

Strong thickness dependence of aurivillius phase formation in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films

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Abstract $\text{Sr}_{0.7}\text{Bi}_{2.4}\text{Ta}_2\text{O}_9$ (SBT) thin films were studied for the dependence of Aurivillius phase formation kinetics on their film thickness. SBT thin films were fabricated using a sol-gel process and spin coating, and their thickness was varied controlling the number of spin coating. The films were first heated at a low temperature for the complete crystallization of amorphous film to fluorite phase and then further heated at different elevated temperatures for the phase transformation to Aurivillius for 40 min. It was found that the phase transformation kinetics apparently increased with thickness up to ~ 390 nm, and then it sharply decreased at higher values. The Aurivillius crystal size decreased and the density of crystals increased with the increase of film thickness up to ~ 390 nm, implying increasing number of nuclei due to the reduced energy barrier for nucleation. Above the critical value both the size and density of crystals decreased. It is suggested that up to ~ 390 nm the tensile strain energy in the films, which was stored by the shrinkage of thin films during the removal of remaining organic components from sol-gel chemistry, plays a major role for determining

the phase transformation kinetics and above the critical value SBT films act as a free bulk material without substrate constraints.

Keywords SBT · Ferroelectric · Thin films · Phase transformation · Thickness

1 Introduction

In recent years, bismuth based layer-structured perovskite compounds, belonging to the so-called Aurivillius class of layered perovskites, have received much attention due to the possibility of applications such as non-volatile memory devices [1–4]. Strontium bismuth tantalate (SBT) has been identified for potential applications, such as a ferroelectric layer in capacitors for non-volatile ferroelectric memories (NvFRAMs) [5–9]. The Pt/SBT/Pt capacitors exhibit almost polarization fatigue free operation for up to $\sim 10^{12}$ switching cycles, low operation voltage, little tendency to imprint, and relatively low leakage, making SBT capacitors one of the strongest candidates for application in the first generation of NvFRAMs. Even though the possible existence of many non-stoichiometric phases, which are stable within the Sr-Bi-Ta-O system has been reported, SBT systems with a near stoichiometric composition ($\text{Sr}_{1-x}\text{Bi}_{2+y}\text{Ta}_2\text{O}_9$) have been found to show significantly improved ferroelectric properties. Refinement of the crystal structure of these phases carried out by Shimakawa et al. [10] indicated that Bi substitution and cation vacancy formation at the strontium sites enhance the structural distortion of the TaO_6 octahedra, leading to a larger ferroelectric spontaneous polarization.

However, the high temperature processing has been a major limiting factor. Therefore, for these systems it is quite necessary that the processing temperature be lowered below

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800°C, since at high temperatures, the reaction at the bottom electrode/thin film interface causes degradation of the electrical properties. Several optimized processes including the rapid thermal annealing (RTA) and annealing of SBT thin films in the oxygen flow, have been successful to lower the crystallization temperature approximately to 650°C [11–14] and to improve the properties of SBT thin films as well. Sung et al. used cation doping for Ta⁵⁺ ions and nanoparticle seeding for SBT thin films, respectively and reported considerable enhancement of Aurivillius phase formation kinetics in both cases [7, 15].

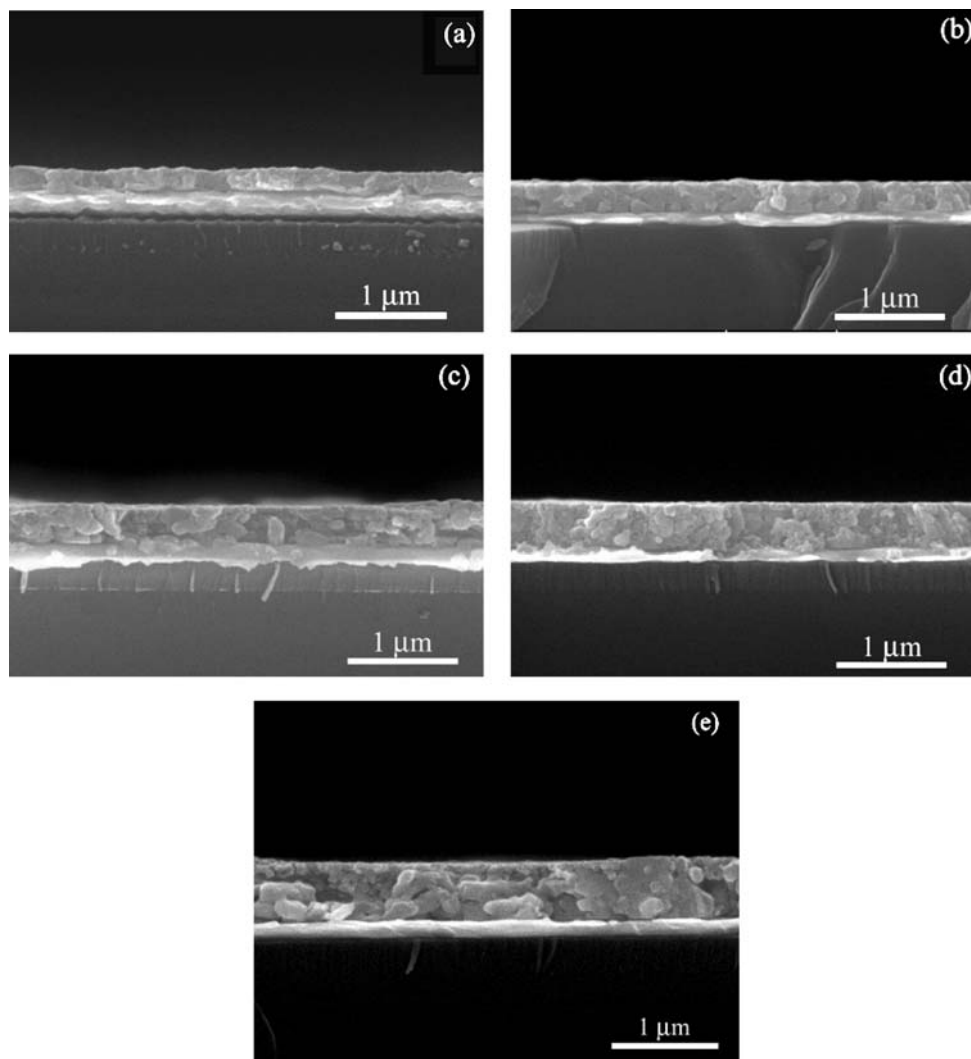
In the present research Sr_{0.7}Bi_{2.4}Ta₂O₉ thin films with different thickness were prepared on Pt/Ti/SiO₂/Si substrates using sol-gel and spin coating techniques. The film thickness was controlled varying the number of spin coating. The variation in the Aurivillius crystal size and fluorite-to-Aurivillius phase transformation was investigated with the SBT film thickness. The control of the film thickness was

suggested as a critical issue to control the Aurivillius phase formation kinetics of SBT thin films.

2 Experimental

The detail preparation route of Sr-Bi-Ta methoxyethoxide stock solution was described in the previous publications [6, 7, 15]. The SBT thin films were prepared on the Pt/Ti/SiO₂/Si wafers with 4 × 4 cm in size using spin coating (Headway Research, Inc., Garland, TX, USA) at a spin speed of 3000 rpm for 30 s. The films were dried in air for 1 min followed by heat-treating at 150°C for 5 min and pyrolysis at 450°C for 10 min in order to remove the organics. The coating process was repeated for 3, 4, 5, 6, and 7 times, respectively to achieve the SBT films with different thickness. SBT thin films prepared were further heat treated at 600°C for 1 h to achieve the complete formation of fluorite phase. In order to maintain consistency in the film thickness, each coated sample

Fig. 1 Scanning electron microscopy (SEM) cross-sectional view images of crystallized Sr_{0.7}Bi_{2.4}Ta₂O₉ (SBT) thin films with different thickness (a) 190, (b) 276, (c) 390, (d) 484, and (e) 585 nm



was split into four small pieces with $\sim 2 \times 2$ cm size for the heat treatment at four different temperatures. To investigate the fluorite-to-Aurivillius phase transformation characteristics, the films were further annealed in the temperature range of 730–760°C at 10°C intervals by giving soaking time period of 40 min. The X-ray diffraction (XRD: Rigaku, Ultima 2000, Tokyo, Japan) was performed using a precision thin film attachment. The incidence beam angle was fixed as 3° and 2 θ scans with a 0.02° step and 5 sec duration were conducted. XRD patterns of these films were recorded and a multi-peak separation program (MDI Jade 5.0, Materials Data, Inc., Livermore, CA, USA) was used to obtain respective integrated intensity of XRD peaks of fluorite (111) planes and Aurivillius (115) planes. The volume fraction values (x_A) of fluorite-to-Aurivillius phase transformation were obtained using a conventional quantitative XRD analysis technique. Scanning electron microscopy (SEM: Philips XL-30 E-SEM, Eindhoven, The Netherlands) was used to examine the crystal morphology and size of thin films.

3 Results and discussion

SBT films with four different thickness values were successfully prepared varying the number of spin coating as 3, 4, 5, 6, and 7. SEM cross-sectional view images of SBT thin films annealed at 600°C for 1 h and subsequently heat-treated at 750°C for 40 min are shown in Fig. 1. The corresponding film thickness values were 190, 276, 390, 484, and 585 nm, respectively. The smoothness of films seems to increase with the increase of film thickness. The phase identification was performed for SBT films heat-treated at 600°C for 1 h and it revealed the complete formation of fluorite phase, which is an intermediate and non-ferroelectric phase forming at a relatively low temperature range [16]. Each fluorite film was further heated at 730, 740, 750, and 760°C for 40 min, respectively and analyzed for fluorite-to-Aurivillius phase transformation using XRD. Figure 2 shows the variation in XRD results of SBT films heated at 750°C for 40 min with film thickness. The Aurivillius (115) and (200) peak intensities increased up to ~ 390 nm and then decreased above this value, which implying that the larger in the film thickness the higher in the phase transformation kinetics up to the thickness value of ~ 390 nm. However, it is also found that above the critical thickness of ~ 390 nm the phase transformation kinetics of the films suddenly decreases. The SEM plan-view images shown in Fig. 3 reveal the enhanced Aurivillius phase formation up to the film thickness of 390 nm and the sudden decrease above this value, which well corresponds to the XRD results. Here, dark and small-size crystallites are fluorite, whereas bright and rod-shape crystals are Aurivillius.

The volume fraction values of phase transformation (x_A) from fluorite to Aurivillius were determined using the

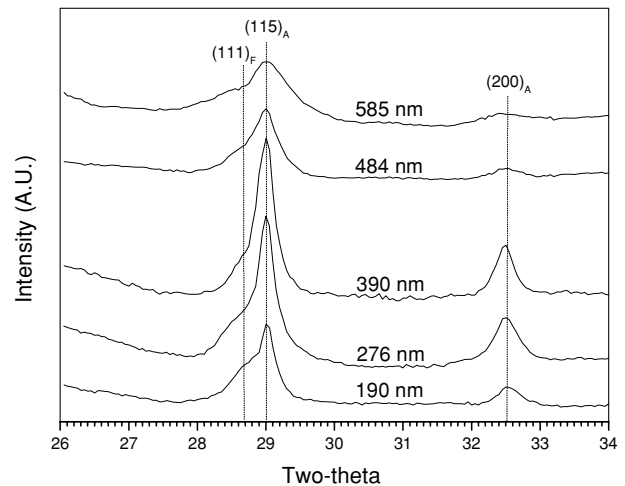


Fig. 2 X-ray diffraction (XRD) patterns of SBT thin films with different thickness. All the films were heated at 600°C for 1 h and further heated at 750°C for 40 min. Here, F(111) denotes the diffraction from fluorite (111) planes, and A(115) and A(200) denote the diffraction from Aurivillius (105) and (200) planes, respectively

following conventional XRD quantitative analysis method [16–18].

$$x_A = \frac{Pw_A}{1 + (P - 1)w_A} \quad (1)$$

where

$$w_A = \frac{I_A(115)}{I_A(115) + I_F(111)} \quad (2)$$

Here, $I_A(115)$ is the integrated intensity of the (115) reflection of the Aurivillius phase. In this study, the coefficient of P , representing the integrated intensity ratio of fluorite (111) reflection to Aurivillius (115) reflection, was determined as 0.833 using the mixtures of standard fluorite and Aurivillius powders. The volume fraction values were plotted as a function of coating numbers and temperature in Fig. 4(a). The five-time coated SBT films with 390 nm thickness showed about 78–91% conversion, while the six- and seven-time coated samples with 484 nm thickness showed the values of about 13–32%. This distinct difference in the phase transformation kinetics of fluorite-to-Aurivillius would be elucidated considering the strain energy stored by the shrinkage of films on the substrates during the annealing at 600°C for the fluorite formation. The possible sol-gel organic components remaining in the films can be further decomposed and removed during the annealing, and films will try to shrink and become dense. In reality, the intermediate annealing at 450°C for 10 min between each coating step would not be enough for the completer pyrolysis of organic components inside the films. The films are constrained to the substrate and can be under a strongly strained condition, especially near

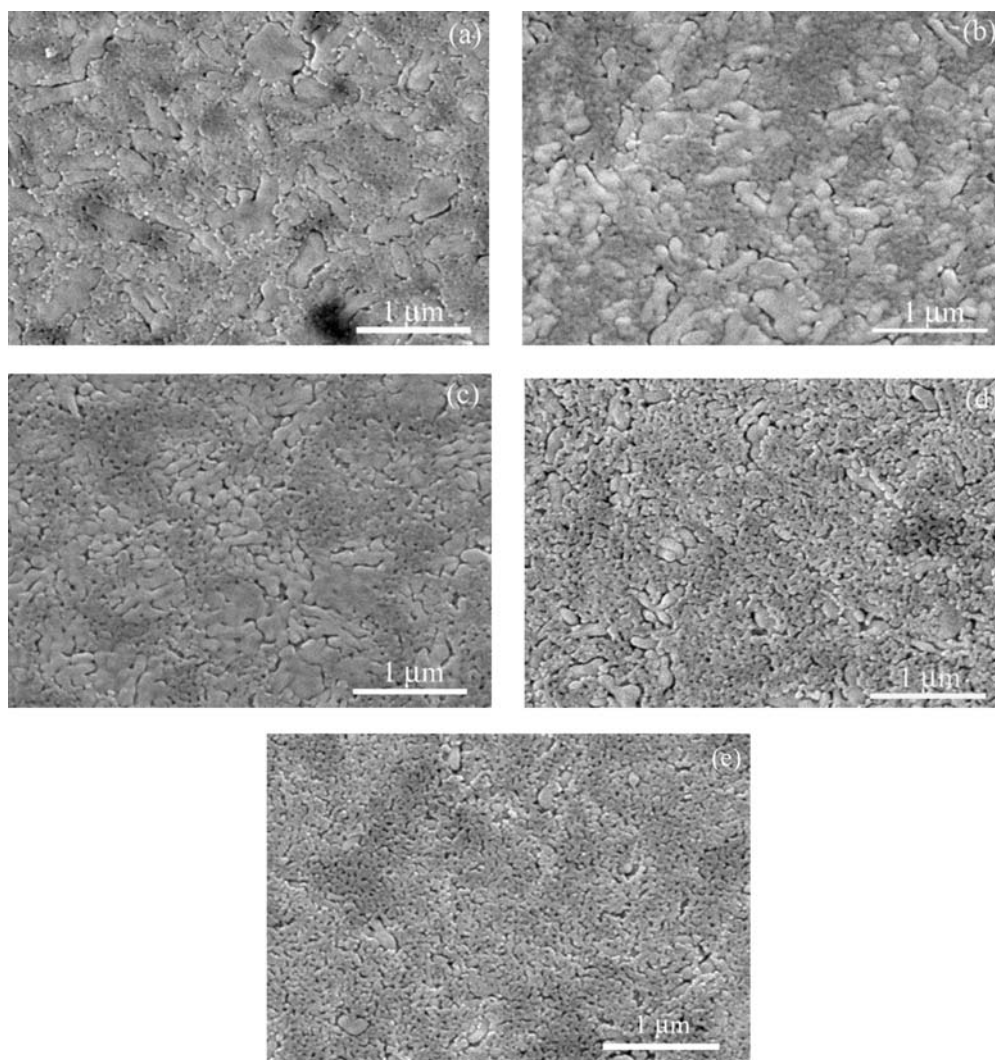


Fig. 3 Scanning electron microscopy (SEM) plan view images of $\text{Sr}_{0.7}\text{Bi}_{2.4}\text{Ta}_2\text{O}_9$ (SBT) thin films with different thickness (a) 190, (b) 276, (c) 390, (d) 484, and (e) 585 nm. Bright and rod-shape crystals are Aurivillius and dark and small-size crystallites are fluorite

the interfacial regions. The larger is the thickness of the SBT film the higher is the accumulated strain energy and this can reduce the energy required for the nucleation of Aurivillius crystals. The tensile strain, from a phenomenological point of view, can assist the dissociation of ionic bonds between cations and anions, and thus diffusion of ions will occur more easily in the highly constrained films. Thus, the fluorite-to-Aurivillius phase transformation kinetics increases with the film thickness. However, above a certain critical thickness value the phase transformation kinetics suddenly drops and saturates, which is probably since the substrate can not give the constraint to thick films any more due to the strong shrinking force and the SBT films could completely relax by overcoming the substrate constraints. Without the accumulated internal strain energy the nucleation and growth rate would be very low due to the high activation energy barrier for the nucleation.

The averaged longitudinal crystal size of each film with different thickness was measured using SEM photos and plotted in Fig. 4(b). The crystal size shows the steady decrease with film thickness and a sharp decrease for the five-time coated samples. This could also be explained using the difference in the stored strain energy. The 5-time coated films have high strain energy accumulated and thus nucleation of Aurivillius crystals can easily occur due to the reduced activation energy barrier for the nucleation. Thus, 5-time coated films show the formation of large number of small-size Aurivillius crystals compared to 3- or 4-time coated samples as shown in Fig. 3. On the other hand, the 3-time coated SBT films show the formation of the relatively large Aurivillius crystals with the lowest density. Due to almost negligible strain energy and thus the high energy barrier the 6- and 7-time coated films show the low crystal growth rate as well

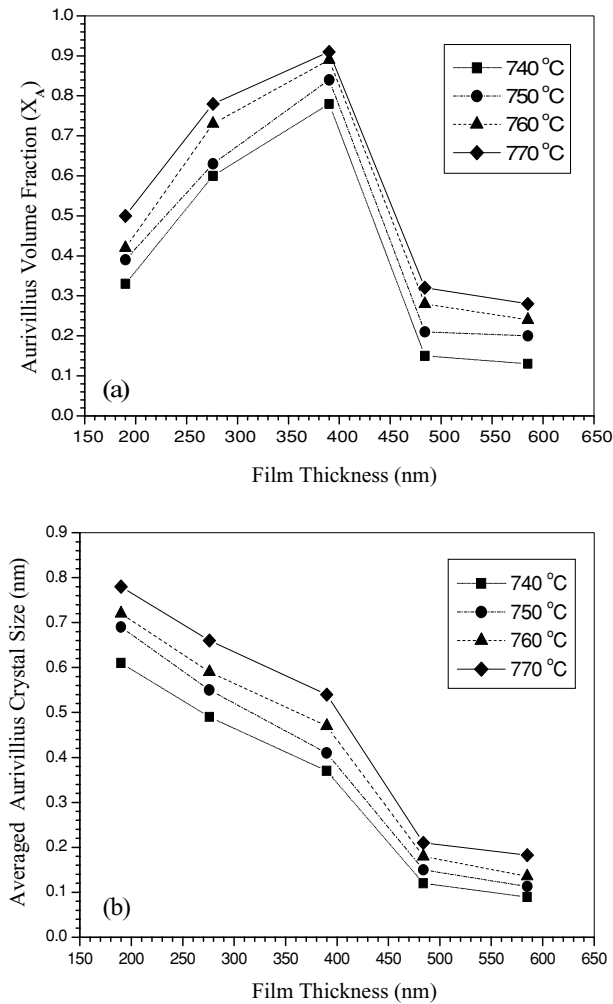


Fig. 4 The variations in (a) the volume fraction of fluorite-to-Aurivillius phase transformation (X_A) and (b) the Aurivillius crystal size with SBT film thickness

as low-density nucleation. Both the fluorite-to-Aurivillius phase transformation and Aurivillius crystal growth were consistently enhanced with temperature increase. The detail kinetics study to estimate the activation energy variation in fluorite-to-Aurivillius phase transformation of SBT films with different thickness is being performed and will be reported later.

4 Conclusions

In this study strong dependence of fluorite-to-Aurivillius phase transformation kinetics on the film thickness was

reported for sol-gel derived SBT thin films. The phase transformation kinetics was proportional to the film thickness, however there was a critical thickness value, above which the kinetics sharply decreases. The film thickness value of 300–400 nm was suggested as an optimum condition for the Aurivillius phase formation in SBT thin films. By using this optimum condition one can reduce the processing temperature, that is, the crystallization temperature for the Aurivillius phase. This approach for the film thickness control would be used as guidance for the control of phase formation kinetics in other sol-gel derived thin films.

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