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Orientation Control of $SrBi_2Ta_2O_9$ Thin Films on Pt (111) Substrates

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The a-axis and c-axis prefer oriented SBT thin films could be deposited on Pt(111)/Ti/SiO_2/Si(100) by radio frequency magnetron sputtering. By using 10 mol% of Sr and 30 mol% of Bi excess target, r.f. sputtered SBT film showed a-axis prefer orientation with good ferroelectric properties. In contrary, by using 30 mol% of Bi excess target, r.f. sputtered SBT film showed high c-axis orientation. The a-axis prefer oriented SBT films is more attractive for memory devices due to lower nucleation and grain growth offset temperature (600~650°C). The c-axis preferred orientation of SBT film can be obtained by Sr deficiency and high compressive stress. However, the a-axis-oriented grains can be formed under stoichiometric Sr content and nearly stress-free state.

Key words: $SrBi_2Ta_2O_9$, a-axis preferred orientation, High c-axis orientation, Intrinsic stress

I. Introduction

In recent years, $SrBi_2Ta_2O_9$ (SBT) thin films have received considerable attention due to their potential application in ferroelectric random access memory (FRAM) as an alternative to $PbZr_{1-x}Ti_xO_3$ (PZT) thin films, which have a fatigue problem with Pt electrodes.[1,2] Although SBT thin films exhibited no fatigue in ferroelectric polarization even after 10^{12} switching cycles, a well-defined hysteresis curve of SBT capacitors can be only obtained after high temperature annealing above 750°C.

Structurally, the continuous perovskite structure occurs in the a-b planes, where unbroken chains of O-Ta-O are present, while the continuity of the perovskite is disturbed by bismuth oxide layer along the c-axis in the bismuth layered ferroelectric materials.[3] Therefore, the ferroelectric properties are strongly dependent on the orientation of the films. Consequently, the ferroelectric properties along the a-axis expect to be better, whereas it is observed that the ferroelectric properties along the c-axis of SBT are not good. However, the crystal orientation effect of SBT has not been well investigated in thin films.

Most previous studies on the oriented growth of SBT thin films were based on the lattice parameter matching between the thin film and the substrate material[4-6]. In order to apply the anisotropic ferroelectric properties of SBT thin films to the memory devices, the studies about the oriented growth of SBT thin films on usual Pt (111)/Ti/SiO_2/Si (100) substrate are needed. Recently, there were reports about the prefer oriented growth of the SBT thin films on Pt (111) electrodes.[7-16] The c-axis prefer oriented SBT films have been mainly observed on thin films with Sr deficient compositions.[11,12] In the case of SBT films with Sr deficient compositions, c-axis oriented growth was also influenced by the mixing process or coordination state of alkoxides in solution.[7,8] The degree of the a-axis orientation was slightly enhanced with increasing Bi content in stoichiometric Sr films.[2] In our previous studies, we could obtain the highly c-axis preferred oriented SBT thin films on usual Pt (111)/Ti/SiO2/Si (100) substrates using the radio frequency(r.f.) sputtering method.[13-15] With increasing the sputtering pressure, the Bi contents in the films increased and the crystal structures of the films were changed from pyrochlore structure, which resulted from Bi deficiency, to c-axis prefer oriented SBT. And the (a00) and (00l) epitaxial SBT thin film on (100) $LaAlO_3$, (100) $SrTiO_3$, and (200) yttria stabilized zirconia (YSZ) single crystal could be grown by the pulsed laser deposition technique[5]. However, the ferroelectric properties of epitaxial films have not been examined and the origins of (a00) oriented epitaxial thin film have not been fully understood.

In this report, the a-axis and c-axis prefer oriented SBT thin films on Pt(111)/Ti/SiO_2/Si(100) were prepared, and ferroelectric properties will be discussed. The factors of the oriented growth, such as composition, stress, and chemical state difference will be observed to understand the preferred orientation.

II. Experimental Procedure

The substrates used in this study were the platinized silicon wafers (Silicon Quest International Inc.), Pt(111) (150 nm)/Ti (50 nm)/SiO_2 (1,000 nm)/Si(100). The mixture of two different gases (Ar, O_2) was used in the r.f. magnetron sputtering process. The polycrystalline SBT ceramic targets which have different Sr content mole ratio (Sr : Bi : Ta=

1 : 2.6:2, 1.1 : 2.6 : 2) with a diameter of 5.08 cm and a purity of 99.9% (Seattle Specialty Ceramics Inc.) were sputtered in an input power of 30 W. The sputtering pressure was 300 mTorr. The deposited thin films were post annealed at 600~800°C for 30~60 min in oxygen flow.

The phase and orientation of the films were characterized by the standard θ-2θ X-ray diffraction (XRD) with Cu K_α radiation. The XRD patterns were indexed by assuming an orthorhombic cell (a=5.5306 Å, b=5.5344 Å, c=24.9839 Å). The biaxial stress in the sputtered SBT films was determined using an α-step surface profile measuring system to measure the curvatures of the 100 μm thickness Si(100) wafer. By subtracting the initial curvature before film deposition from that measured after the deposition, we can evaluate the film stress from Stoney's equation.[17] The surface morphologies of SBT thin films were observed by scanning electron microscope (SEM). The compositions of thin films were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES). The compositions and chemical states of the surfaces of the films were determined by x-ray photoelectron spectroscopy (XPS, Phi 5700). Patterned platinum top electrodes were produced using dc magnetron sputter deposition method in conjunction with a lift-off method. The metal-ferroelectric-metal (MFM) capacitors were reannealed in O_2 flow at 700°C for 30 minutes to improve the contact between SBT and Pt electrode. The characterization of the ferroelectric properties of the capacitors was performed by using a RT66A ferroelectric tester (Radiant technologies).

II. Results and Discussion

1. Film Structure of the SBT Films

Fig. 1 illustrates the XRD patterns of the SBT thin films.

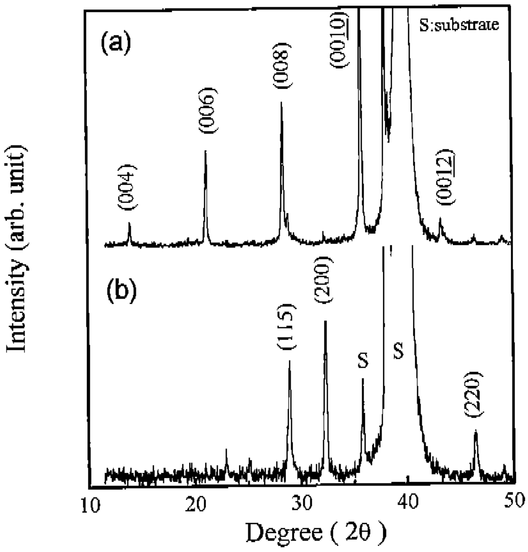

Fig. 1. X-ray diffraction pattern of SBT films deposited from two targets having a composition of (a) a-type (Sr : Bi : Ta= 1.0 : 2.6 : 2.0) and (b) b-type (1.1 : 2.6 : 2.0). The films were post annealed at 800°C for 30 min.

One is an a-type film deposited from target, which have composition of 30 mol% of Bi excess, and the other is a b-type film deposited from 10 mol% of Sr excess and 30 mol% of Bi excess target. The a-type film exhibits strong (00l) peaks (l=4, 6, 8, 10, 12) with the c-axis oriented normal to the substrate. In contrast, the b-type film has stronger (200) peak. The crystal orientation of these two films is completely different. Therefore, the target composition is a very important factor in controlling the crystal orientations of r.f. sputtered SBT thin films.

Fig. 2 shows SEM surface micrographs of the SBT film. Both films exhibit very different grain growth behavior. In a-type, bimodal grain size distribution consisting of elongated grains and small globular grains,[14,15,18,19] which was observed at the films post-annealed at 650°C, is shown in 2(b). When the annealing temperature increased, small globular grains in the matrix were changed to uniform elongated grains. Unlike the c-axis prefer oriented a-type film, however, uniform grain distribution and lower nucleation and grain growth offset temperature (about 600°C) could be seen in the a-axis prefer oriented b-type SBT film.

2. Ferroelectric Properties of the SBT Films

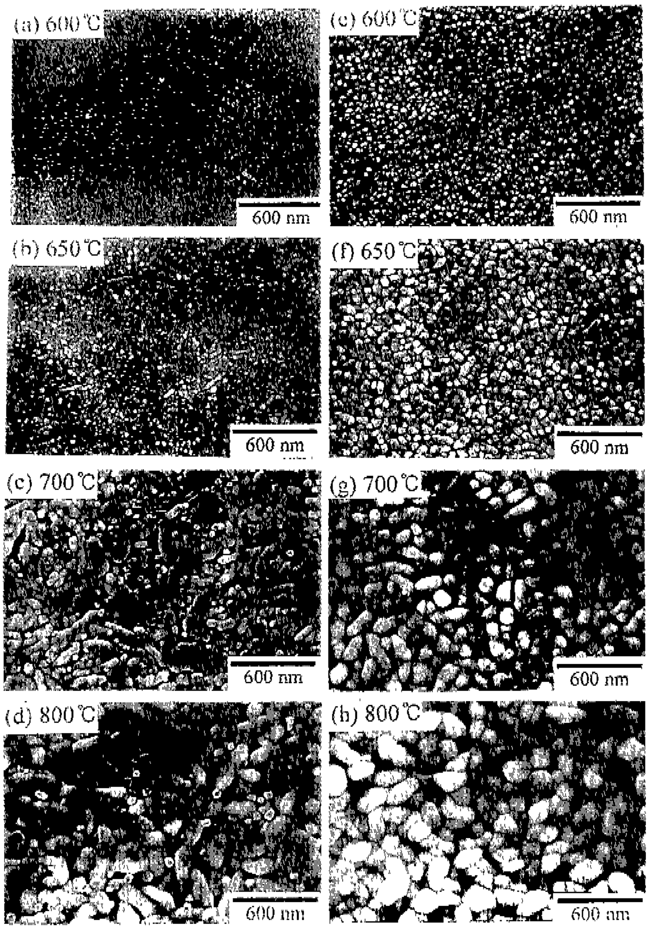

Fig. 2. SEM surface micrographs of the SBT thin film annealed at various temperature. where. (a)-(d): a-type and (e)-(h): b-type.

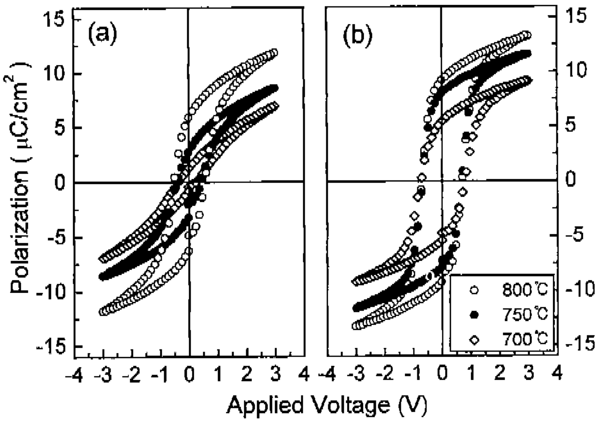

Fig. 3. Hysteresis loops of Pt/SBT/Pt capacitor using excitation voltage of 3V. where, (a) a-type and (b) b-type.

Fig. 3 shows the hysteresis loops of the a- and b-type films at applied voltage of 3 V. The polarization values of the b-type SBT films are greater than those of a-type, but the coercive fields of the b-type are slightly higher than a-type through all annealing temperatures. Also the signal to noise ratio (r) defined by Mihara *et al.*[20] was 1.03 for a-type and 4.42 for b-type, respectively. The b-type film annealed at 700°C shows good ferroelectric properties (Pr=5.5 μC/cm²) applicable to FRAM device.

The fatigue characteristics of the films are shown in Fig. 4. Neither film exhibits any change up to 10^{11} switching cycles. Therefore, crystal orientation has no effect on the fatigue characteristics of the SBT films.

3. SBT Film Composition

We determined the composition of the SBT films by using the ICP method to investigate differences between the a-type and b-type films. The atomic ratio of Sr, Bi and Ta, Sr : Bi : Ta is 0.9 : 2.6 : 2.0 for the a-type and 1.0 : 2.5 : 2.0 for the b-type, respectively. Based on the above results, the Sr contents were different. Therefore, the difference in crystal orientation between the a-type and b-type films is caused by Sr content difference. We could infer that the c-axis preferred orientation is formed with deficient Sr content, and a-axis preferred orientation may be obtained with stoichiometric Sr content and excess Bi.

4. Intrinsic Stress and Chemical State of As-deposited Amorphous SBT Films

Residual stress was measured at room temperature. Both of as-deposited SBT films exhibit compressive stress. In sputtering method, as-deposited films are usually under compressive stress due to high energy of deposition species and the bombarding of hot electrons or negative oxygen.[21] Therefore, the stress of the sputtered films showed to be influenced by sputtering parameters. During the a-type film deposition, higher dc self-bias was generated presumably due to different target composition. The a-type film shows higher compressive stress (−970 MPa) than the b-type(−50 MPa).

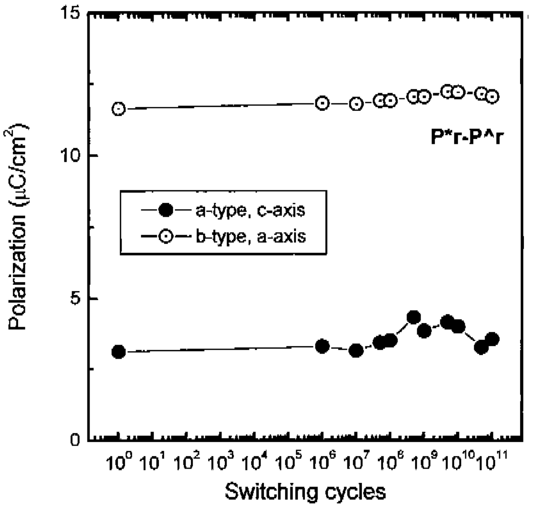

Fig. 4. Fatigue characteristics of the SBT films. The capacitors (area is 5.027 μm²) were switched using square pulse with peak-to-peak voltage of 6 V at 1 MHz.

The influence of the bonding states of as-deposited film on the orientation of the SBT thin film was investigated by XPS analysis. The XPS spectra in the Bi 4f peak region and Sr 3d peak region are shown in Fig. 5 (a,b) and (c,d), respectively. The spectra are deconvoluted into peaks assuming a Gaussian-type shape. Compared to both type films, Bi state is almost similar, but Sr state is quite different. The high binding-energy peak (133.7 eV) shown in the decomposition of the Sr 3d peak (Fig. 5 (c,d)) is considered to be metallic Sr state. We found that the atomic fraction of metallic Sr was higher in the a-type film than b-type.

The effect of the stress and bonding state on the crystal orientation of SBT film was not fully understood so far. But, further study about the stress and bonding state effect must be needed to control the orientation of SBT film.

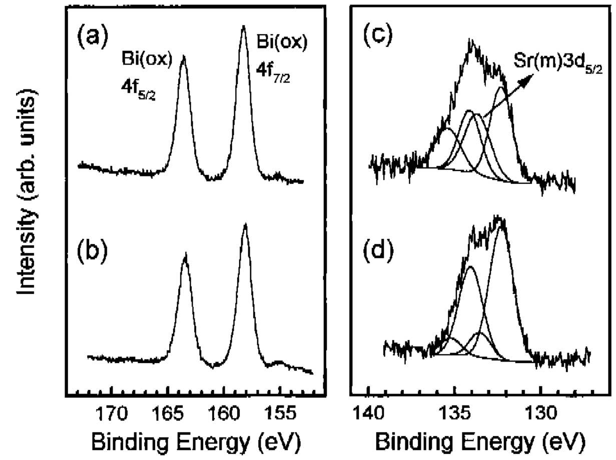

Fig. 5. (a, b) Bi 4f and (c, d) Sr 3d XPS spectra obtained from the SBT films as-deposited at room temperature. where, (a), (c) : a-type and (b), (d) : b-type.

IV. Conclusion

The a-axis and c-axis prefer oriented SBT thin films could be deposited on Pt(111)/Ti/SiO_2/Si(100). By using 10 mol% of Sr and 30 mol% of Bi excess target, r.f. sputtered SBT film showed a-axis prefer orientation with good ferroelectric properties. In contrary, by using 30 mol% of Bi excess target, r.f. sputtered SBT film showed high c-axis orientation. The a-axis prefer oriented SBT films is more attractive for memory devices due to lower nucleation and grain growth offset temperature (600~650°C). The c-axis preferred orientation of SBT film could be obtained by Sr deficiency and high compressive stress. But, the a-axis oriented grains could be synthesized when Sr is stoichiometric and nearly stress-free. In addition, the difference of bonding state were also detected, but further study must be need in details for the understanding of correct effect of bonding state on the preferred orientation.

Acknowledgement

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