Influence of oxygen partial pressure on magnetron sputtered Sr$_{0.8}$Nd$_{0.3}$Bi$_{2.5}$Ta$_2$O$_{9+x}$ ferroelectric thin films

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Abstract

During magnetron sputtering deposition of SrBi$_2$Ta$_2$O$_9$ thin films, oxygen gas is introduced in the deposition chamber to compensate the oxygen loss during sputtering. In this paper, the influence of oxygen partial pressure is systematically investigated in sputtering of Sr$_{0.8}$Nd$_{0.3}$Bi$_{2.5}$Ta$_2$O$_{9+x}$ thin films, using X-ray diffraction, X-ray photoelectron spectroscopy and field emission scanning electron microscopy. The studies confirm that at various oxygen partial pressure Nd$^{3+}$ ions substitute into the bismuth layered perovskite structure, preferentially at the Sr$^{2+}$ site. The deposition rate, composition, microstructure and polarization properties of the films highly depend on the oxygen partial pressure.

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1. Introduction

Ferroelectric thin films have remnant polarization with two distinct states which can be reversed by an applied electric field. Thus they have the potential for non-volatile random access memory (NvRAM) application. Among ferroelectric thin films, layered bismuth oxide ferroelectric materials based on SrBi$_2$Ta$_2$O$_9$ (SBT) have attracted ever increasing attention because they exhibit fatigue-free property up to $10^{12}$ cycles even on Pt bottom electrode, excellent retention characteristics, and low leakage current [1].

SBT consists of two SrTaO$_3$ perovskite-like units between (Bi$_2$O$_2$)$_2^{2+}$ layers along the $c$ axis [2], having two polar axes ($a$ or $b$ axis) [3,4] so that no spontaneous polarization contribution comes from $c$ axis direction. As a consequence, the stoichiometric SBT film with random orientation has very low remnant polarization. Previous studies show that substitution at A or B site could effectively modify its polarization properties. For A site (Sr$^{2+}$), Ca$^{2+}$, Bi$^{3+}$ or La$^{3+}$ substitutions in both thin films [5] and bulk ceramics [6,7], whose radii are very close, show significant modification of polarization properties. Praseodymium- or neodymium-doped SBT bulk ceramics also experience significantly improved polarization properties [8,9]. As a result of trivalent ion (Bi$^{3+}$, La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$) replacing divalent Sr$^{2+}$ ion, a large amount of Sr vacancies is induced in the perovskite blocks of SBT. The vacancies of cations as well as oxide ions play an important role in polarization-switching properties of ferroelectrics [10–12].

SBT thin films and derivatives have successfully fabricated by sol–gel [13], pulsed laser ablation [14,15], metal organic chemical vapor deposition [16], and magnetron sputtering [17–19]. During sputtering deposition of oxide thin film, the oxygenic loss tends to take place, leading to oxygen deficiency (oxygen vacancies) in film composition, which aggravates fatigue and reliability problem in ferroelectric films [20,21]. Therefore, during sputtering deposition of SBT ferroelectric thin films, oxygen gas should be introduced with Ar gas. The concentration of oxygen in the sputtering plasma is one of the most important factors.
Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure (×10⁻⁴ Pa)</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Process pressure (Pa)</td>
<td>1.5</td>
</tr>
<tr>
<td>Power density (W/cm²)</td>
<td>2.3</td>
</tr>
<tr>
<td>Oxygen percentage in total gas (%)</td>
<td>0; 10; 25; 33; 50</td>
</tr>
<tr>
<td>Target-to-substrate distance (mm)</td>
<td>40</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>Room temperature</td>
</tr>
</tbody>
</table>

However, a systematic study of the effect of oxygen partial pressure during rf magnetron sputtering on the microstructure and polarization properties of Sr₀.₈Nd₀.₃Bi₂.₅Ta₂O₉₊ₓ (SNBT) thin films is generally lacking. This paper focuses on the study of the influence of oxygen partial pressure on deposition rate, composition, microstructure and polarization properties of sputtered SNBT thin films.

2. Experimental

SiO₂ film of 350 nm was thermally grown on Si (1 0 0) wafers; then, Tantalum film of around 120 nm in thickness was sputtered on top; Pt (1 1 1) of 80 nm in thickness was subsequently sputtered to form the Pt(1 1 1)/Ta/SiO₂/Si(1 0 0) "substrate". SNBT films were sputtered on the substrate from sintered target of Sr₀.₈Nd₀.₃Bi₂.₅Ta₂O₉₊ₓ with a purity of 99.9% (Super Conductor Materials Inc., Tallman, NY). The deposition conditions were listed in Table 1. During deposition, the pressure was maintained at 1.5 Pa by a pressure controller. The total gas flow of argon and oxygen was fixed at 60 sccm. The crystallization of as-deposited films was realized through rapid thermal processor (RTP) (JIPLEC, JETFIRST100) at 800 °C for 5 min under oxygen atmosphere of 1 atm. The ramping rate used was 20 °C/sec. The phase and crystal orientation of the films were analyzed by grazing incidence X-ray diffraction (GIXRD) with Cu Kα radiation (λ = 1.5406 Å) (Philips, X’pert) at 40 kV and 35 mA. The surface morphology and cross-sectional image were observed using field emission scanning electron microscopy (FESEM, JEOL JSM-6340F, Japan). The chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA). The energy scale of the XPS spectra is calibrated with the binding energy of the C 1s peak due to the surface contamination.

After crystallization, a top Pt electrode was DC-sputtered onto the films through a shadow mask to produce a circular diode of 0.2 mm diameter. This metal-ferroelectric metal (MFM) capacitor was re-annealed in O₂ flow at 500 °C for 30 min to improve the ohmic contact between the SNBT film and the Pt electrode. Measurement of the P–E hysteresis loops was then carried out at the RT6000HV A ferroelectric tester (Radiant Technologies Inc.) in a virtual ground mode.

3. Results and discussion

3.1. Deposition rate

The thickness of SNBT thin films is measured through the FESEM cross-sectional image of the as-deposited SNBT thin film, as depicted in Fig. 1 (the corresponding deposition parameters are listed in the inset). The thickness of the thin film is about 230 nm and the deposition duration is 80 min, thus the average deposition rate is around 2.8 nm/min. The deposition rates at various oxygen partial pressures are also calculated in the same way and plotted in Fig. 2. It is seen that the deposition rate gradually decreases (dropping from 3 to 1.8 nm/min) as oxygen partial pressure increases. The drop of deposition rate is believed to relate to the oxygen partial pressure. During sputtering, the target atoms are subject to collisions with gas atoms or molecules left in the chamber and other ejected atoms, resulting in a partial loss of energy and direction on their way to the substrate [22]. Because oxygen gas is bi-atom molecule and its radius is much larger than Ar (0.140–0.122 nm), the sputtered particles suffer from more collision when more oxygen partial pressure is introduced. This reduces the deposition rate. Furthermore, at a given rf power density of 2.3 W/cm², the thermalization region shifts toward the target by increasing oxygen partial pressure [23], leading to the oxidation of the target [24,25] and possible re-sputtering of the film [26] that would compound the decrease in the deposition rate.

3.2. Crystal structure

Fig. 3 shows the GIXRD profiles of the films (annealed at 800 °C at RTA) deposited at various oxygen partial pressures, indexed by assuming an orthorhombic cell (a = 5.531 Å, b = 5.534 Å, and c = 24.98 Å [27]). All the films are single
phase with polycrystalline, i.e., no secondary phase (such as pyrochlore) diffraction peaks are detected. In comparison with the patterns of stoichiometric SBT thin films and SBT powder, a systematic shift of diffraction lines towards higher diffraction angle is observed: a clear indication of a decrease of orthorhombic lattice parameters, which is mainly attributed to the smaller ionic radii of Nd\(^{3+}\) (1.11 Å) comparing to that of Sr\(^{2+}\) (1.27 Å).

The relative intensity of (2 0 0) and (1 1 5) is presented in Fig. 4. As the oxygen partial pressure increases, the ratio of \(I_{(200)}\) and \(I_{(115)}\) initially goes down and subsequently rises, reaching a minimum at 25% oxygen partial pressure. This differs from Tsai and Tseng’s result: the (2 0 0) peak intensifies all the way as the oxygen partial pressure increases [28]. The variation of diffraction peaks intensities relates to the variation in film composition resulting from the oxygen partial pressure, which will be discussed later. The variation is expected to affect the polarization properties of the film.

3.3. Chemical stoichiometry

Fig. 5 is the XPS spectra at various oxygen partial pressures. The Nd 3d\(_{5/2}\) and Nd 3d\(_{3/2}\) peaks all appear at 982.1 and 1004.6 eV without fail. Note that in pure Nd\(_2\)O\(_3\), the peaks attributed to Nd\(^{3+}\) appear at around 980.8 and 1003.3 eV, respectively [29]. The peak-fitting analysis of the Nd-substituted SBT spectrum suggests that Nd\(^{4+}\) is not present. The results of GIXRD and XPS analyses confirm that the trivalent cations Nd\(^{3+}\) preferentially substitute Sr\(^{2+}\) thus the formation of V\(_{Sr}\) compen-

![Fig. 3. GIXRD patterns (incidence angle is 2°) of thin films deposited at various oxygen partial pressures: (a) 0%; (b) 10%; (c) 25%; (c) 33%; (d) 50%.](image1)

![Fig. 4. Relative intensity ratio of (2 0 0) and (1 1 5) as deposited at various oxygen partial pressures.](image2)

![Fig. 5. X-ray photoelectron spectra of core-level scan of Nd peaks for the films deposited at different oxygen partial pressures: (a) 0%; (b) 10%; (c) 25%; (d) 33%; (e) 50%.](image3)

![Fig. 6. Compositional change of the films as a function of oxygen partial pressure.](image4)
sates the charge deference between Sr$^{2+}$ and Nd$^{3+}$. This is in good agreement with the Nd-doped SBT bulk: the single-phase layered perovskite structure is still preserved when Nd$^{3+}$ concentration is up to 70 at.% [30]. Substitution of Nd at A site in ABO$_3$ structure materializes via

$$\text{Nd}_2\text{O}_3 \rightarrow 2\text{Nd}_{\text{Sr}} + 3\text{O}_2^- + V'_{\text{Sr}}$$

where Nd$_{\text{Sr}}$ stands for Nd$^{3+}$ at the Sr$^{2+}$ site (A site), O$_2^-$ denotes O$^{2-}$ at the oxygen site and $V'_{\text{Sr}}$ represents the Sr$^{2+}$ vacancy. It is also worth mentioning that the Nd 3d intensity becomes weaker as the oxygen partial pressure increases, qualitatively indicating the Nd concentration is reduced.

XPS quantitative analysis determines the chemical compositions of the films as plotted in Fig. 6, where Bi/Ta and Nd/Ta gradually decrease (For Bi/Ta: dropping from 1.21 to 0.98; for Nd/Ta: from 0.12 to 0.05) while Sr/Ta increases (from 0.28 to 0.34) and (Nd + Sr)/Ta ratio almost keeps a constant ($\sim$0.4). This is a result of the increase of Sr/Ta and decrease of Nd/Ta. These observations also indicate that more oxygen introduced is ben-
eficial to sputter Sr and Ta atoms while makes against the Bi and Nd sputtering. The compositions at different oxygen partial pressures are different from target composition, which results from the different striking coefficients and variation in sputtering yields of the constituent elements. Combining Fig. 3, Fig. 5 with Fig. 6, it is concluded that within the range (0.12–0.05) of Nd concentration, the Nd$^{3+}$ substituted Sr$^{2+}$ and it does not cause formation of any unwanted phase.

### 3.4. Microstructure

The FESEM images of SNBT thin film, presented in Fig. 7, display different surface morphology at various oxygen partial pressures. At 0% O$_2$, i.e., pure argon atmosphere, shown in Fig. 7(a), the surface is relatively dense and most of the grains are rod-like. With increasing oxygen partial pressure, the amount of the rod-like grains reduces while more equal axial grains appear, e.g., Fig. 7 (b), (c) and (d). At 50% O$_2$ oxygen flow, the microstructure is completely overtaken by the equal axial grains. It is believed that the evolution of the surface morphology is related to the variation of oxygen partial pressure. From Fig. 6, it is noticed that the oxygen partial pressure causes the compositional change of thin films. The variation in composition (especially Bi concentration) may result in the different surface morphologies: higher Bi concentration tends to form rod-like grains [31].

### 3.5. Ferroelectric properties

Fig. 8(a) plots the polarization hysteresis loops of the films at an applied field of 220 kV/cm (5 V over 230 nm in thickness) at 25°C. All films present ferroelectric characteristics: the remnant polarization values are larger than that of pure SBT (8 μC/cm$^2$ [32]). Fig. 8(b) presents the $2P_r$ and $2E_c$ curves of the films at different oxygen partial pressures. The $2P_r$ has basically no change from 0% to 10% and then decreases sharply between 10% and 25% oxygen before slightly increasing again at 25–50% O$_2$. The $2E_c$ shows a “bathtub” shape with the increasing oxygen partial pressure. At no oxygen, $E_c$ of 114 kV/cm is high and not beneficial to the domain switching. At the oxygen partial pressure of 10%, the $2P_r$ obtained a maximum value of 16.4 μC/cm$^2$, at the same time the $2E_c$ dropped to 79.5 kV/cm, which is more desirable in FeRAM devices. The higher remnant polarization at 0% and 10% is attributed to the substitution of higher Nd$^{3+}$ concentration (see Fig. 6: the Nd content is highest among all the ratios). The large $2E_c$ is ascribed to oxygen vacancies involved in the film. At 0%, no oxygen in the chamber causes the oxygen loss during sputtering leading to oxygen vacancies. The oxygen vacancies may pin down the domains thus result in larger coercivity [30]. At 25%, both $2P_r$ ($2P_r = 9.8$ μC/cm$^2$) and $2E_c$ (74 kV/cm) reach the minimum. As the oxygen partial pressure goes up, both the $2P_r$ and $2E_c$ rise. The increasing $2P_r$ comes from the improved (200) orientation (see Fig. 4) However, at 50%, the $2E_c$ increases due to lower Nd concentration substitution (see Fig. 6: Nd/Ta ratio is only 0.05).

### 4. Conclusion

During sputtering deposition of Sr$_{0.8}$Nd$_{0.3}$Bi$_{2.5}$Ta$_2$O$_{9+x}$ ferroelectric thin films, oxygen partial pressure has an important effect on deposition rate, chemical composition, microstructure and ferroelectric properties. As the oxygen partial pressure increases, the deposition rate decreases; $I_{(200)}/I_{(115)}$ shows a “V” shape; both Bi/Ta and Nd/Ta decrease while Sr/Ta increases and (Nd + Sr)/Ta almost keeps a constant. Within the range of 0.05–0.12 in Nd/Ta ratio, Nd$^{3+}$ ions preferentially substitute the Sr$^{2+}$ ion, which is in good agreement with the result of Nd-doped SBT ceramics bulk. The coercivity displays a “bathtub” curve as oxygen partial pressure increases. At the oxygen partial pressure of 10%, the film shows an improved polarization property ($2P_r = 16.4$ μC/cm$^2$) with a reduced coercivity ($2E_c = 79.5$ kV/cm).

### References