Nd-substituted SrBi$_2$Ta$_2$O$_9$ ferroelectric thin films prepared by radio frequency magnetron sputtering

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Abstract

Nd-substituted SrBi$_2$Ta$_2$O$_9$ (SNBT) thin films are sputtered on Pt/Ta/SiO$_2$/Si substrates. X-ray diffraction and x-ray photoelectron spectroscopy studies indicate that Nd$^{3+}$ is substituted into the bismuth layered perovskite structure, preferentially at the Sr$^{2+}$ site. The annealed thin film is polycrystalline with plate/needle-like grain microstructure. Secondary ion mass spectrometry results show that elements in SNBT thin film homogeneously distribute along film depth and interfacial diffusion takes place during post annealing. The Nd substitution leads to enhanced remnant polarization ($P_r = 18 \ \mu$C/cm$^2$) and reduced coercivity ($E_c = 64$ kV/cm) at 180 kV/cm measured at 25 °C. After $10^{10}$ switching cycles, around 9% remnant polarization is decreased.

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1. Introduction

Utilization of ferroelectric thin films for nonvolatile random access memory applications has been under intensive investigation. Films for transistor-type memory require possessing these properties: a large remnant polarization ($P_r$), a low coercive field ($E_c$), sufficient fatigue endurance against repetitive polarization switching. 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].

However, for high density RAM applications of SBT thin films, there are two major problems to overcome: the low remnant polarization ($2P_r < 12 \ \mu$C/cm$^2$) and high annealing temperature ($> 800$ °C). Because SBT has only two polar axes ($a$ or $b$ axis), so that no remnant polarization contribution comes from $c$ axis, growing (200) or (020) orientation is expected. However, (200) or (020) oriented SBT thin films are extremely difficult to grow due to great mismatch between SBT and Pt bottom electrode (in general, a Pt layer on a Ta/SiO$_2$/Si substrate tends to show a (111) plane orientation, which has a relatively large mismatch with low index planes of SBT thin films [2]). On the other hand, previous studies [3–8] show that substitution at A or B site can effectively modify polarization properties. For A site (Sr$^{2+}$), Ca$^{2+}$, Bi$^{3+}$ and La$^{3+}$ substitutions with Sr$^{2+}$, whose radii are very close, have been widely investigated and showed significant modification of polarization properties. Similar to PbTiO$_3$ that accommodate the cation vacancies created by La substitution, a large amount of Sr vacancies can be induced in the perovskite blocks of SBT by substitution with trivalent cations. The vacancies of cations as well as oxide ions strongly affect the polarization-switching properties of ferroelectrics [9–11]. Substitution with Bi$^{3+}$ at the Sr$^{2+}$ site induces A-site vacancies to satisfy charge neutrality, and pushes up the amount of cation vacancies to about 9% at the A site ($A = Bi_{0.18} \ Sr_{0.82}$), where □ denotes the Sr vacancies [12,13]. This leads to an increase in Curie temperature ($T_c$) from 295 °C (SBT) to 430 °C, and a large $P_r$ was observed in both thin films [14] and bulk ceramics [12]. Investigation of praseodymium...
substituted SBT bulk ceramic also showed that low-field polarization properties were significantly improved due to the praseodymium substitution, which presents an advantage over SBT and Bi-substituted SBT for a low-voltage operating ferroelectric-memory material [15]. These results suggest that Sr vacancies play an essential role in the polarization-switching behavior of SBT system. However, until now, no report is available to study the substitution of neodymium in SBT thin films.

In this letter, Nd-substituted SBT (SNBT) thin films were deposited using radio frequency magnetron sputtering. The microstructure and polarization properties of thin films were investigated.

2. Experimental details

SNBT films were sputtered from sintered target of Sr0.8-Nd0.2Bi1.3Ta2.5Ox with a purity of 99.9% (Super Conductor Materials Inc. Tallman, NY). The deposition conditions were listed in Table 1. Pt(111)/Ta/SiO2/Si(100) was used as substrate. Tantalum is a refractory metal proven to possess outstanding adhesion and barrier properties [16] thus it is used as an adhesion layer. Tantalum of around 100 nm in thickness was deposited on SiO2 film grown on Si(100) wafer. Then, Pt(111) was layered before deposition of the SNBT film. The amorphous as-deposited films were crystallized at 850 °C under oxygen atmosphere for 30 min at a ramping rate of 20 °C/min. The phase and crystal orientation of the films were analyzed by (grazing incidence) x-ray diffraction (GIXRD) with Cu Kα radiation (X-ray diffraction, PANalytical, Netherlands) with a purity of 99.9%. The films were crystallized at 850 °C which is attributed to the smaller ionic radius of Nd3+ (1.11 Å) compared to that of Sr2+ (1.26 Å) [18]. No formation of secondary phase such as pyrochlore detected by XRD demonstrates that with partial substitution of Sr ions by Nd ions up to 20 at.%, the single-phase layered perovskite is still preserved.

Table 1: Typical sputtering conditions of SNBT films

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<th>Parameters</th>
<th>Conditions</th>
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<tr>
<td>Base pressure (Pa)</td>
<td>&lt;3×10^-4</td>
<td></td>
</tr>
<tr>
<td>Process pressure (Pa)</td>
<td>1.5 Pa</td>
<td></td>
</tr>
<tr>
<td>Power density (W/cm²)</td>
<td>2.3 W/cm²</td>
<td></td>
</tr>
<tr>
<td>Gas flow rate (Ar/O2, sccm)</td>
<td>54/6</td>
<td></td>
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<tr>
<td>Target-to-substrate distance (mm)</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>Room temperature</td>
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The top Pt electrode was sputtered onto the crystallized SNBT films through a shadow mask to produce a circular diode of 0.2 mm diameter. The metal-ferroelectric metal capacitors were re-annealed in O2 flow at 600 °C for 30 min to improve the contact between SNBT and Pt electrode. Measurement of the polarization hysteresis loops was carried out with a RT6000HVA ferroelectric tester (Radiant Technologies Inc.) in a virtual ground mode. Fatigue characteristics were examined by using rectangular alternative pulses at 500 kHz and 180 kV/cm.

3. Results and discussion

SNBT thin film exhibits an orthorhombic crystal structure with space group A21am at room temperature and transforms to tetragonal structure with crystal symmetry I4/mmm at or above the transition temperature. The XRD patterns of the films were indexed by assuming an orthorhombic cell (a = 5.531 Å, b = 5.534 Å, and c = 24.98 Å [17]). The XRD patterns (θ-2θ scanning mode; 2θ scanning mode: incidence angle α=3°) of SNBT thin film in Fig. 1 indicates that the annealed thin film is of single phase with A21am orthorhombic symmetry. The fully crystallized film is polycrystalline. A systematic shift of diffraction lines towards higher diffraction angle is a clear indication of a decrease of orthorhombic lattice parameters, which is attributed to the smaller ionic radius of Nd3+ (1.11 Å) compared to that of Sr2+ (1.26 Å) [18]. No formation of secondary phase such as pyrochlore detected by XRD demonstrates that with partial substitution of Sr ions by Nd ions up to 20 at.%, the single-phase layered perovskite is still preserved.

Fig. 2 is the XPS spectra of SNBT thin film before and after etching by Ar ions. In SNBT, the Nd3d5/2 and Nd3d3/2 peaks (Fig. 2a) before or after etching appear at 892.2 eV and 1004.6 eV while in pure Nd2O3, the peaks attributed to Nd3+ appear at around 980.8 eV and 1007.3 eV, respectively [19]. The peak-fitting analysis of the SNBT spectrum suggests that Nd4+ is not present. The results of x-ray diffraction and XPS analyses confirm that Nd is preferentially substituted at the Sr site as trivalent cations thus the formation of O2⁰⁻ compensates the charge deference between Sr2++ and Nd3+ Substitution of Nd at A site materializes via

\[ \text{Nd}_2\text{O}_3 \rightarrow 2\text{Nd}^{3+} + 3\text{O}^{2-} + \text{V}^{\text{S}^{2+}} \]

where Nd3+ stands for Nd3+ at the Sr2+ site (A site), O2⁻ denotes O2⁻ at the oxygen site and V^S is represents the Sr2⁺ vacancy. XPS quantitative analysis indicates that the chemical composition of sputtered films is determined as Sr0.8Nd0.2Bi1.3Ta2.5Ox, a little different from target composition, which results from the different striking coefficients and variation in sputtering yields of the constituent elements. After etching by Ar ions, the shift in Nd 3d peaks relative to those before etching is ignorable. This implies that Ar ions sputtering did not almost cause any change of the Nd–O bond. However, Bi 4f core levels are quite different before and after etching, as shown in Fig. 2b. Before etching, the 7/2 and 5/2 spin-orbit doublet components of the Bi
4f core level photoelectron do appear, while after 5 min of sputtering, an additional spin-orbit doublet emerges dominantly, overlapping with the major Bi 4f photoelectron at the low binding energy side. These new peaks are assigned to a metallic bismuth state reduced by Bi–O bonding breakage and oxygen dissociation during the etching process [20]. The photoelectron spectra of Sr 3d core levels for SNBT films before and after five-minute sputtering (Fig. 2c) present that Sr 3d peaks not only shift but also broaden due to enhancement of spectral weight at a higher binding energy region after sputtering. The fitting results imply that very small fraction (around 2%) of Sr is assigned to a metallic Sr (5/2 = 134.3 eV and 3/2 = 136 eV). Ta 4f core levels also present the shifting behavior after etching (Fig. 2d) and also a small fraction of metallic Ta is involved. The comparison among Bi 4f, Sr 3d and Ta 4f core level spectra suggests that the oxygen ions at the SrTa2O7 perovskite layers are much more stable than the oxygen ions at the Bi2O2 layers. Thus, it is included that oxygen vacancies seem to be preferably

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Fig. 1. XRD patterns of the Nd-substituted SBT thin film annealed at 850 °C for 30 min using conventional furnace annealing.

Fig. 2. XPS spectra before and after etching: (a) Nd 3d (b) Bi 4f; (c) Sr 3d; (d) Ta 4f.
present near the Bi ions at the Bi₂O₂ layers. On the other hand, for SNBT thin film, after five-minute sputtering, very weak photoelectron peaks of Sr 3d or Ta 4f belonging to metallic state provide evidence that few oxygen vacancies may appear in SrTa₂O₇ perovskite layers. This lightly differs from pure SBT thin film: in pure SBT thin films, almost no oxygen vacancy is located at SrTa₂O₇ perovskite layers thus fatigue free property is present [21]. These results suggest that Nd incorporation leads to a little change in Ta–O, Sr–O bonds.

The SIMS depth profiling was conducted to investigate the elemental distribution and interfacial diffusion. Normalized SIMS results show that SNBT layer, platinum (bottom electrode) layer and tantalum adhesion layer are clearly defined in Fig. 3. After annealing, the composition at the SBT–Pt interface changes gradually due to inter-diffusion (Fig. 3). Within the SBT layer, Sr, Nd, Bi and Ta are basically homogeneous. However, Bi suffers from severe diffusing towards the surface due to volatility of Bi₂O₃, and at the same time, diffusing into the Pt layer at the SBT/Pt interface. In fact, this is picked up in XRD results shown in Fig. 1: a weak diffraction peak from Bi₂Pt appears at 29.9° (2θ), coincident with earlier reports [22,23]. The inter-diffusion layer, occurring during annealing, has a reverse effect on the ferroelectric properties [22]. Therefore, it is expected to avoid or reduce this inter-diffusion phenomenon. During annealing (under O₂ atmosphere), metallic Bi diffuses out of the film and oxidizes into volatile Bi₂O₃ at the surface. This reduces the chemical potential of Bi metal, creating the driving force for more Bi to migrate from the film towards the surface [23] (where more oxygen is available). Besides, the interface between Pt and Ta layer becomes not sharp after annealing as well as that before annealing: Pt concentration extends through to Ta layer, indicating that the inter-diffusion between Pt and Ta layers also takes place at high temperature.

Fig. 4a depicts the FESEM micrograph showing the surface morphology of the SNBT thin film after annealing. The film is relatively dense and the grains (around 200–300 nm) are plate/rod-like. The cross-sectional image displayed in Fig. 4b shows the thickness of the SNBT film (around 220 nm). The layered (SNBT/Pt/Ta/SiO₂) structure is still identifiable although there exists inter-diffusion, while the interface becomes blurry in comparison with the as-deposited sample (not shown here). These observations are in good agreement with SIMS depth profiling results.
The polarization hysteresis loop (labeled as initial) in Fig. 5 of typical 220 nm Nd–SBT films was measured at an applied field of 180 kV/cm at 25 °C. A significant improvement of remnant polarization of 18 μC/cm² (2P_r) is obtained. This value is much larger than that of pure SBT (2P_r=11 μC/cm² [24], 8 μC/cm² [25]), also higher than that of Sr-deficient/Bi-excessive SBT thin films (2P_r=11.6 μC/cm²) reported by our group [26]. The improvement of P_r in SNBT thin film is ascribed to larger grains size and substitution effect. The larger grain size (shown in Fig. 4) due to annealing at high temperature may cause higher remnant polarization [27]. On the other hand, a small fraction of oxygen vacancies present in the cation vacancies generated. The higher valent substituents (96 kV/cm) [26]. The lower coercive field is possibly related to the barrier required for the nucleation of domains is significantly reduced. Switching cycles, around 9% remnant polarization is decreased. In ferroelectric thin films, results in a larger remnant polarization. At the same time, the SNBT has a 2E_c of 64 kV/cm, much smaller than that of the pure SBT (108 kV/cm) and Bi-substituted SBT thin films (96 kV/cm) [26]. The lower coercive field is possibly related to the cation vacancies generated. The higher valent substituents and associated cation vacancies tend to form dipolar defects, which are quenched above the ferroelectric transition temperature due to their extremely low mobility [10]. The activation barrier required for the nucleation of domains is significantly lowered by the random field near dipolar defects, leading to a lower E_c [28]. Fatigue property was measured by applying rectangular alternative pulses at 4 V amplitude. After 10^10 switching cycles, the hysteresis loop is also shown in Fig. 5. It can be seen that a little degradation (around 9% reduction) of remnant polarization is visible. In ferroelectric thin films, fatigue failure is related to the oxygen vacancies generated in ABO_3 perovskite structure [29,30]. As discussed in XPS results, oxygen vacancies are preferably present near the Bi ions at the Bi_2O_3 layers, which could not lead to the fatigue failure. However, a small fraction of oxygen vacancies present in SrFeO_3 perovskite layers caused by Nd incorporation may be the reasonable explanation for the light degradation of remnant polarization. Overall, these findings conclusively demonstrate that SNBT thin film is more promising over sputtered SBT and Bi-substituted SBT for a low-voltage-operating ferroelectric-memory material in the form of thin films.

4. Conclusions

In summary, Nd^{3+} has been substituted into the bismuth layered perovskite structure via magnetron sputtering method, preferentially at the Sr^{2+} site (perovskite A site) accompanied by the creation of Sr vacancies to meet the requirement of charge neutrality. After annealing, the film is polycrystalline and suffers from interfacial diffusion. Polarization measurements reveal that trivalent Nd substitution improves the remnant polarization (2P_r) (18 μC/cm² at an electric field of 180 kV/cm) and reduces coercive field (2E_c=64 kV/cm). After 10^10 switching cycles, around 9% remnant polarization is decreased.

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