Film Growth of Perovskite Oxides by Real-time X-ray Scattering

Perovskite oxides is a class of materials with a wide range of interesting properties in ferroelectric, dielectric, semiconducting, superconducting, and optical properties. Thin films of perovskite oxides have been extensively studied for device applications such as microelectronic, memory, sensor, microwave and optical devices. The properties of perovskite oxide films grown under different conditions generally depart significantly from those of corresponding bulk materials. Thus, the understandings of the growth mechanism and the film structure of this class of materials are of great interest.

Molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) are the common ways of growing epitaxial films of complex oxides. Both methods have the advantages of maintaining control in stoichiometry, crystal structure, and crystal orientation. However, in sight of the compatibility to the industrial fabrication processes, the growth of high quality oxide films by radio frequency (RF) magnetron sputtering deposition is highly desirable. But, the growth parameters in RF sputtering are complex, which include working pressure, gas composition, substrate temperature, and deposition rate. In order to investigate the film growth process during sputtering, we have employed synchrotron X-ray scattering technique as a real-time probe. Using *in-situ* X-ray measurements, we can efficiently search for the optimal conditions for growing films of special morphology. In this article, we report the recent results of our two studies on the growth behavior of the perovskite-type oxide thin films by RF magnetron sputtering technique. The first work is the study of homoepitaxial growth of $SrTiO_3$ (STO) and the second is of heteroepitaxial growth of $LaNiO_3$ (LNO) on STO substrate.

The sputtering cell was mounted on a Huber 8-circle diffractometer as displayed in Fig. 1. Two 0.5 mm thick Be windows on the sputtering cell allow the entrance and exit of X-rays. The sputtering was carried out at a power density of 0.5 w/cm^2 under a working pressure of 15 mTorr and a gas mixature of O_2 (25%) and Ar (75%). Substrate temperature can be varied from room temperature to 750 ℃. The growth rate is about 1.5 Å/min as estimated from the X-ray reflectivity measurements. The growth experiments were carried out on wiggler beamline BL17B. In the scattering measurements, typical wave vector resolution was set at ~ 0.001 Å^{-1} by using two pairs of slits between sample and detector.

The *in-situ* monitoring of the growth is carried out by measuring the intensity oscillation in real time at different diffraction points of the specularly reflected X-rays. Figure 2 shows such measurements of STO on STO at the anti-Bragg position (0 0 0.5) and Fig. 3 of LNO on STO at (0 0 0.75). For STO on STO, the damping rate of intensity observed implies that the surface becomes rougher

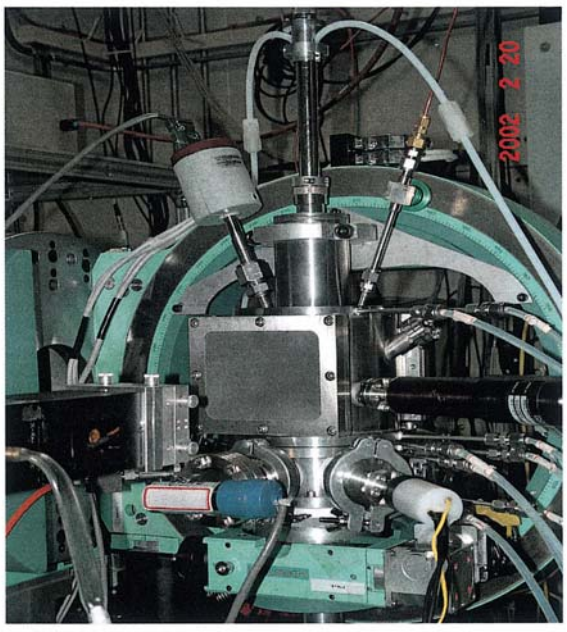

Fig. 1: The oxide growth chamber mounted on a Huber 8-circle diffractometer.

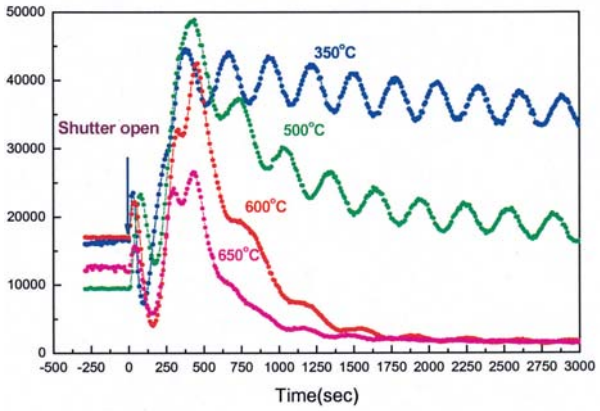

Fig. 2: Real-time measurement of the X-ray intensity at anti-Bragg point (0 0 0.5) of STO on STO deposition by sputtering with different substrate temperatures.

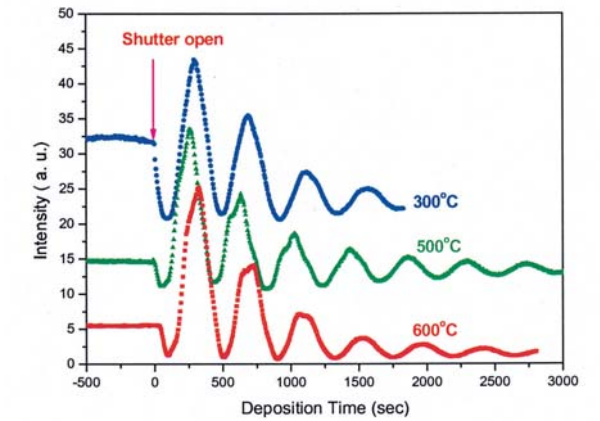

Fig. 3: Real-time intensity oscillations at (0 0 0.75) of LNO on STO substrate during RF sputtering with different substrate temperatures.

with increased substrate temperatures. The lengthening of oscillation period with elevated substrate temperature indicates that STO grows slower with increased temperature.

Interestingly, the growth of LNO on STO behaves quite differently. For all temperatures, the specular intensity oscillations show remarkable similarity, i.e. the dependence of surface roughness with deposition temperature is relatively weak as compared to STO on STO. The difference of the growth behavior between the two cases is also observed at the initial stage of the deposition. For LNO on STO, the reflectivity immediately drops after the shutter was opened. The oscillations reveal layer-by layer growth with the decrease in oscillation amplitude, indicating that the surface becomes rough over time. For STO on STO, the growth oscillation curves exhibit very different profiles with deposition temperature, indicating complicated surface morphology dependence with temperature at the initial growth.

The *ex-situ* studies of the grown films indicate that the films with good reflectivity oscillation are indeed epitaxial with the STO substrate. The epitaxial relation is studied by in-plane X-ray scans on these films using grazing incident scattering geometry. A typical curve of such scan around (200) from a STO film deposited at 750℃ is shown in the inset of Fig. 4. The broad peak is ascribed to the Bragg peak of the deposited layer while the sharp peak from the substrate. We note that the peak is down shifted by 1% from the bulk value which is attributed to the deficiency in density of the deposited films as discussed in detail elsewhere (Ref. 3). The detailed profiles near total reflection angle of the X-ray reflectivity curves are illustrated in Fig. 5. The graduate decrease of the critical angle with decreasing deposition temperature manifests that the density of low temperature (≦ 250 ℃) deposited films are much lower than that of the films deposited at high temperatures (≧ 500 ℃), which in turn is slightly lower than that of STO substrate, ρ. Most evidence of epitaxy is revealed in the azimuthal scan around surface Bragg peak which shows clearly an 4-fold symmetry.

For the LNO on STO growth, Fig. 6 compares

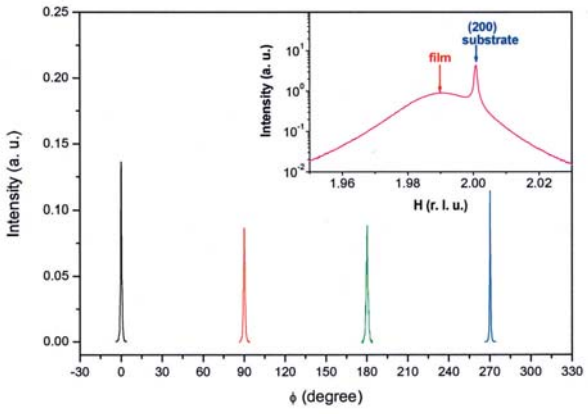

Fig. 4: The azimuthal scan around the surface (200) peak of a STO film deposited at 750℃. Inset: In-plane diffraction profile of (200) reflection.

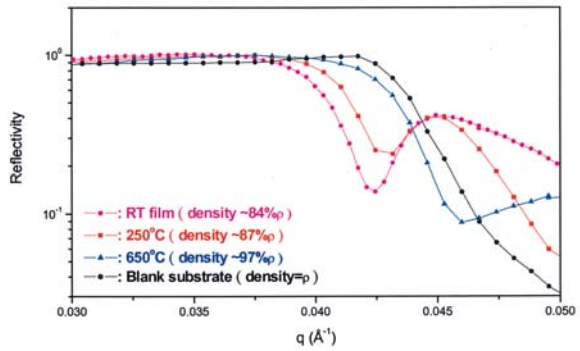

Fig. 5: The detailed profile near total reflection angle of X-ray reflectivity curves for different STO films.

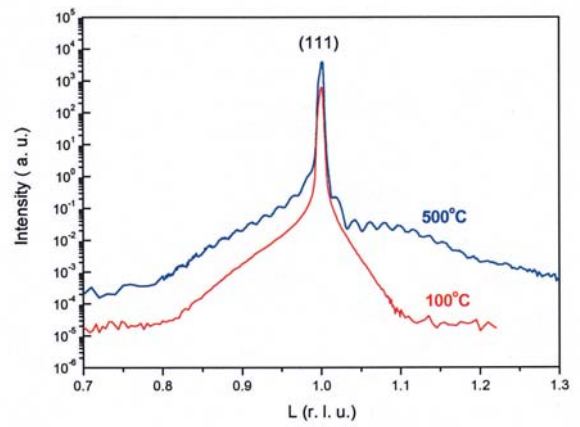

Fig. 6: Profiles of the (111) crystal truncation rod of two LNO films on STO substrates grown at 100 ℃ and 500 ℃.

the crystal truncation rod measurements taken around (111) Bragg peak for the 100 ℃ and 500 ℃ deposited films. The distinct interference fringes are observed for the film deposited at 500 ℃ but not for 100 ℃, elucidating that epitaxial relation along (111) plane with the substrate can be achieved at high temperature deposition.

In summary, we have demonstrated that the real-time synchrotron X-ray scattering under *in-situ* sputtering conditions is a very powerful tool to study the growth behavior of perovskite oxides. Using *in-situ* X-ray technique, we have successfully found the conditions of RF sputtering growth for high quality homoepitaxial STO and heteroepitaxial LNO films on STO substrates.

Beamline:

17B1 W20/X-ray Scattering beamline

Experimental Station:

8-circle diffractometer end station

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Publications:

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