2} + 2\rho_1(\rho_2-\rho_1)\cos(q_z d) e^{-q_z^2(\sigma_1^2+\sigma_2^2)/2}\right]\delta(\mathbf{q}_\parallel),$$

where $q_z(\mathbf{q}_\parallel)$ is x-ray momentum transfer along the surface normal (in-plane) direction, $\rho_1(\rho_2)$ is the electron density of BST (MgO), $\sigma_1(\sigma_2)$ is the root-mean-squared surface (interface) roughness, and d is the average film thickness.

Figure 3 shows the x-ray reflectivity curves of 550 Å and 5500 Å thick films measured during the annealing. The thickness of the films was determined by the period of the intensity oscillations Δq in the reflectivity curve by $2\pi/\Delta q$, except for the 5500 Å thick film where the oscillation was not observed. Usually the intensity oscillation becomes weak in case of thick films, since the oscillation period becomes very small and the roughness increases. As indicated by the

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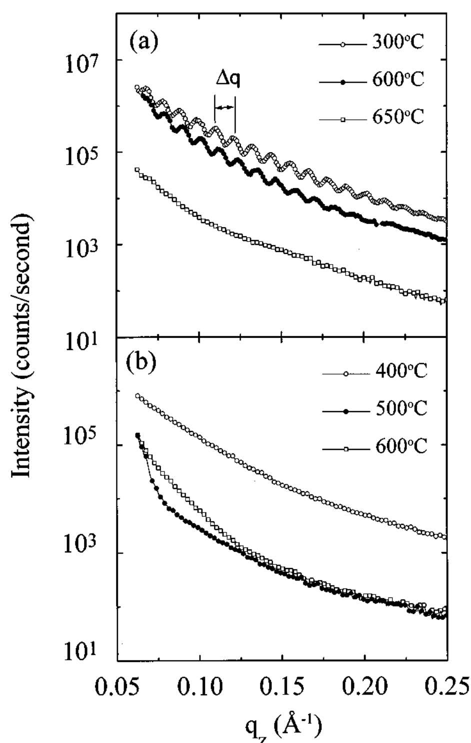

FIG. 3. The x-ray reflectivity curves of (a) the 550 Å thick film, and of (b) the 5500 Å thick film at temperatures below and above the nucleation of the intermediate phase.

above equation, the amplitude of the intensity oscillation and the overall intensity depend strongly on the roughness of the interface and of the surface.

The reflectivity decreased dramatically in both films as they were annealed to the temperature at which the intermediate phase was formed. In the 550 Å thick film, the intensity oscillation was also disappeared at the same time. The decrease of the reflected intensity indicated that the interface became rough as the intermediate phase was formed. A fit to the above equation suggested that the interfacial roughness was larger than 20 Å when the intermediate phase was formed. We conjecture that the intermediate phase was nucleated at the interface, which made the interface rough. If the nucleation of the intermediate phase occurred at the interface, it is natural that the transformation temperature from the amorphous to the intermediate phase would not strongly depend on the film thickness. A transmission electron microscopy (TEM) study has reported the observation of a similar intermediate phase near the interface.[8]

We explain the observed crystallization behavior as follows. In thin films, the intermediate phase nucleated at the interface propagated throughout the whole film. The energy barrier between the intermediate phase and the perovskite phase raised the crystallization temperature to much higher temperature. We also believe that the interface acts as the nucleation center for the perovskite phase from the intermediate phase in thin films. The [001]-oriented texture of the thin films, which is supported by the fact that there are only the Bragg peaks parallel to the [001] direction in Fig. 1(a), could be explained by this. In thick films, however, the perovskite phase started to nucleate in the bulk of the film simultaneous to the nucleation of the intermediate phase at the interface. Since the nucleation happens in the bulk of the film randomly, the crystalline orientation must also be random. The perovskite Bragg peaks of various orientations shown in Fig. 1(b) support the random orientation of the crystalline direction in the thick film. This is consistent with the crystalline domain structure observed in the TEM studies.[8,10]

In conclusion, we revealed the detailed process of the crystallization of amorphous BST films using real-time synchrotron x-ray scattering measurements. Our study shows that a metastable intermediate phase, that was nucleated at around 500–600 °C at the interface in all the films, plays a crucial role in the crystallization process. The nucleation of the perovskite phase in the thick 5500 Å film started at around 550 °C in the bulk of the film simultaneous to the nucleation of the intermediate phase near the film-substrate interface. In the thin 550 Å film, however, the transition occurred at much higher temperature near 700 °C due to the extra energy barrier between the perovskite phase and the intermediate phase. Further study is required to elucidate the detailed nature of the intermediate phase.

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