

Adsorption-controlled growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by reactive MBE

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Adsorption-controlled conditions have been identified and utilized to grow epitaxial bismuth titanate thin films by reactive molecular beam epitaxy. Growth of stoichiometric, phase pure, *c*-axis oriented, epitaxial films is achieved by supplying a large overabundance of bismuth and ozone continuously to the surface of the depositing film. Titanium is supplied to the film in the form of shuttered bursts each containing a three monolayer dose of titanium to grow one formula unit of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. It is seen from measured film thickness, Rutherford backscattering spectrometry composition measurements, monitoring of reflection high-energy electron diffraction half-order intensity oscillations during growth, and *in situ* flux measurements using atomic absorption spectroscopy that at suitable temperature and ozone background pressure, the titanium sticking coefficient approaches one and the excess bismuth desorbs from the surface. Film growth proceeds by the formation of mounds whose step heights are predominantly integral multiples of a half-unit cell. © 1998 American Institute of Physics. [S0003-6951(98)01222-4]

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an attractive ferroelectric material for use in nonvolatile memories because of its demonstrated fatigue resistance.^{1,2} Additionally, its highly layered perovskite structure makes it ideally suited for study using the atomic-scale layering capabilities of molecular beam epitaxy (MBE). Epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been grown on various substrates by sputtering,³ laser ablation,⁴ and by laser MBE.⁵ We have used adsorption-controlled growth conditions to accurately and reproducibly grow stoichiometric films.

The EPI 930 MBE system⁶ used for this study is described in detail elsewhere.⁷ The (001) SrTiO_3 wafers utilized in this study are etched with a buffered-HF solution prior to growth⁸ exposing the TiO_2 -terminated surface. During growth, bismuth and ozone are supplied to the surface of the film continuously while the substrate temperature is maintained at 600–660 °C. The ozone background pressure used during growth is 2×10^{-5} Torr, which represents an incident flux of ozone hundreds of times greater than the flux incorporated into the growing film. Similarly, bismuth is supplied at an incident flux 2 to 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. Adsorption-controlled growth is achieved under these conditions. The average growth rate we have investigated is ~ 0.5 Å/s.

Using the growth conditions described above it is possible to use a range of bismuth incident fluxes and substrate temperatures and still obtain phase-pure material. Rutherford backscattering spectrometry (RBS) measurements indicate that the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films are stoichiometric within the error of the measurements. Results obtained from film thicknesses

calculated from x-ray diffraction peak widths and thickness fringes of ultrathin 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 indicate that the incident titanium flux determines the growth rate of the films. The excess bismuth and oxygen desorb from the surface. A similar adsorption-controlled growth mechanism was shown to be operative by de Keijser and Dormans⁹ for $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ thin films grown by organometallic chemical vapor deposition (OMCVD). They found that by using a range of lead precursor partial pressures, it was possible to obtain stoichiometric films.

Adsorption-controlled growth was first successfully utilized for the MBE synthesis of epitaxial GaAs thin films nearly 30 years ago.¹⁰ This growth mechanism relies on the volatility of the group V component. In the case of GaAs, the equilibrium vapor pressure of gaseous $\text{As}_{4(g)}$ over pure, solid $\text{As}_{(s)}$ is about ten orders of magnitude higher than the equilibrium vapor pressure of gaseous $\text{As}_{2(g)}$ over a gallium-rich GaAs surface at 600 °C.¹¹ As a result, stoichiometric films are easily grown by supplying an excess of arsenic to the surface of the depositing film.

For the case of bismuth titanate its heat of formation is unknown, so we cannot make a thermodynamic assessment of its adsorption-controlled growth. But we have demonstrated the ability to synthesize stoichiometric films under adsorption-controlled conditions. At the incident bismuth flux and growth temperatures employed, elemental bismuth will not condense on the substrate surface¹² and must first be oxidized. Although $\text{Bi}_2\text{O}_{3(s)}$ does not evaporate congruently, the primary oxide species present in the vapor phase under growth conditions that we typically employ are BiO , Bi_4O_6 , and Bi_2O_3 .¹³ It is the volatility of these oxides that must be

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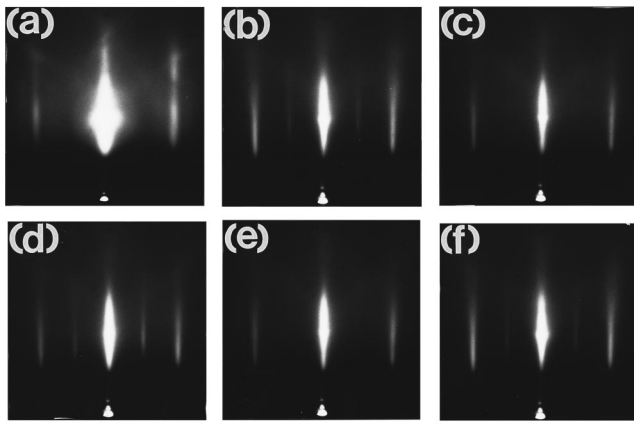


FIG. 1. RHEED patterns with the electron beam incident along the $[110]$ azimuth of the $(001)\text{SrTiO}_3$ substrate for (a) the bare etched $(001)\text{SrTiO}_3$ substrate at $\sim 640^\circ\text{C}$ during exposure to 2×10^{-5} Torr of ozone, (b)–(d) during deposition of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ perovskite sheets showing the $\sqrt{2} a_p$ to a_p to $\sqrt{2} a_p$ transition in the surface periodicity (with concomitant disappearance of half-order streaks), and (e)–(f) during the deposition of the Bi_2O_2 planes where the faded half-order streaks (e) could result from bismuth adatoms reordering on the surface.

considered to take the place of the group V molecules during adsorption-controlled growth. Our achievement of adsorption-controlled growth indicates that the equilibrium vapor pressure of these bismuth oxide complexes over pure $\text{Bi}_2\text{O}_{3(s)}$ is much higher than over a titania-rich $\text{Bi}_4\text{Ti}_3\text{O}_{12(s)}$ surface.

Prior to the initiation of growth, the continuous exposure of ozone and bismuth on the substrate surface is established. This aids in the cleaning of the substrate surface.¹² No change in the RHEED pattern is observed until the titanium flux is initiated. Below we describe the temporal evolution of the RHEED pattern during the deposition of one-half unit cell where we have utilized changes in surface symmetry as a means of controlling shutters.

Figure 1(a) shows the RHEED pattern of the bare etched SrTiO_3 substrate at $\sim 640^\circ\text{C}$ during exposure to 2×10^{-5} Torr of ozone. Figures 1(b)–1(f) show the evolution of the RHEED pattern during the deposition of one-half-unit cell of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ oriented with its c -axis normal to the substrate surface (c -axis oriented). The half-order streaks present along the substrate $[110]$ azimuth [Fig. 1(b)] are due to the epitaxial relationship between the cubic substrate and pseudorthorhombic film² where $\text{Bi}_4\text{Ti}_3\text{O}_{12} [100] \parallel \text{SrTiO}_3 [110]$. With each opening of the titanium shutter, the half-order streaks disappear after a period of time that corresponds to the deposition of 1.5 monolayers of titania as shown in Fig. 1(c). After the deposition of 3 monolayers of titania, the half-order streaks again reappear, as shown in Fig. 1(d), and the titanium shutter is closed. The disappearance of the half-order streaks halfway through the titanium burst of each formula unit could be due to the reduced distortion of the centermost layer of TiO_6 octahedra in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystal structure. The octahedra in this central layer, unlike those on either side of the Bi_2O_2 layers, are not rotated about the c axis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.^{1,14} The square surface mesh of the central TiO_6 layer has a perovskite lattice spacing (a_p) like the substrate and thus produces no half-order streaks. However, due to the $\sim 7^\circ$ antiphase rotation of the TiO_6 octahedra in the other two layers,^{2,18} they have a lattice spacing of $\sim \sqrt{2} a_p$

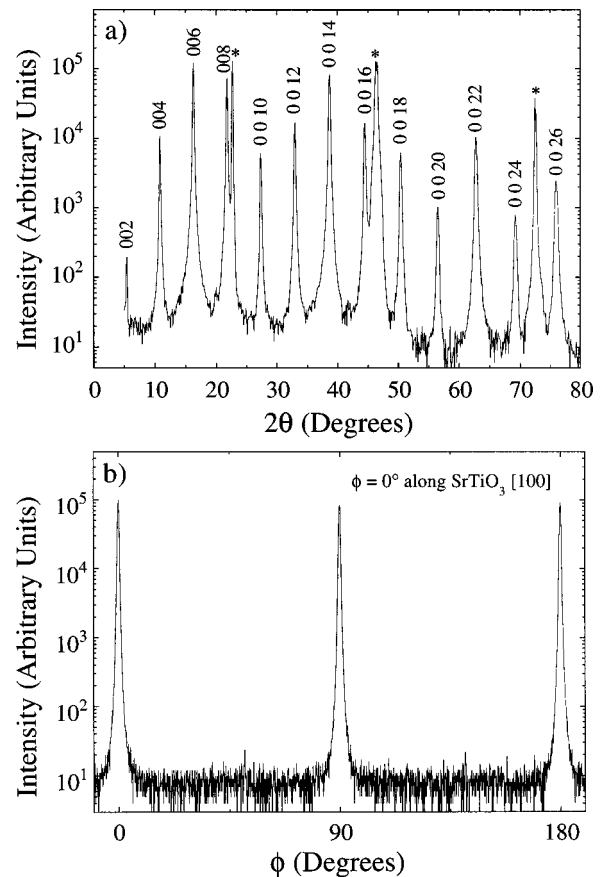


FIG. 2. Four-circle x-ray diffraction scans of a 1000 \AA thick (001) -oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on $(001)\text{SrTiO}_3$. (a) θ - 2θ scan indicating that the c axis of the film is $32.6 \pm 0.1 \text{ \AA}$. The substrate peaks are marked by an asterisk (*). (b) Azimuthal scan (ϕ -scan) of the 117 reflections indicating that the in-plane lattice constants of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film are $a \approx b \approx 5.50 \pm 0.04 \text{ \AA}$.

and a surface mesh that yields half-order streaks.

If the titanium shutter is not closed following the initial reappearance of the halforder streaks [Fig. 1(d)], the film surface quickly roughens and the RHEED pattern becomes spotty. The spotty RHEED pattern observed is consistent with the formation of anatase (TiO_2), which has been conclusively identified in subsequent four-circle x-ray diffraction measurements.

Although we argue that the sticking coefficients of bismuth oxide complexes to pure $\text{Bi}_2\text{O}_{3(s)}$ are negligible under adsorption-controlled conditions, one Bi_2O_2 double layer is incorporated with each $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ perovskite sheet to form $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ during growth. This behavior is consistent with maintaining charge neutrality—one $(\text{Bi}_2\text{O}_2)^{2+}$ is incorporated to neutralize each $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ sheet.

The adsorption-limited incorporation of bismuth was also recently demonstrated for the growth of the superconductor $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ by MBE.¹⁵ Migita *et al.*¹⁵ found that under adsorption-limited growth conditions bismuth incorporation was limited to two BiO layers per formula unit of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, despite their flooding the film surface with excess bismuth. This observation is also consistent with our hypothesis of adsorption-limited incorporation to achieve charge neutrality.

In Fig. 2(a) the θ - 2θ four-circle x-ray diffraction scan (using $\text{Cu } K\alpha$ radiation) of a 1000 \AA thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on $(001) \text{SrTiO}_3$ is shown. Intense 00ℓ peaks indicate

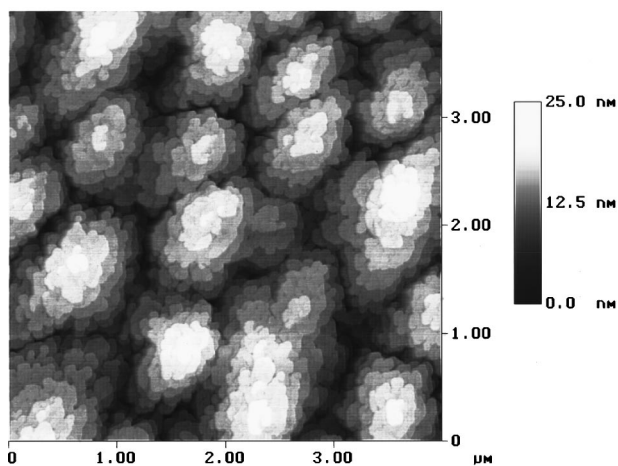


FIG. 3. An AFM image of the surface of a 1000 Å thick $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown on (001) SrTiO_3 .

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° in ω and 0.25° in 2θ showing minimal out-of-plane misalignment. Figure 2(b) shows the azimuthal scan (ϕ -scan) of the 117 reflections of this same film. The peaks indicate a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [110] \parallel SrTiO_3 [010] orientation relationship with a FWHM of 0.4° in ϕ , indicating little variation in the in-plane alignment. These peak widths are all comparable to the instrumental resolution of our Picker four-circle diffractometer. RBS channeling results for this film showed a minimum channeling yield (χ_{\min}) of 0.20 for the bismuth signal behind the surface peak, which is the lowest reported value for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films.

An atomic force microscopy (AFM) image of the surface of this same film is shown in Fig. 3. Clearly visible on the surface are micron-sized mounds that protrude approximately 100–200 Å out of the film. The terraces making up these mounds have step heights that are predominantly integral multiples of a half-unit cell (the height of a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formula unit). The surface morphology revealed by AFM is reminiscent of that of layered perovskite superconductor films,^{16,17} although it is unclear if oppositely-signed screw dislocations are present within each mound or if the mounds arise due to limited surface diffusion across Ehrlich–Schwoebel step-edge barriers.^{18,19}

Figure 4 is a high resolution transmission electron microscopy (HRTEM) micrograph of this same film viewed along the [100] $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ zone axis. Figure 4(b) is an enlarged view from the middle of Fig. 4(a). This image was taken at a defocus value of about -40 nm with a JEOL-4000EX high resolution electron microscope. Figure 4 shows the lattice image corresponding to the projected structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ along the [100] direction. From Fig. 4(b) it is seen that the Bi_2O_2 double layers (indicated by two white arrows) and the three perovskite sheets (marked by the black arrows) alternate along the [001] direction of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film. No stacking faults or other defects were found along the entire film studied with TEM.

In conclusion, we have grown epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films by reactive MBE under conditions of ozone background pressure and temperature where an adsorption-controlled

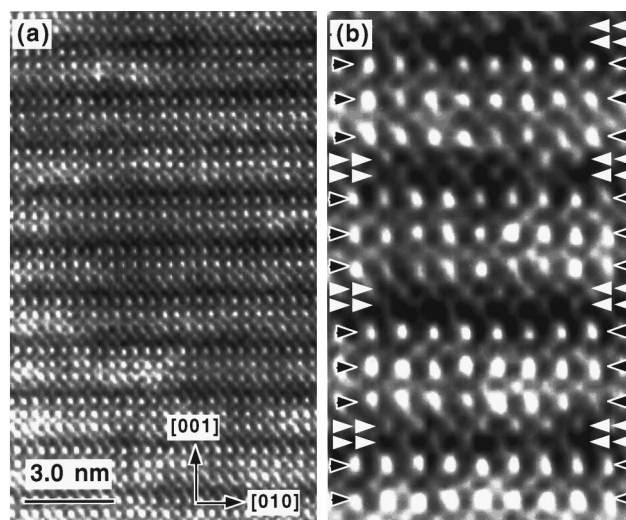


FIG. 4. HRTEM micrographs of a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film with the electron beam parallel to the [100] direction. (b) is an enlarged image from the middle of (a). The Bi_2O_2 double layers are indicated by the white double arrows, while the three perovskite sheets are indicated by the black arrows.

growth mechanism dominates, i.e., the excess bismuth, bismuth oxides, and ozone desorb from the surface leaving behind a phase pure, stoichiometric crystal.

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