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Adsorption-Controlled Growth of Ferroelectric pbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Films for Nonvolatile Memory Applications by MBE

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ADSORPTION-CONTROLLED GROWTH OF FERROELECTRIC PbTiO_3 AND $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ FILMS FOR NONVOLATILE MEMORY APPLICATIONS BY MBE

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ABSTRACT

Epitaxial PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films have been grown on (100) SrTiO_3 and (100) LaAlO_3 substrates by reactive molecular beam epitaxy (MBE). Titanium is supplied to the film in the form of shuttered bursts each containing a one monolayer dose of titanium atoms for the growth of PbTiO_3 and three monolayers for the growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Lead, bismuth, and ozone are continuously supplied to the surface of the depositing film. Growth of phase pure, *c*-axis oriented epitaxial films with bulk lattice constants is achieved using an overpressure of these volatile species. With the proper choice of substrate temperature (600 - 650 °C) and ozone background pressure ($P_{\text{O}_3} = 2 \times 10^{-5}$ Torr), the excess of the volatile metals and ozone desorb from the surface of the depositing film leaving a phase-pure stoichiometric crystal. The smooth PbTiO_3 surface morphology revealed by atomic force microscopy (AFM) suggests that the PbTiO_3 films grow in a layer-by-layer fashion. In contrast the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films contain islands which evolve either continuously or around screw dislocations via a spiral-type growth mechanism.

INTRODUCTION

PbTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are well known ferroelectric oxides and are both members of the $(\text{Bi,Pb})_{n+1}\text{Ti}_n\text{O}_{3n+3}$ Aurivillius homologous series [1]. PbTiO_3 is the $n = \infty$ member of this series and has the largest remanent polarization ($80 \mu\text{C}/\text{cm}^2$) of any known ferroelectric [2]. PbTiO_3 has a tetragonal unit cell at room temperature with $a = b = 3.90 \text{ \AA}$ and $c = 4.15 \text{ \AA}$ [3]. At the other end of this homologous series, $n = 3$, lies the highly layered compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ which has lower remanent polarization ($\sim 50 \mu\text{C}/\text{cm}^2$ of which the component along the *c*-axis is $\sim 4 \mu\text{C}/\text{cm}^2$ [3]), but can withstand far more polarization reversals before it fatigues [4]. The structure consists of Bi_2O_2 layers separated by $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ perovskite sheets. It is orthorhombic at room temperature with lattice constants $a = 5.41$, $b = 5.45$ and $c = 32.83 \text{ \AA}$ [3]. The resistance to fatigue of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and other Aurivillius phases make these materials of interest for use in non-volatile ferroelectric random access memories (FRAMs). On the other hand the high P_r of PbTiO_3 makes it of interest for superconducting field effect transistors (SuFETs) [5]. We are interested in the variation of properties that occur in the $(\text{Bi,Pb})_{n+1}\text{Ti}_n\text{O}_{3n+3}$ homologous series and describe below the preparation of the two end members of this series by MBE.

EXPERIMENTAL

Bismuth and lead titanate are grown using reactive MBE. The system used for this study is described in detail elsewhere [6]. Lead and bismuth are continuously supplied to the surface of the depositing film from low-temperature effusion cells. Titanium is sublimated onto the film from a titanium sublimation pump. The Ti-Ball™ [7] is powered by a low noise DC power supply. The resulting titanium flux has a maximum peak-to-peak variation of $\pm 2.5\%$ over 5 hours [8] (about five times longer than the time needed to grow a 1000 \AA thick PbTiO_3 or $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film).

The fluxes of all depositing species are monitored *in situ* using atomic absorption spectroscopy (AA). Oxygen is supplied to the film in the form of $\sim 80\%$ pure distilled ozone. Film growth is monitored continuously using reflection high energy electron diffraction (RHEED). The substrate heater-block temperature is measured by an optical pyrometer. (100) LaAlO_3 and (100) SrTiO_3 substrates are used. The SrTiO_3 wafers are etched with a buffered-HF solution prior to growth [9]. The substrates are attached to heater blocks using silver paint.

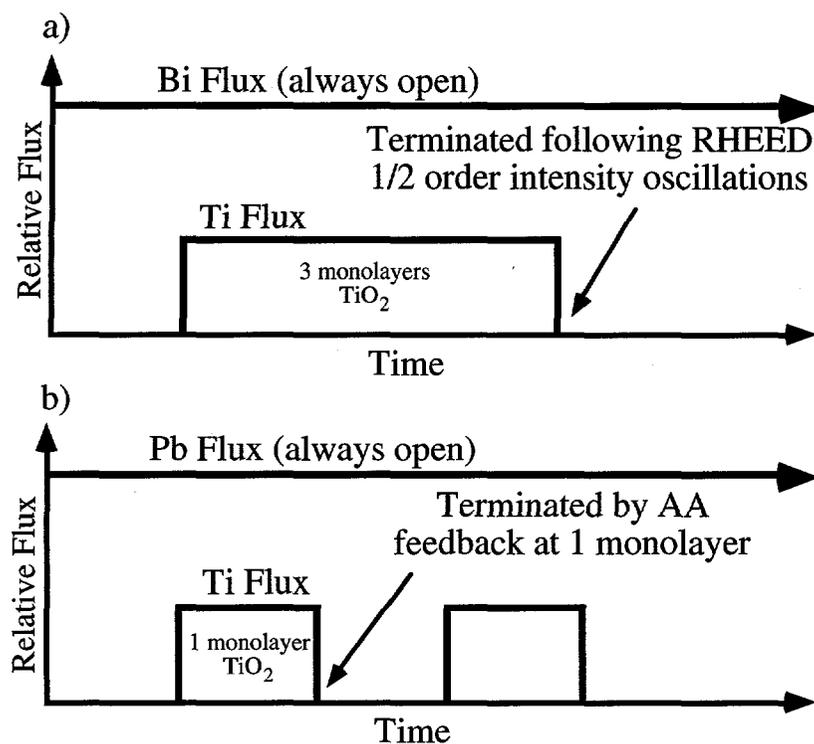


Fig. 1. Flux vs. time for a typical MBE growth of (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ or (b) PbTiO_3 . Ozone is supplied continuously to the surface of the depositing film.

Figure 1(a) shows the depositing flux as a function of time used for the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ growths. Bismuth and ozone are supplied to the surface of the film continuously while the substrate temperature is maintained at $\sim 640^\circ\text{C}$. The ozone background pressure for a typical growth is 2×10^{-5} Torr which represents an incident flux of ozone hundreds of times greater than required for a stoichiometric crystal. Similarly, bismuth is supplied at an incident flux $\sim 2 - 5$ times greater than the average titanium incident flux. Titanium is supplied in shuttered doses each containing three monolayers of titania which make up the $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ perovskite sheets. The titanium dose is terminated by the evolution of RHEED half-order streaks present along the substrate [110] azimuth. The oscillating half-order streaks, which are not damped throughout film growth, are due to the epitaxial relationship between the cubic substrate and orthorhombic film where $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [100] // SrTiO_3 [110]. The disappearance of these oscillating half-order streaks could be a manifestation of the higher symmetry of the centermost TiO_6 octahedra which are not tilted with respect to c -axis or rotated with respect to the a - b plane of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [10]. As the film growth proceeds in the c -axis direction, the tilt and rotation of the TiO_6 octahedra on either side of the Bi_2O_2 layers, which yields the orthorhombic symmetry of the unit cell, could result in the reappearance of the half-order streaks.

Figure 1(b) shows the depositing flux as a function of time for a typical PbTiO_3 growth. The typical substrate temperature is $\sim 630^\circ\text{C}$. Again, lead and ozone are supplied to the surface of the film continuously, while the ozone background pressure is maintained at 2×10^{-5} Torr. The lead flux is maintained at a rate of incidence 2 - 5 times greater than the titanium flux. The titanium is shuttered to deliver individual TiO_2 monolayers using direct feedback from the AA signal.

RESULTS AND DISCUSSION

Using the growth conditions described above it is possible to use a range of lead and bismuth incident fluxes and still obtain phase pure material. Rutherford backscattering spectrometry (RBS) measurements indicate that the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and PbTiO_3 films are stoichiometric within the error of the measurement. A similar mechanism was shown to be operative by de Keijser and Dormans [11] for

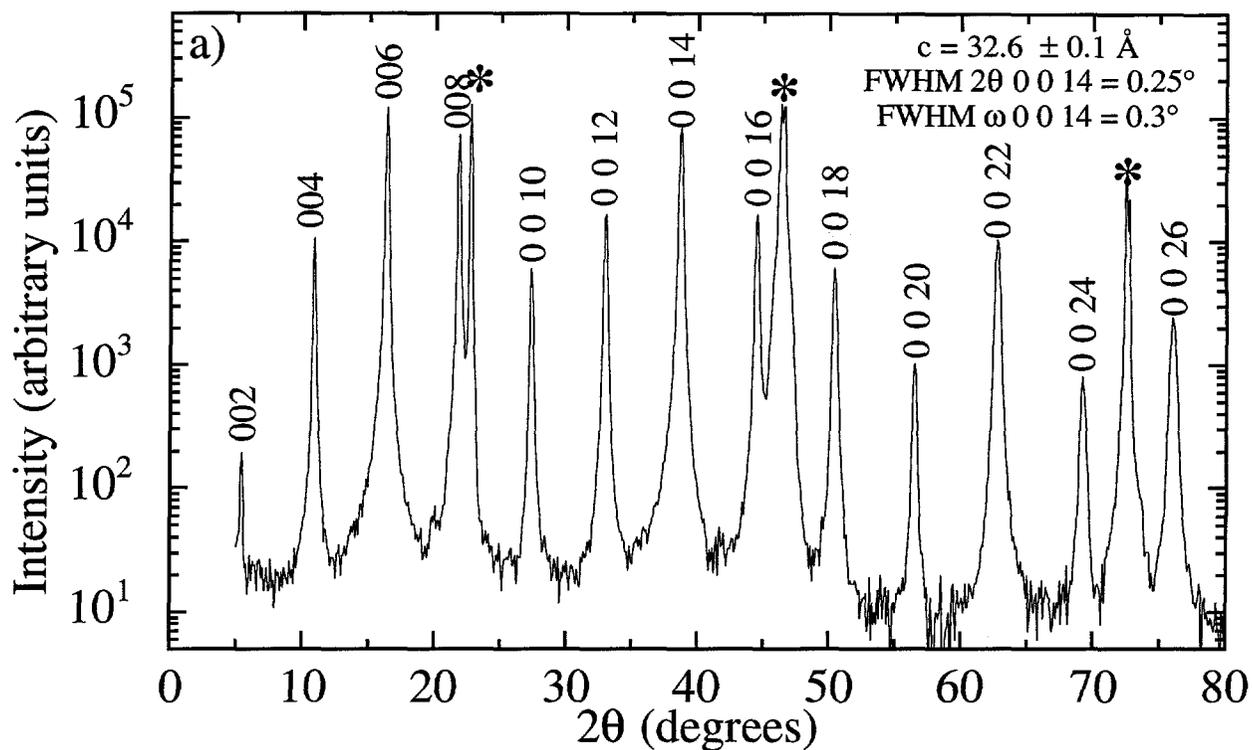


Fig. 2(a) θ - 2θ scan of a 1000 Å thick film of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ on a (100) SrTiO_3 substrate (* indicates substrate reflections).

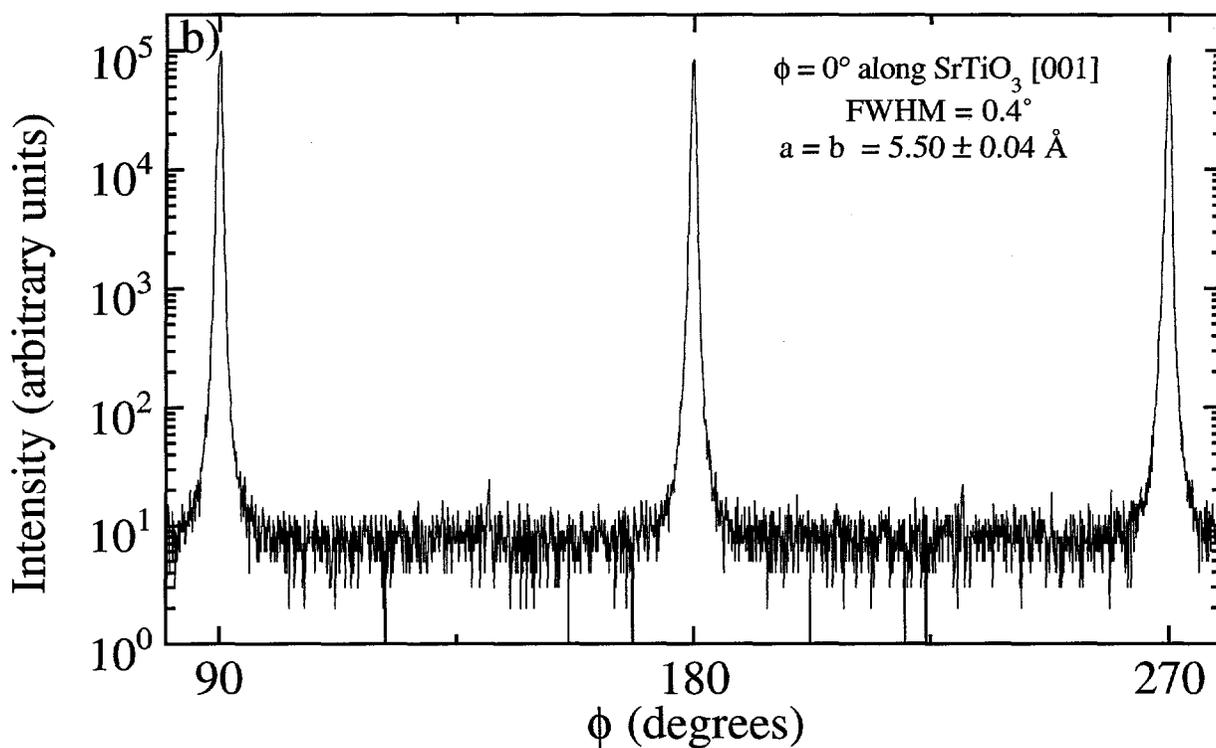


Fig. 2(b) Azimuthal ϕ -scan of a 1000 Å thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film; 117 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ reflections.

organometallic chemical vapor deposited PZT thin films. They found that by using a range of lead precursor partial pressures, it was possible to obtain stoichiometric films [11]. This adsorption controlled growth mechanism is reliant on the presence of a volatile metal — metal-oxide system. We attribute this adsorption-controlled mechanism, under the proper choice of background pressure and substrate temperature, to conditions where the sticking coefficient of lead or bismuth to the TiO_2 layer approaches unity while the sticking coefficient of lead or bismuth to the PbO_x or BiO_x surface is negligible. The near unity sticking coefficient of titania is substantiated by the film thickness calculated from the x-ray diffraction peak widths and thickness fringes of ultrathin $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films, RBS composition measurements, counting RHEED half-order intensity oscillations during growth, and *in situ* flux measurements using a quartz crystal thickness monitor and AA spectroscopy. All of these indicate that the incident titanium flux determines the growth rate of the titanate films. The excess of the volatile cations and the excess ozone present desorb from the surface. Similar to the MBE growth of GaAs films where arsenic is supplied in massive overabundance, the adsorption-controlled growth mechanism generates phase pure single crystal films eliminating many of the difficulties associated with accurate composition control.

Figure 2(a) is a θ - 2θ 4-circle x-ray diffraction scan of 1000 Å thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on (100) SrTiO_3 . Intense $00l$ peaks indicate that the film is pure *c*-axis oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The rocking curve full width at half maximum (FWHM) of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 0014 reflection is measured to be 0.3° showing minimal out-of-plane misalignment. Figure 2(b) is an azimuthal scan (ϕ -scan) of the 117 reflections of this same film. The peaks show a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [110] // SrTiO_3 [010] orientation with a FWHM of 0.4° in ϕ , indicating little variation in the in-plane alignment. These peak widths are all comparable to the instrument resolution of our Picker 4-circle diffractometer. RBS channeling results for this film showed a minimum channeling yield (χ_{\min}) of 0.2, which is the lowest reported value for epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Figure 3 is an AFM image of the surface of this same film. Clearly visible on the surface are micron size islands that protrude $\sim 100 - 200$ Å out of the film. The terraces making up these islands have step heights that are integral multiples of a half

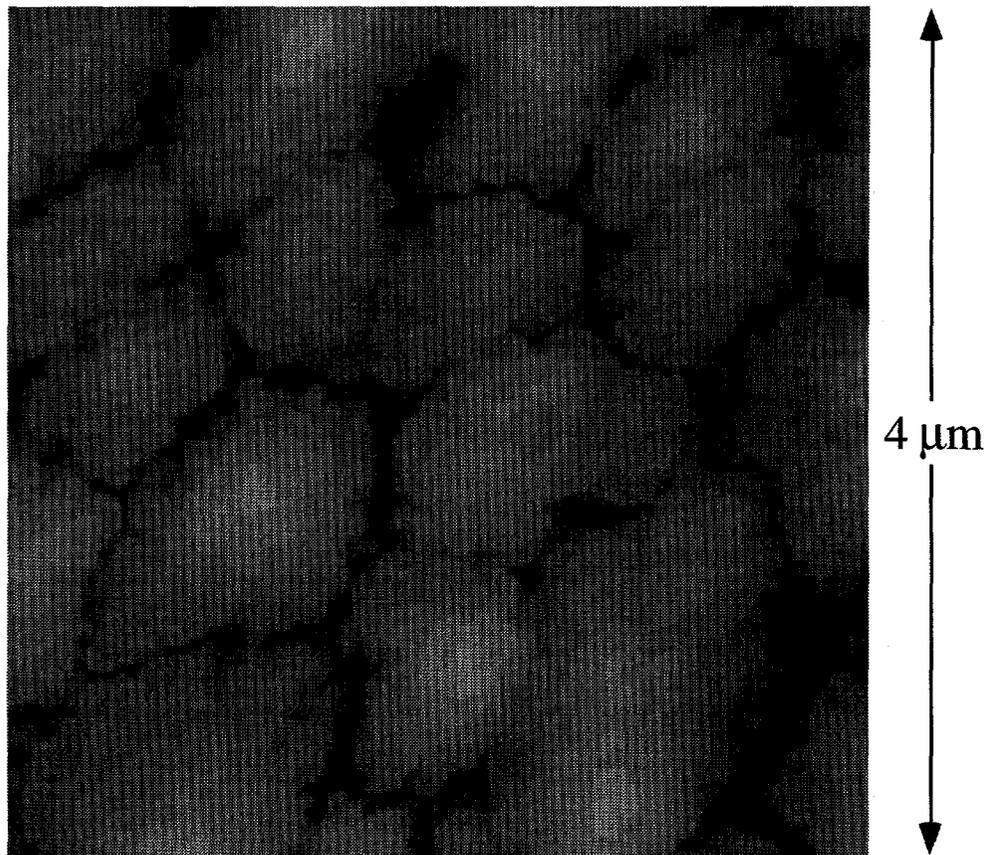


Fig. 3 AFM image of the surface of 1000 Å thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on SrTiO_3 .

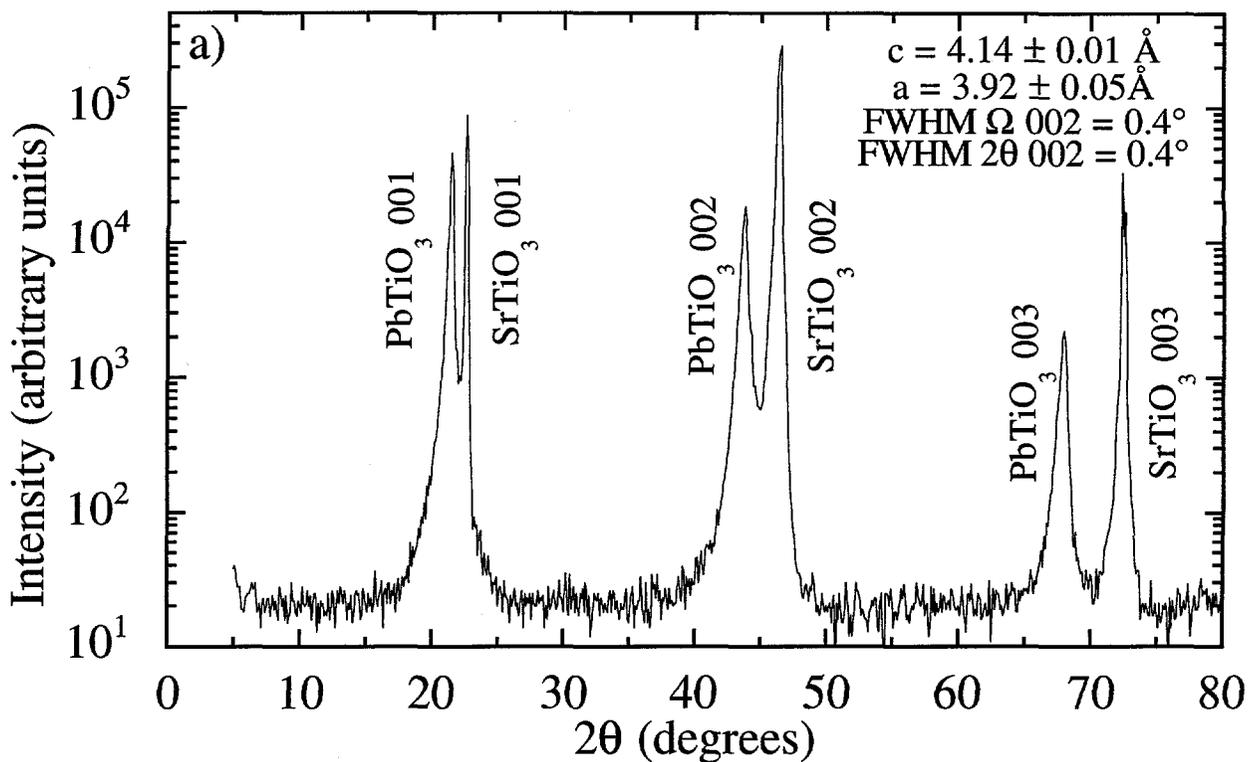


Fig. 5(a) θ - 2θ scan of a 1000 Å thick film of PbTiO₃ on a (100) SrTiO₃ substrate.

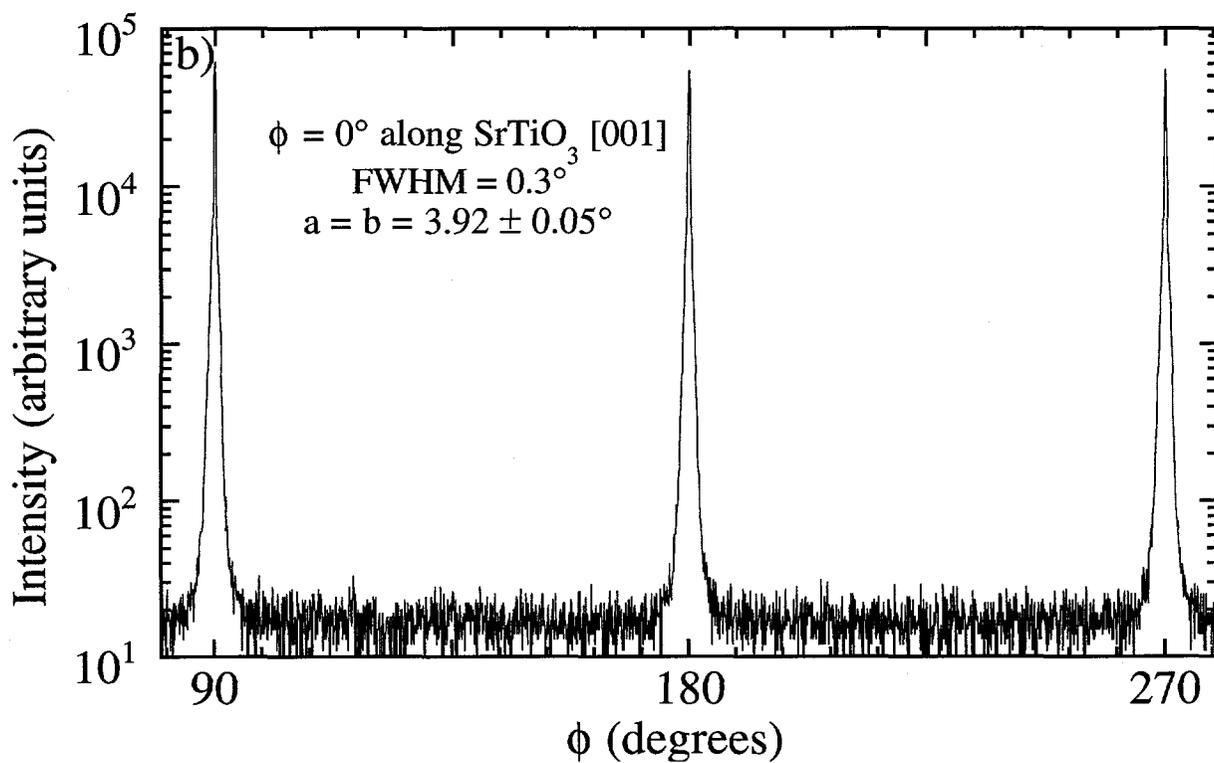


Fig. 5(b) Azimuthal ϕ -scan of a 1000 Å thick PbTiO₃ film; 101 PbTiO₃ reflections.

unit cell. The surface morphology revealed by AFM is reminiscent of that of layered perovskite superconductor films [12,13], although it is unclear if oppositely-signed screw dislocations are present within each mound or if the mounds are screw dislocation-free islands that arise due to limited surface diffusion.

In Fig. 5(a) a θ - 2θ 4-circle x-ray diffraction scan of a 1000 Å thick film of PbTiO₃ grown on (100) SrTiO₃ is shown. Intense 00 l peaks indicate that the film is pure *c*-axis oriented PbTiO₃; additional scans showed no evidence of *a*-axis oriented domains. The ϕ -scan in Fig. 5(b) demonstrates that the film is epitaxial with a cube-on-cube orientational relationship between film and substrate and a FWHM in ϕ of 0.3°. AFM images of the PbTiO₃ film surface show extremely smooth morphologies with a root mean square (RMS) roughness of < 5 Å. This surface structure is indicative of a layer-by-layer growth mechanism.

CONCLUSIONS

We have grown epitaxial PbTiO₃ and Bi₄Ti₃O₁₂ films by reactive MBE. Under conditions of ozone background pressure and temperature where an adsorption-controlled growth mechanism dominates, we believe that the sticking coefficient of the volatile metal cations is close to one on TiO₂ surfaces and negligible on other adsorbed species. The excess of lead, bismuth, and ozone desorb from the surface leaving behind a phase pure, stoichiometric crystal. AFM analysis indicates that the PbTiO₃ has a smooth surface morphology (RMS roughness < 5 Å). Bi₄Ti₃O₁₂ films have micron sized islands present at the surface that span 100 - 200 Å from top to bottom. These morphologies are consistent with either a spiral-type growth mechanism where film growth normal to the substrate surface is mediated by screw dislocations or an island-type growth mechanism.

ACKNOWLEDGMENTS

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