Substrate temperature studies of SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ grown by pulsed laser ablation deposition

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Ferroelectric SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ (SBNT) thin films were deposited on Pt/TiO$_x$/SiO$_2$/Si substrates at various substrate temperatures by the pulsed laser ablation deposition method. X-ray diffraction shows that the film has a fluorite structure at a substrate temperature of 500 °C. The fluorite structure was transformed into perovskite phase at 550 °C and was fully crystallized at temperatures >700 °C, with a secondary phase present. Secondary ion mass spectroscopy and x-ray photoelectron spectroscopy studies reveal that the secondary phase was a nonferroelectric Bi-deficient pyrochlore phase at the SBNT/Pt interface and the film surface. The pyrochlore structure has a detrimental effect on the ferroelectric properties (i.e., the remanent polarization, coercive field, leakage current and fatigue) of the film. The remanent polarization and coercive field for the film grown at a substrate temperature of 700 °C were 4.79 mC/cm$^2$ and 68.68 kV/cm, respectively, with leakage current <10$^{-7}$ A/cm$^2$ even at an applied voltage of 8 V and 30% degradation in endurance against fatigue after 2 × 10$^{12}$ switching cycles. © 2002 American Vacuum Society. [DOI: 10.1116/1.1426364]

I. INTRODUCTION

In recent years, there has been growing interest in ferroelectric thin films due to their potential application in nonvolatile memory devices. Nonvolatile memory is superior to dynamic random access memory (DRAM) because memory is kept without a power source. In particular, Pb(Zr,Ti)O$_3$ (PZT) thin films have been intensely studied for application in nonvolatile memory devices. However PZT has problems of fatigue of the ferroelectric hysteresis. It has been reported that bismuth layer-structured ferroelectric (BLSF) materials show good endurance against fatigue. BLSF materials have a general formula of (Bi$_2$O$_3$)$_{2m+2}$($A_{m-1}B_mO_{3m+1}$)$_2$, where $A$=Ba, Pb, Sr, Bi, K, or Na, $B$=Ti, Nb, or Ta and $m=2$, 4, or 5.

To date, several film deposition methods have been used to deposit SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ (SBNT) thin films including sol gel, metalorganic deposition, radio-frequency magnetron sputtering, and pulsed laser ablation deposition (PLD). Recently, the ferroelectric properties of SrBi$_2$Ta$_2$O$_9$ (SBT) with partial replacement of Ta by Nb have been investigated. It was discovered that the SBNT films with a Ta/Nb ratio of 3:1 demonstrates maximum resistance against hydrogen reduction and gives maximum polarization. Others have reported that SBNT films could reduce the processing temperature and improve the ferroelectric properties, as well as achieve higher remanent polarization ($P_r$), and higher Curie temperature than conventional SBT. In this article, we successfully synthesize SBNT ferroelectric thin films using in situ PLD at various substrate temperatures and employ x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and secondary ion mass spectrometry (SIMS) to analyze the film properties.

II. EXPERIMENTAL DETAILS

SBNT films were deposited on Pt/TiO$_x$/SiO$_2$/Si substrates at substrate temperatures $T_s$ ranging from 450 to 750 °C by the in situ PLD method. Pt was used as the bottom electrode because of its high conductivity and chemical inertness, especially to oxygen, even at high annealing temperatures. The adhesion of Pt to conventional dielectrics such as SiO$_2$ is poor and TiO$_x$ provides an excellent adhesion layer between Pt and SiO$_2$. In addition, TiO$_x$ acts as a diffusion barrier between Pt and SiO$_2$, preventing the formation of platinum silicides at temperatures as low as 200 °C. SiO$_2$ was selected as a buffer layer because of its excellent, stable performance at the Si–SiO$_2$ interface. The main advantages of laser ablation are its capability to transfer the target stoichiometry to the film and its capability to deposit oxide films at lower temperatures because evaporated particles have high energy and require a lower substrate temperature for crystallization. In addition, it offers the advantages of in situ epitaxial growth of films, compatibility with semiconductor technology, and the capability to deposit a wide range of materials over a broad pressure regime. The chamber was pumped down to a base pressure of 7.5 × 10$^{-6}$ Torr. A 1 in. SBNT ceramic target was ablated by a KrF (248 nm) excited laser source (Lambda Physik Ind. Co.). The energy density of the laser pulse was 96 mJ/cm$^2$ and its pulse frequency was 4 Hz with a 30 ns duration. The substrate was positioned at a distance of 4 cm directly opposite the SBNT target, which was rotated and cooled during deposition. Ablation was done in an oxygen ambient of 150 mTorr for 20 min. Since phase formation of the SBNT film was achieved directly during the deposition process, no postannealing was necessary.
The SBNT thin film phase and orientation were identified by XRD using a Philips PW1729 x-ray diffractometer. The surface morphology and roughness of the films were investigated by an AFM (Digital Instruments D3000) in tapping mode. The elemental distribution as a function of depth as well as interdiffusion behavior at the SBNT/Pt interface were studied by SIMS using a Cameca IMS-6f instrument. A 7.5 keV O$_2^-$ primary ion beam was used. The surface chemical composition of the SBNT films was analyzed by XPS. The relative atomic sensitivity factors used for Bi 4$f$, Ta 4$f$, Nb 4$f$, and O 1$s$ are 24.88, 9.07, 8.46, and 2.85, respectively. The XPS binding energies were calibrated to the C 1$s$ peak (at 284.8 eV) of adventitious carbon. The electrical properties of the films were measured using a RT 6000S ferroelectric tester (Radiant Technology) operating in virtual ground mode after the deposition of $4 \times 10^{-4}$ cm$^2$ gold counter electrodes by e-beam evaporation through a shadow mask.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of SBNT thin films deposited by PLD as a function of the substrate temperature ($T_s$). The SBNT film orientations (hkl) were indexed by assuming the films are orthorhombic, with lattice constants of $a = 5.515$ Å, $b = 5.520$ Å, and $c = 25.02$ Å. The formula that relates interplanar spacing $d$ with lattice parameters for orthorhombic symmetry was applied, i.e., $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$. The XRD patterns show that the film grown at $T_s = 450$ °C was amorphous and only (111) and (200) peaks corresponding to the Pt lower electrode were observed. The film started to crystallize, having a fluorite structure at substrate temperatures as low as 450 °C and was fully crystallized at 500 °C and had a predominant (111) peak and secondary (220) and (222) peaks. The fluorite structure exists as an intermediate phase between the amorphous and perovskite phases of SBNT. As the substrate temperature was increased to 550 °C, the intensity of the fluorite (111) peak decreased and its 2$\theta$ position shifted toward a larger angle, indicating breakdown of the fluorite structure and initial formation of perovskite phase. The perovskite phase was fully formed at $T_s = 700$ °C with a predominant (115) peak and secondary (113), (0010), (208), (2010), and (315) peaks. This indicates that the films are polycrystalline. In addition, a peak corresponding to a secondary phase, indicated by an asterisk, appears at the higher 2$\theta$ component of the (115) peak at $T_s = 700$ and 750 °C (indicated in the inset). This peak has been attributed to distortion of the perovskite unit cell, while other authors indexed it as the ferroelectric SrTa$_4$O$_{11}$, SBT (107), and Bi$_4$Ti$_3$O$_{12}$ (171). We note that the appearance of this peak coincides with a reduction of the (115) peak intensity. As we will show later, this peak corresponds to a nonferroelectric phase and the formation of this peak suppresses growth of the ferroelectric (115) peak, which in turn affects the remanent polarization of the SBNT film. To investigate the origin of this phase at 700 and 750 °C, it is important to understand the distribution of elements in the film at these substrate temperatures. SIMS depth profiling was performed to examine changes of the elemental distribution in the multilayers, and XPS was used to examine chemical changes on the film surface.

The intensity of secondary ion signals Sr$^+$, Pt$^+$, Ti$^+$, Bi$^+$, Ta$^+$, and Nb$^+$ as a function of the sputtering time (and hence depth) were monitored during SIMS depth profiling. The degree of diffusion for each element was quantified using the decay length, defined as the depth for which the signal decays to 1/e of its original value. The thickness of each layer was measured by cross-sectional field emission scanning electron microscopy and we assumed a constant ion sputtering rate within each layer. Figures 2(a)–2(c) show SIMS depth profiles of Pt$^+$, Ti$^+$, and Bi$^+$ intensities, respectively, as a function of time (and hence depth) and the substrate temperature using a O$_2^-$ primary beam. Table I summarizes the decay lengths for elements Sr, Bi, Ta, and Nb into Pt, Pt into SBNT film, and Ti into Pt at substrate temperatures of 500, 700, and 750 °C. The Pt$^+$ profile in Fig. 2(a) has an M-shaped curve because of matrix enhancement at the interfaces. A sharp rise in the Pt concentration occurs at the SBNT/Pt interface at 500 °C, indicating that there is little Pt diffusion into the SBNT film at 500 °C. The decay length for Pt in SBNT was calculated to be 17.7 nm. Our previous study of SBT films show similar decay lengths for room temperature growth, indicating that there is minimal diffusion at the SBNT/Pt interface at 500 °C. The profile broadening observed is attributed to SIMS instrumental ef-
The Pt profile broadened when the film was further annealed, resulting in a significant increase in decay length to 33.9 and 45.2 nm at 700 and 750 °C, respectively. Diffusion of Pt into the TiOₓ layer was also observed at 700 °C and above. Figure 2~b~ shows the diffusion behavior of Ti. The decay length of Ti into Pt at 500 °C of 35.6 nm is significantly higher than that in our previous work~23.3 nm~ on room temperature growth of SBT, suggesting Ti diffusion into Pt occurs at 500 °C. The diffusion of Ti into Pt is more pronounced at higher temperatures, with the decay length increasing to 42.3 nm at 700 °C and to 54.3 nm at 750 °C. It should be noted that the change in Ti⁺ intensity at the SBNT/Pt interface is due to a matrix-dependent ionization effect that causes an abrupt change in the ionization yield. Even though Ti diffuses into Pt significantly high temperature, Ti does not diffuse into the SBNT film at 750 °C and we conclude that the secondary phase observed in the XRD data is not due to Ti diffusion, as previously reported.²² Ti diffusion into Pt has been reported to cause an increase in surface roughness in the Pt layer and this will in turn cause the surface roughness of SBNT film to increase,²³ as will be seen later. This increase in surface roughness will be shown to affect the leakage current density of the SBNT film. Figure 2(c) shows the Bi diffusion behavior in Pt. The abrupt interface at Tₐ = 500 °C is evidence of a sharp drop in the Bi⁺ secondary ion signal. The Bi⁺ profile subsequently broadens upon further annealing, resulting in an increase in decay length from 56.7 nm at 700 °C to 94.6 nm at 750 °C. This suggests either significant diffusion of Bi into Pt,²⁴ and/or extraction of Bi by Pt in the Pt layer.²⁵ Of all the elements, Bi shows the largest decay length (~94.6 nm) at 750 °C. The active diffusion of Bi at high temperature is due to its low melting point that causes Bi to diffuse across the interfaces into the electrode. From Table I, we see that the decay length of Sr, Ta, and Nb into Pt increases from ~16–19 to ~20–22 nm, indicating that diffusion of these elements into the Pt layer does not increase significantly upon annealing to 750 °C. It was reported in our previous study that the interdiffusion behavior of Bi, Ti, and Pt affects the ferroelectric properties of the SBT film.²⁴ Figure 2(c) also shows a decrease in Bi⁺ intensity at the SBNT/Pt interface at Tₐ = 700 °C, indicating that the SBNT film is Bi deficient there. One possible consequence is the formation of a Bi-deficient pyrochlore structure that makes the pure SBNT phase difficult to obtain at the interface. As a result, a non-

![SIMS depth profiles](image)

**Table 1.** Decay lengths for elements Sr, Bi, Ta, and Nb into Pt, Pt into SBNT film, and Ti into Pt at substrate temperatures of 500, 700, and 750 °C.

<table>
<thead>
<tr>
<th>Tₛ (°C)</th>
<th>500 (nm)</th>
<th>700 (nm)</th>
<th>750 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta in Pt</td>
<td>18.2</td>
<td>19.5</td>
<td>21.2</td>
</tr>
<tr>
<td>Sr in Pt</td>
<td>18.6</td>
<td>19.1</td>
<td>20.0</td>
</tr>
<tr>
<td>Nb in Pt</td>
<td>16.5</td>
<td>18.2</td>
<td>20.6</td>
</tr>
<tr>
<td>Bi in Pt</td>
<td>17.0</td>
<td>56.7</td>
<td>94.6</td>
</tr>
<tr>
<td>Pt in SBNT</td>
<td>17.7</td>
<td>33.9</td>
<td>45.2</td>
</tr>
<tr>
<td>Ti in Pt</td>
<td>35.6</td>
<td>42.3</td>
<td>54.3</td>
</tr>
</tbody>
</table>
ferroelectric SBNT layer will develop and the existence of such a layer has been reported to dampen the remanent polarization of SBT films. Another possible consequence is the formation of a Bi–Pt alloy in the Pt layer which may affect the electrical properties of Pt. We have previously reported that Bi and Ti diffusion into the Pt layer may degrade Pt as a bottom electrode for SBT thin films.

Figure 3 shows the surface composition ratio of Nb:Ta of SBNT film at various substrate temperature \( T_s \) determined by XPS. The Nb:Ta ratio remains approximately 0.43 (or Nb/Ta = 1.4/0.6) at all substrate temperatures used. This shows that partial Nb substitution in the Ta site is stable and unaffected by substrate temperature. The composition of the Nb:Ta ratio calculated is close to the desired ratio for maximum resistance against hydrogen reduction. Figure 3(b) shows the surface composition of Bi/(Ta+Nb) of the SBNT film as a function of the substrate temperature. Figure 3(b) reveals that Bi/(Ta+Nb) shows only a slight deviation (~1.96) from stoichiometric SBNT at 450 °C. The Bi/(Ta+Nb) ratio decreases with an increase in substrate temperature to 1.73 at \( T_s = 750 ^\circ C \). This indicates that the SBNT film surface was Bi deficient at high temperature. The decrease in Bi content is probably due to the volatile nature of Bi2O3 at high temperature. The evaporation of Bi2O3 results in the presence of undesirable oxygen vacancies in the perovskite lattice and leads to fatigue. It can be inferred that Bi deficiency may lead to a change in the SBNT structure at the surface or near surface region, resulting in a nonferroelectric layer at the top metal electrode/SBT interface.

Figure 4 shows XPS Bi 4f spectra at substrate temperatures of 500, 700, and 750 °C. Metallic Bi 4f peaks are observed at \( T_s = 750 ^\circ C \).

The XPS and SIMS results show that the Bi concentration was deficient at the SBNT film surface and SBNT/Pt interface at \( T_s > 700 ^\circ C \). As a result, a Bi-deficient pyrochlore structure develops which corresponds to the secondary peak that we identified in the XRD data. As will be shown later, the results of the combination of XPS, AFM, and electrical data strongly suggest that this structure is nonferroelectric and may degrade the ferroelectric properties of the SBNT film.

Figures 5(a)–5(f) show 1 \( \mu m \times 1 \mu m \) AFM micrographs of the surface morphology of the SBNT film as a function of the substrate temperature. The surface morphology at \( T_s = 450 ^\circ C \) is generally smooth and without any distinct grain structure. The surface of SBNT films grown at \( T_s = 500 ^\circ C \) consists of small spherical grains ~32 nm in size. The small spherical grains form aligned structures by coalescing with other grains at \( T_s = 550 ^\circ C \). We suggest the alignment of grains corresponds to the transition from the fluorite to the perovskite structure as observed in XRD. These aligned grains fuse and form larger grains at \( T_s > 650 ^\circ C \). Two types of grains were observed when \( T_s \approx 700 ^\circ C \), rod-like grains and spherical grains. The number of rod-like grains increases from 1.2/\( \mu m^2 \) at 700 °C to 2.7/\( \mu m^2 \) at 750 °C. It is not likely that the rod-like grains contribute to the ferroelectric (115) peak since its XRD intensity decreases when the substrate
temperature increases from 700 to 750 °C. We suggest that the rod-like grains correspond to the bismuth-deficient pyrochlore phase discussed earlier, since there is a corresponding increase in intensity in XRD and the number of rod-like grains. We assign the spherical grains to the ferroelectric phase. Figure 6 shows the grain sizes as a function of the substrate temperatures. The plot shows that the spherical grain size increases with an increase in temperature except at 750 °C where there is a slight decrease in grain size. It has been reported that the grain size is related to ferroelectric properties of the SBNT film. Hence, the decrease in grain size at $T_s = 750 °C$ might be related to degradation of the ferroelectric film’s properties. Also in Fig. 6, it is seen that the length of the rod-like grains increases with an increase in substrate temperature while the width remains fairly constant. We deduce that the length of the rod-like grains is dependent upon the amount of Bi-deficient pyrochlore phase.

Figure 7 shows the influence of the substrate temperature on the average surface roughness of SBNT film. As expected, the surface roughness increases with an increase in substrate temperature. The roughness of SBNT grown between 450 and 600 °C was less than 5 nm, but increased sharply at 650 °C and above. The sharp increase in roughness at $T_s = 700 °C$ could be due to the change in surface roughness of the Pt interface caused by Ti diffusion into the Pt electrode. It has been observed that the increase in surface roughness causes increased leakage current in the SBT thin film. Note that, even though the roughness increases from $T_s = 700$ to 750 °C, the grain size decreases. Figures 8(a) and 8(b) show cross-sectional AFM line profiles of the films at 700 and 750 °C, respectively. Although the grain size and surface roughness are interdependent parameters, the increase in surface roughness with a corresponding decrease in grain size at 750 °C is attributed to larger background undulation, depicted by the dotted line. This suggests that the Pt interface has indeed become roughened, resulting in a rougher SBNT film.

Figure 9 shows $P−E$ hysteresis loops for the SBNT films grown at $T_s = 700$ and 750 °C at an applied voltage of 5 V. Hysteresis loops were obtained for both films. However, the ferroelectric properties (i.e., remanent polarization, coercive field, leakage current, and fatigue) of the film that was deposited at $T_s = 700 °C$ was found to be superior to that grown...
at $T_s = 750 \, ^\circ C$. The $2P_r$ and $2E_c$ for films deposited at $T_s = 700$ and $750 \, ^\circ C$ are $4.79 \, \mu C/cm^2$ and $68.68 \, kV/cm$ and $4.36 \, \mu C/cm^2$ and $73.67 \, kV/cm$, respectively. The SBNT film grown at $T_s = 700 \, ^\circ C$ has larger remanent polarization and a smaller coercive field compared to that at $T_s = 750 \, ^\circ C$. The $P_r$ is lower than that obtained by rf sputtering in our previous studies. The smaller $P_r$ value is possibly due to Bi deficiency in the SBNT film. The decrease in $P_r$ at $T_s = 750 \, ^\circ C$ is attributed to the decrease in grain size as observed in AFM. Figure 9 also shows the ferroelectric hysteresis loops of both films before and after fatigue cycling up to $2 \times 10^{12}$ switching cycles performed at an amplitude of $\pm 5 \, V$ and a frequency of $1 \, MHz$. The films grown at $T_s = 700$ and $750 \, ^\circ C$ show $30\%$ and $75\%$ degradation in polarization after fatigue cycling, respectively. The fatigue could be due to the presence of oxygen vacancies in the film due to the volatility of Bi$_2$O$_3$ at high annealing temperatures, as well as oxygen diffusion into the Pt layer and the presence of Bi-deficient pyrochlore phase.

Figure 10 shows the leakage current characteristics of SBNT films at $T_s = 700$ and $750 \, ^\circ C$. The leakage current was measured by applying a $0$–$10 \, V$ dc bias to the top electrode with the bottom electrode grounded. The film deposited at $T_s = 700 \, ^\circ C$ shows a slight increase in leakage current density with an increase in applied voltage, whereas the film deposited at $T_s = 750 \, ^\circ C$ shows a sharp increase in leakage current density at an applied voltage of $2.5 \, V$. Taking the breakdown voltage to be the voltage at which the leakage current density is greater than $5 \times 10^{-7} \, A/cm^2$, the film grown at $T_s = 700 \, ^\circ C$ has a breakdown voltage of $>8 \, V$ and exhibits excellent insulating properties whereas the film grown at $T_s = 750 \, ^\circ C$ has a breakdown voltage of $4 \, V$, which is below the current operating voltage of memory devices of $5 \, V$. The high leakage current density of film grown at $T_s = 750 \, ^\circ C$ is consistent with the previous suggestion that metallic Bi forms a pathway for leakage current to flow and increases surface roughness of the film by Ti diffusion into the Pt layer. This shows that SBNT films grown by PLD at $700 \, ^\circ C$ have potential in nonvolatile random access memory applications.
IV. CONCLUSIONS

SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ thin films were deposited on Pt/TiO$_x$/SiO$_2$/Si substrates by pulsed laser ablation deposition. The SBNT film grown at 500 °C showed a fluorite structure. The fluorite phase breaks down and transforms into perovskite phase at 550 °C that crystallized fully at 700 °C. The secondary phase found at $T_s$ ≥ 700 °C is a Bi-deficient pyrochlore phase, which formed as a result of Bi diffusion into the Pt layer and/or extraction of Bi by Pt in the Pt layer. The Bi-deficient phase is detrimental to the ferroelectric properties of the SBNT film. The grain size increases with the substrate temperature except at $T_s$ = 750 °C. The decrease in grain size correlates to the decrease in remanant polarization for the film grown at 750 °C. The rod-like grains are attributed to the Bi-deficient phase. The SBNT film grown at 750 °C shows higher leakage current, lower remanent polarization, and lower fatigue resistance compared to the film grown at 700 °C. The remanent polarization and coercive field for the film grown at 700 °C were 4.79 μC/cm$^2$ and 68.68 kV/cm, respectively, with leakage current of <10$^{-7}$ A/cm$^2$ at an applied voltage of 8 V with 30% degradation in endurance against fatigue after 2 × 10$^{12}$ switching cycles.