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$SrBi_2Ta_2O_9$ thin films fabricated by alternate deposition of $SrTa_2O_6$ and Bi_2O_3 layers

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Strontium bismuth tantalate (SBT), a bismuth-layer-structured perovskite, has become one of the most fascinating materials for non-volatile ferroelectric random access memory devices due to its fatigue-free property with Pt electrodes. Of the available thin-film preparation methods, chemical solution deposition (CSD) offers advantages such as easy composition control and flexible operation. The only real limitation in the use of SBT is that its processing temperature is rather high (ca. 800 °C) [1]. As far as drop in processing-temperature is concerned, a few new deposition processes have been suggested. Many literatures proposed that drop in processing-temperature could be realized by modifying the post-annealing process. Ogata *et al.* suggested that low oxygen-pressure annealing results in the reduction of SBT crystallization temperature [2], whereas Song *et al.* argued that high oxygen-pressure annealing led to a drop in the ferroelectric SBT phase formation temperature [3]. As a typical example of modifying the post-annealing process, Aizawa *et al.* proposed a face-to-face annealing technique, in which the SBT films were crystallized at 750 °C without Bi atoms volatilization [4]. Recently, seeding layers were introduced into the fabrication of SBT thin films. Leu and co-workers were able to use a magnetron sputtered Ta-seeding-layer to improve the crystallinity and ferroelectric properties of SBT films [5]. Jung *et al.* were the first to deposit SBT films on the pre-crystallized SBT seed layer using sol-gel and spin coating methods, resulting in the enhancement of the fluorite-Aurivillius phase transformation kinetics [6]. However, no significant reduction was found in the processing temperature with seed layer (not lower than 740 °C). In this letter, we report the preparation of SBT thin films at temperature lower than 700 °C by a new CSD technique, in which SBT films were fabricated by alternate deposition of $SrTa_2O_6$ and Bi_2O_3 layers. The effect of deposition order of $SrTa_2O_6$ and Bi_2O_3 layers on the crystallization and microstructure will be discussed.

The starting solutions were prepared with strontium isopropoxide, tantalum ethoxide, and bismuth 2-ethylhexanoate. Ethoxyethanol was used as the solvent and tetrahydrofuran was used as the chelating reagent. A solution with Sr/Ta = 1/2 molar ratio, so-called $SrTa_2O_6$ (ST) precursor, was prepared. In order to prepare Bi_2O_3 (B) precursor, glacial acetic acid was used as the anticatalyzer. The concentration of both solutions was the same. The substrate used was $Pt/Ti/SiO_2/Si$ wafer. Two different SBT thin films were prepared by spin coating ST and B precursors at 6000 rpm, with the same volume (30 microlitre) and in different orders. One was prepared in B/ST/B/ST... deposition order, and another in ST/B/ST/B... deposition order. For each deposition order, heat treatment at 650 °C immediately after ST precursor spin coating and heat treatment at 150 °C immediately after B precursor spin coating were carried out, spending 1 hrs. The SBT film deposited in ST/B/ST/B... order was obtained without post-annealing, whereas the SBT film deposited in B/ST/B/ST... order was obtained with additional firing at 650 °C for 1 hrs.

Figs 1 and 2 show the X-ray diffraction (XRD) patterns of the SBT thin films deposited in different orders. The indexed planes in the XRD patterns were done assuming an orthorhombic unit cell [7]. It was observed that the SBT films fabricated in both deposition orders were polycrystalline. The variation in $I_{(115)}/I_{(220)}$ intensity ratio indicated that the films deposited in different orders were grown with different textures. Furthermore, the Bi_2Pt second phase was observed in the XRD pattern of SBT films deposited in ST/B/ST/B... order. Despite the additional heat treatment, no second phase was observed in the film deposited in B/ST/B/ST... order.

In order to investigate the influence of the deposition order on the microstructure and texture of the SBT films, atom force microscope (AFM) identification was carried out. Figs 3 and 4 illustrate the comparisons of AFM images between the first layer and the final film

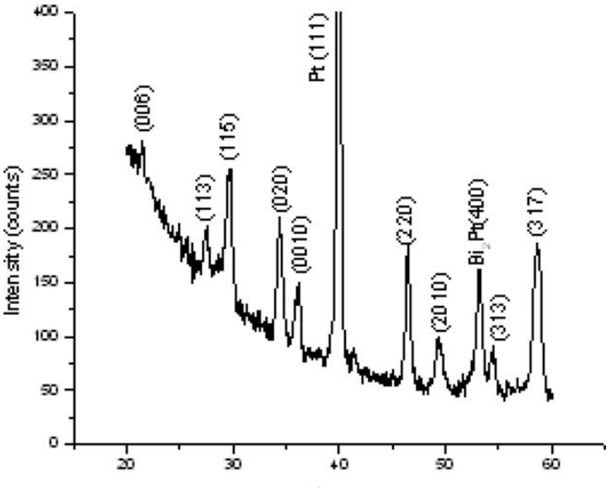

Figure 1 XRD pattern for SBT film deposited in ST/B/ST/B... order.

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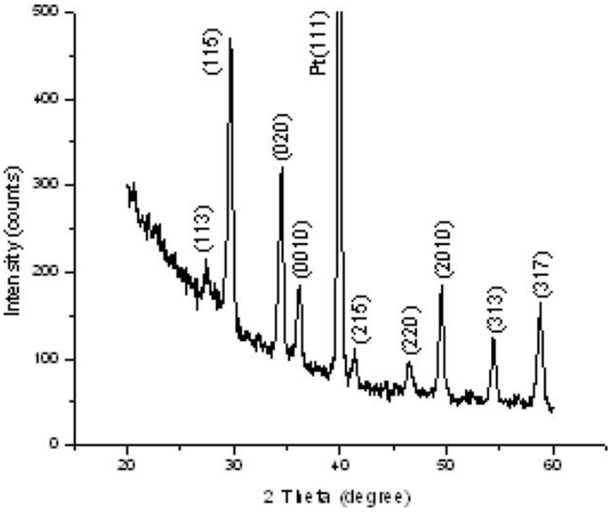

Figure 2 XRD pattern for SBT film deposited in B/ST/B/ST. . . order.

for both films. Fig. 3 indicates that the micrographs of the final film deposited in ST/B/ST/B. . . order was very different from that of the first layer, whereas Fig. 4 indicates that those two micrographs were similar for the film deposited in B/ST/B/ST. . . order. For the deposition in ST/B/ST/B. . . order, the first layer was composed of agglomerated Bi_2O_3 particles (Fig. 3a) because of the low temperature heat treatment at 150 °C. In the subsequent deposition processing, Bi_2O_3 would react with bottom electrode Pt at 650 °C. Then the Bi_2Pt second phase was formed. The interfacial Bi_2Pt layer in SBT films with Pt bottom electrodes was reviewed by J. F. Scott [8]. Clearly, the SBT film deposited in ST/B/ST/B. . . order was grown in the existence of Bi_2O_3 particles and Bi_2Pt second phase. Unfortunately, both phases have different symmetry with SBT. For the deposition in B/ST/B/ST. . . order, the first layer was a crystallized $SrTa_2O_6$ layer because of the relatively high temperature heat treatment at 650 °C. However, $SrTa_2O_6$ has the same symmetry with SBT. The film deposited in B/ST/B/ST. . . order was grown with a lattice-matched layer while another case was not. Consequently, the growth conditions would be different for both deposition orders. The microstructure and texture would be different for both SBT films because of lattice matching.

On the other hand, heat treatment at high temperature above 450 °C after spin-coating of the Bi_2O_3 layer resulted in non-crystallized SBT films. No crystallized

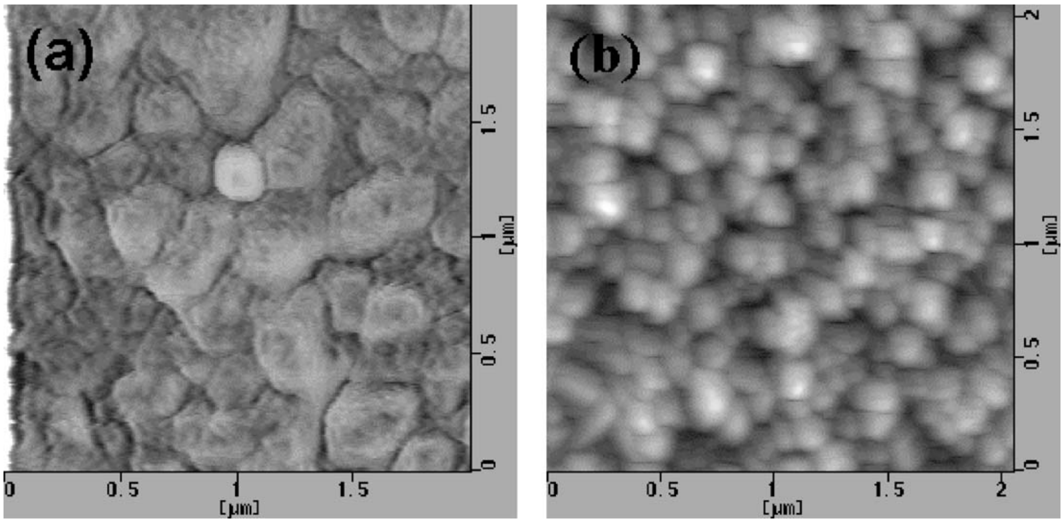

Figure 3 AFM images for SBT film deposited in ST/B/ST/B. . . order: (a) the first layer and (b) the final film.

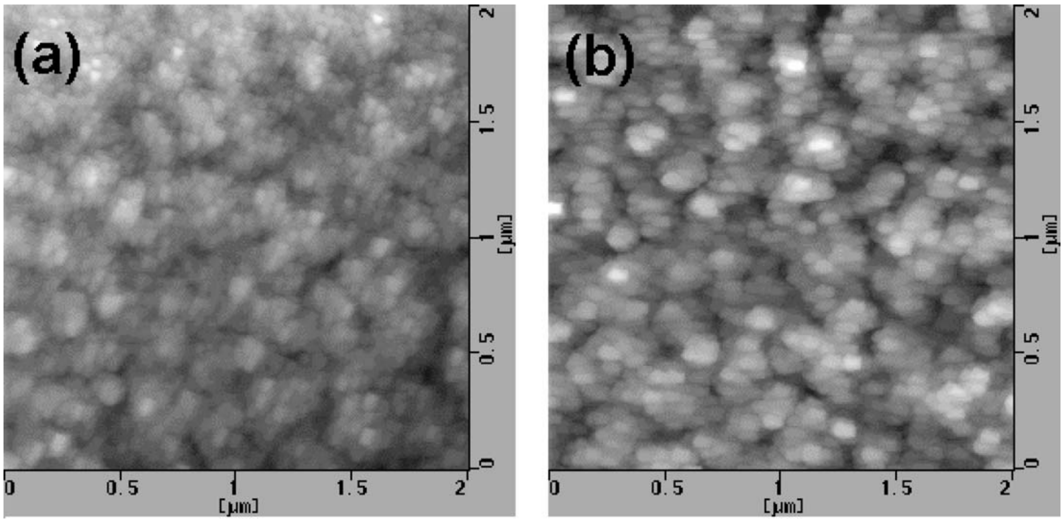

Figure 4 AFM images for SBT film deposited in B/ST/B/ST. . . order: (a) the first layer and (b) the final film.

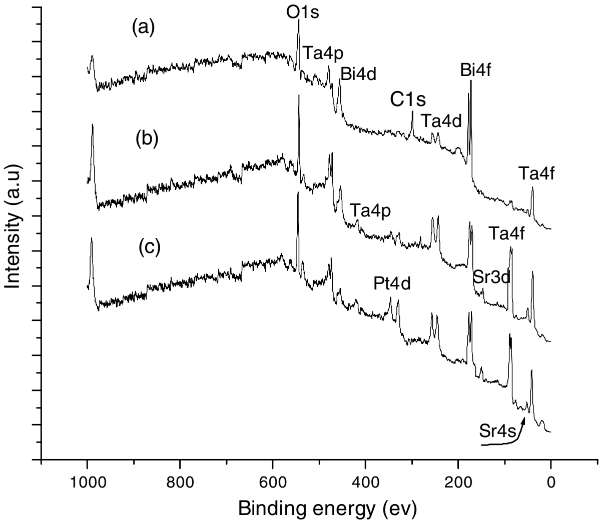

Figure 5 XPS spectra for SBT film deposited in ST/B/ST/B... order: (a) without bombardment, (b) bombarded by Ar^+ for 10 min, and (c) for 20 min.

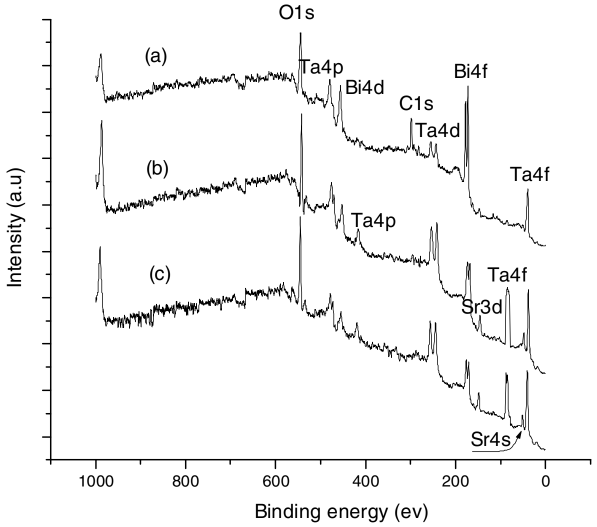

Figure 6 XPS spectra for SBT film deposited in B/ST/B/ST... order: (a) without bombardment, (b) bombarded by Ar^+ for 10 min, and (c) for 20 min.

SBT phase was observed in the XRD pattern (figure not shown). This may be explained using the various symmetries of Bi_2O_3 phase crystallized at high temperature. Bi_2O_3 has various symmetries such as monocline [9], cubic [10] and tetragonal [11], but none of these was the same as the SBT. In the conventional CSD fabrication of SBT film, high baking temperature was found leading to easy formation of Bi_2O_3 second phase and difficult crystallization of SBT phase [12].

Depth profiles of constituent elements in both SBT films were performed by X-ray photoelectron spectroscopy (XPS). Typical results are shown in Figs 5 and 6. The enrichment of bismuth, deficiency of oxygen and absorbed carbon were observed on the surfaces of both films. For the film deposited in ST/B/ST/B... order, platinum was detected when the film was bombarded for 20 min (Fig. 5). This corresponded to the XRD analysis of the same film (Fig. 1). However, no platinum was detected in the film deposited in B/ST/B/ST... order even though the film was bombarded for the same time. Therefore, deposition in B/ST/B/ST... order resulted in the suppression of the formation of Bi_2Pt second phase. Except for the surface, the peak areas of Ta, Sr, Bi and O elements became uniform in the both bulk films as a function of depth. It indicates that the diffusion reaction between Bi_2O_3 and $SrTa_2O_6$ layers was sufficient at a relatively lower temperature of 650 °C. The easy crystallization of SBT films grown with alternate deposition may be attributed to the ultra thin layers and hyperfine particles of Bi_2O_3 and $SrTa_2O_6$, which were formed by high-speed spin-coating and a very small volume of precursor solutions. Because of the relatively higher activity of the ultra thin layers and hyperfine particles, the crystallization of SBT phase was favored by the alternate deposition of Bi_2O_3 and $SrTa_2O_6$ layers.

In summary, SBT films were successively fabricated using the alternate deposition of Bi_2O_3 and $SrTa_2O_6$ layers. The films prepared in different deposition orders showed different microstructure and texture. Deposition in B/ST/B/ST... order brought about a lattice-matched $SrTa_2O_6$ layer for the SBT film growth; whereas deposition in ST/B/ST/B... order resulted in the formation of Bi_2Pt second phase besides a non-lattice-matched Bi_2O_3 layer. The different growth conditions caused by the different deposition orders were responsible for the different microstructure and texture. Alternate deposition of $SrTa_2O_6$ and Bi_2O_3 layer favored the crystallization of SBT phase because of the ultra thin layers and hyperfine particles, which were formed by high-speed spin-coating and a very small volume of precursor solutions.

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