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Citation: Appl. Phys. Lett. **74**, 2933 (1999); doi: 10.1063/1.123970
View online: http://dx.doi.org/10.1063/1.123970
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v74/i20
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APPLIED PHYSICS LETTERS VOLUME 74, NUMBER 20 17 MAY 1999

Elliptical grain growth in the solid-phase crystallization of amorphous $SrBi_2Ta_2O_9$ thin films

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(Received 4 January 1999; accepted for publication 19 March 1999)

During the crystallization process of amorphous $SrBi_2Ta_2O_9$ (SBT) thin films at 800 °C in a dry O_2 ambient, we have found elliptical nuclei in the initial nucleation state. These elliptical grains are preferentially oriented to [110] direction in the $[1\bar{1}0]$ direction of projection. Elliptical grain growth keeps [110] as increasing the annealing time at 800 °C. Transmission electron microscopy and selected-area electron diffraction pattern indicate that the origin of $\langle 110 \rangle$-oriented crystallization is due to the highest ionic packing (001) SBT plane which includes TaO_6 octahedra and the nearest bonding direction of TaO_6 octahedra in SBT plane is the $\langle 110 \rangle$ direction. © *1999 American Institute of Physics.* [S0003-6951(99)00320-4]

$SrBi_2Ta_2O_9$ (SBT) thin films have received great attention because Pt/SBT/Pt capacitor shows excellent fatigue resistance for over 10^{12} cycle and has long retention and very low leakage current density.[1,2] Particularly, using SBT thin film as a gate material in the metal/ferroelectric/semiconductor field effect transistor nonvoltaile ferroelectric random access memory devices has been developed.[2–4] The SBT thin films have been mainly prepared by sol-gel,[5] metal organic decomposition (MOD),[6] and metal organic chemical vapor deposition.[7] Then, the MOD method is known to be a simple and excellent method to control the composition of the SBT film precisely.

However, there is no report regarding the origin of crystallization process of the amorphous SBT film provided by the MOD method although the electrical properties of the SBT films have been intensively investigated.[1–7] The understanding of crystallization behavior of ferroelectric SBT film is very useful for preparing epitaxial growth or solid-phase crystallization of the SBT films because we can predict the inherent crystallization direction during the deposition or annealing process. Therefore, in this work we have prepared the amorphous SBT film by the MOD method and studied the nucleation and grain growth phenomena in the amorphous SBT thin films during the annealing process by a transmission electron microscopy (TEM).

For the deposition of the SBT films on Si substrate, we used a 0.1 mol SBT solution diluted by butylacetate. After preparing the SBT thin film on Si by MOD method, we annealed these thin films at 400 °C for 5 min in ambient atmosphere. The thickness of SBT film is about 500 Å. To study the crystallization process, we annealed again these samples at 800 °C for 5, 15, 30, and 60 min, respectively. TEM and selected-area electron diffraction (SAD) pattern have been employed to characterize the preferential orientation of SBT grains. Plan-view TEM specimens were prepared by mechanical polishing and the argon ion milling at liquid-nitrogen temperature. The crystal structure of the annealed SBT thin films was determined by x-ray diffraction method and the preferential orientation and microstructure were analyzed by high-resolution transmission electron microscopy (HRTEM) (JEOL 2000EX) that was operated at 200 kV.

Figure 1(a) is a bright-field TEM image observed in the [001] projection which shows a grain in the SBT thin film annealed at 800 °C in a dry O_2 ambient for 5 min. The grain is well distinguished from the surrounding contrast. The grain has a circular shape and the grain size is about 160 nm. The circular grain is surrounded with very fine grains and amorphous matrix. Sizes of fine grains are smaller than 30 nm. A SAD pattern obtained near the grain in Fig. 1(a) by inserting a field-limiting aperture of which diameter is about 300 nm. In the diffraction pattern, spots A, B, and C, indicated by arrows are diffracted from the SBT lattice planes (200), (020), and (220), respectively. These lattice planes have the zone axis of the [001] direction, meaning that the grain in Fig. 1(a) orients in the [001] direction. The ring

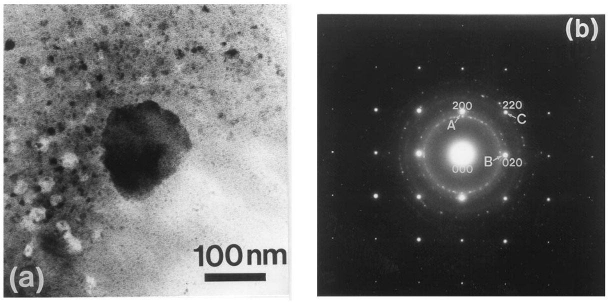

FIG. 1. (a) Bright-field TEM image in the [001] projection showing a circular grain in the SBT film annealed at 800 °C in a dry O_2 ambient for 5 min and (b) a selected-area electron diffraction pattern of which zone axis is [001].

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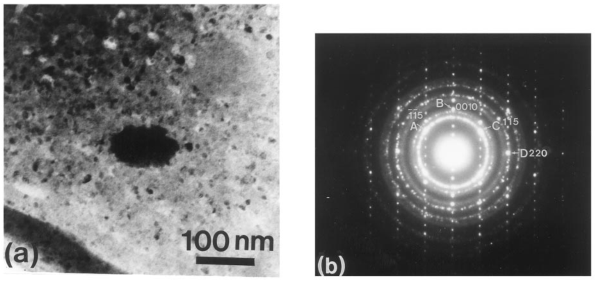

FIG. 2. (a) Bright-field TEM image in the $[1\bar{1}0]$ projection showing an elliptical grain in the SBT film annealed at 800 °C in a dry O_2 ambient for 5 min and (b) a selected-area electron diffraction pattern of which zone axis is $[1\bar{1}0]$.

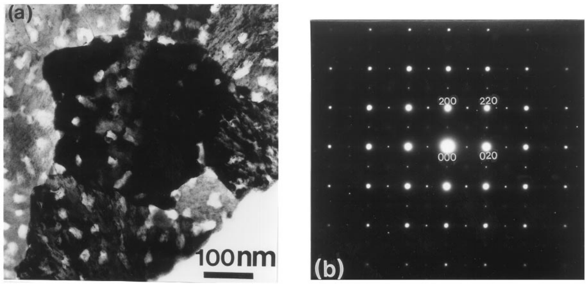

FIG. 3. (a) Bright-field TEM image in the [001] projection showing a circular grain in the SBT film annealed at 800 °C in a dry O_2 ambient for 60 min and (b) a selected-area electron diffraction pattern of which zone axis is [001].

pattern in Fig. 1(b) clearly reveals that the SBT film is still in amorphous or microcrystalline phase. Comparing this diffraction pattern with the shape of the grain in Fig. 1(a) shows no preferential orientation of SBT grain through the [001] projection since the lattice constants a, b, and c equals to 5.5306, 5.5344, and 24.9839 Å, respectively, which reveals that there is little difference between a and b in electron diffraction pattern. This means that the lattice structure is approximately tetragonal although the SBT film normally has orthorhombic lattice structure. Figure 2(a) is another bright-field TEM image in the $[1\bar{1}0]$ projection, showing a different shaped grain. Figure 2(b) is a SAD pattern obtained near the grain in Fig. 2(a). The grain size is about 130 nm along a long axis, and 70 nm along a short axis. The size of the long axis is 1.9 times that of the short axis, forming the elliptical-shape grain. The size of smaller grains surrounding the elliptical grain is about 30 nm. In Fig. 2(b), spots A, B, C, and D are diffracted from the SBT lattice planes $(\overline{11}5)$, (0010), (115), and (220), respectively. These lattice planes have the zone axis of the $[1\bar{1}0]$ direction. It means that the elliptical grain is preferentially oriented along the [110] direction. In the diffraction pattern the spots in [001] direction lie very closely, meaning that since the c axis lattice constant is extremely greater than those of a and b axis, the diffraction spots in the reciprocal lattice space appear very closely in contrast to those of the real lattice space. From Figs. 1 and 2, the circular grain in the [001] projection indicates that there is no preferential direction for the grain growth during the annealing process at 800 °C. However, in the $[1\bar{1}0]$ projection that is perpendicular to [001], the elliptical grain growth along the $\langle 110\rangle$ direction suggests that the $\langle 110\rangle$ is preferential direction.

To determine the preferential grain growth direction during the continuing annealing time from 5 to 60 min at 800 °C the samples are analyzed by TEM. Figure 3(a) is a bright-field TEM image of the SBT thin film annealed for 60 min. The size of the circular grain increases to about 360–430 nm and the circular shape is slightly distorted, but it remains in circular shape. Figure 3(b) is the SAD pattern obtained near the grain in Fig. 3(a). The pattern is diffracted by the planes of zone axis of [001], which is identical with the pattern of Fig. 1(b). Figures 3(a) and 3(b) show that there is no preferential orientation in the [001] projection since the large grain has an equivalent length along both directions of $[1\bar{1}0]$ and [100] although the length to the $[1\bar{1}0]$ direction is slightly longer than the length of [100] direction. However, when we observe the same sample in the $[1\bar{1}0]$ projection elliptically grain growth is clearly shown in Fig. 4(a). The length of the [110] axis is about 580 nm and the short length of the [001] axis is about 170 nm. The long axis is 3.4 times the short axis, meaning the elliptical-shape grain to be greater than that of Fig. 2(a). Figure 4(b) is the corresponding SAD pattern obtained near the grain in Fig. 4(a). This pattern is diffracted by the planes of zone axis $[1\bar{1}0]$. Figures 4(a) and 4(b) clearly indicate that [110] is the preferential direction since the grain growth toward the [110] direction increases from 1.6 to 3.4 times of the growth along the [001] as increasing the anealing time from 5 to 60 min.

Figure 5(a) shows the ionic arrangements of (110) plane of SBT crystal through $[1\bar{1}0]$ projection, depicting the perovskite-unit and the bismuth oxide layers. This ionic arrangement shows that cation Sr is located at the center of the

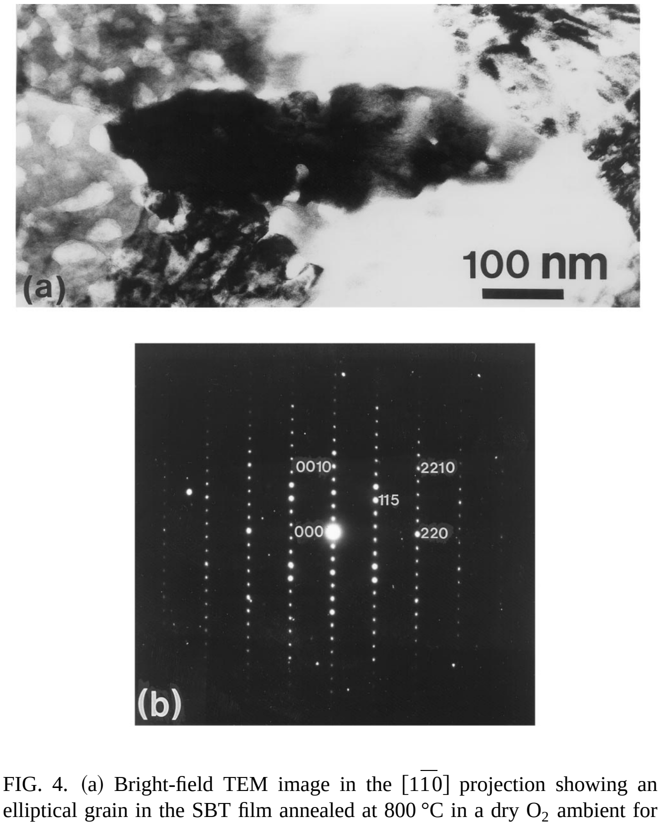

FIG. 4. (a) Bright-field TEM image in the $[1\bar{1}0]$ projection showing an elliptical grain in the SBT film annealed at 800 °C in a dry O_2 ambient for 60 min and (b) a selected-area electron diffraction pattern of which zone axis is $[1\bar{1}0]$.

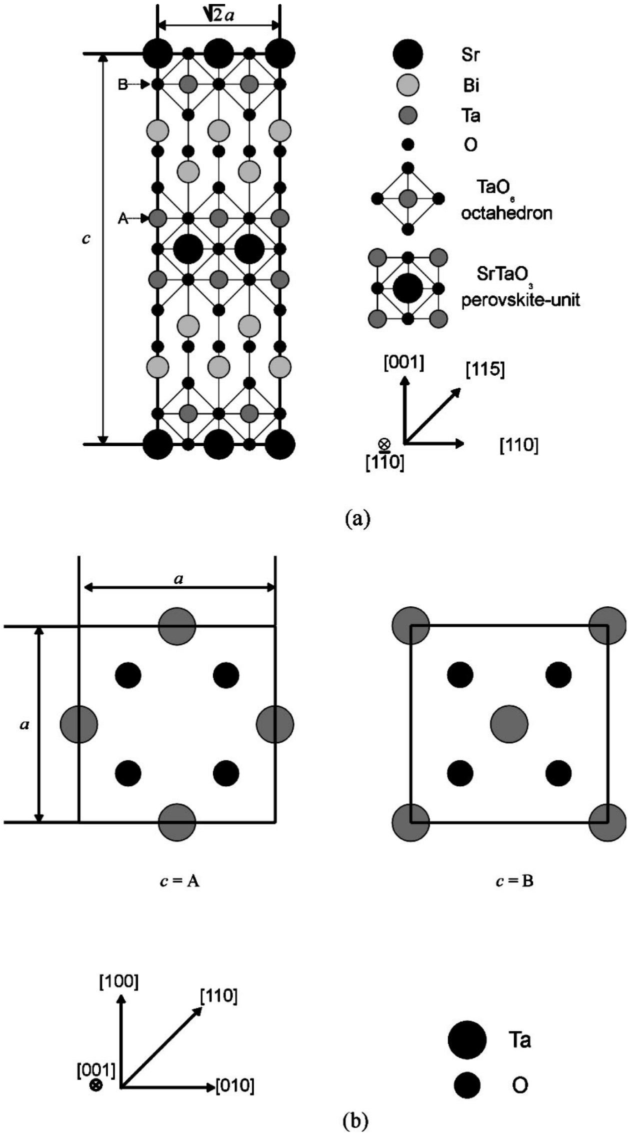

FIG. 5. (a) A schematic ionic arrangement of (110) plane of SBT crystal structure in the $[1\bar{1}0]$ projection depicting the perovskite-unit and the bismuth oxide layers and (b) the highest ionic packing (001) planes with a height of c axis, A=0.5783 and B=0.9217.

perovskite-unit and the TaO_6 octahedra are connected with each other in the same manner of the perovskite type. These perovskite-unit layers are alternated by Bi_2O_2 layers. For the (001) planes, A and B planes in Fig. 5(a) have different heights, $c=0.5783$ and 0.9217, respectively. Then, these A and B planes have the maximum number of ions per unit area and no other plane has more numbers of ions per unit area than these planes. This means that the interfacial energy of these planes is the lowest among those of $\{hkl\}$ planes. Therefore, the highest ionic packing planes are (001) planes and their heights are 0.5783 and 0.9217. The grain growth is determined by packing of these planes. Figure 5(b) shows the highest ionic packing planes, the SBT (001) planes with heights, $c=\text{A}$ (0.5783) and $c=\text{B}$ (0.9217). These planes have four oxygen ions and two Ta ions, totally 6 ions per unit area a^2 and have a center of TaO_6 octahedra in $SrTaO_3$ perovskite structure. In the highest ionic packing plane of (001) plane, the shortest bonding direction is Ta-O bonding in $SrTaO_3$ perovskite-unit, which is the $\langle 110\rangle$ direction of SBT crystal. Therefore, bonding to the $\langle 110\rangle$ direction is easier than the bonding on any other direction. Therefore the shape of grain is elliptical along the [110] direction observed in $[1\bar{1}0]$ the projection. The four-family of $\langle 110\rangle$ direction is isotropic in Fig. 5(a), which results in the circular shaped grain in [001] direction.

In this work, TEM study of the solid-phase crystallization of amorphous $SrBi_2Ta_2O_9$ (SBT) thin films after annealing at 800 °C in a dry O_2 ambient reveals the origin of the elliptical SBT grain growth. The ionic arrangement for the (110) plane of SBT suggests that the highest ionic packing planes are the (001) planes and their heights of c axis are 0.5783 and 0.9217. In this highest ionic packing planes the interfacial energy is the lowest among the other (001) planes and the nearest direction of Ta-O bonding is the $\langle 110\rangle$ direction. Therefore, it is concluded that the amorphous SBT films can be grown keeping the $\langle 110\rangle$ direction preferentially and it would be expected to be useful for epitaxial growth of SBT thin films providing the $\langle 110\rangle$-oriented substrate.

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