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Control of Crystallographic Orientation in Ferroelectric $Bi_{3.15}La_{0.85}Ti_3O_{12}$ Thin Films by Rapid Thermal Annealing

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Ferroelectric $Bi_{3.15}La_{0.85}Ti_3O_{12}$ (BLT) thin films were fabricated on $SiO_2/Si_3N_4/SiO_2$ substrates by a sol-gel spin coating method. The orientations of the BLT thin films were controlled by an intermediate rapid thermal annealing (RTA) process. The BLT thin films prepared using the RTA process at $<$400°C showed the (117) preferred orientation, while films preannealed at $\geqslant$450°C showed a stronger (006) peak than a (117) peak. A nearly perfect *c* axis orientation was obtained by RTA at $>$500°C and a subsequent furnace annealing at 700°C. It was found that 400 Å thin BLT films with one layer coating were partially crystallized at even for a rapid thermal process temperature lower than 500°C. Transmission electron microscopy analysis indicated that *c* axis oriented nuclei were formed at 500°C RTA and these nuclei function as seeds in the growth of BLT films with an almost perfect *c* axis orientation during the final furnace annealing stage. The surface morphology of *c* axis oriented BLT thin films showed smooth and plate-like grains while rod-like shapes were observed in the (117) oriented films.
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Ferroelectric random access memory (FeRAM) with metal/ferroelectric/semiconductor field-effect transistor (MFSFET) structures have the advantages of saving electrical power and decreasing memory cell size and this type of memory utilizes the remanent polarization of a ferroelectric thin film to control the surface potential of a silicon substrate. MFSFETs may be operated in the form of a nondestructive readout (NDRO) scheme. However, this structure has not yet been demonstrated due to difficulties in forming reliable ferroelectric thin films directly on a silicon surface. Elements in the film may diffuse into silicon,[1] forming an uncontrollable oxide layer, thus degrading the interface characteristics. To solve these problems, a metal/ferroelectric/insulator/semiconductor field-effect transistor (MFISFET) structure has been proposed and has been studied extensively. The most commonly used insulators (interdielectric layers) for the study are silicon nitride, Y_2O_3, CeO_2, and ZrO_2.[2-6] Recently lanthanum-substituted bismuth titanate (BLT) thin films have attracted considerable attraction for use in switching polarization parts in MFIS structures due to their low process temperature and good ferroelectric properties.[7,8] However, like $Bi_4Ti_3O_{12}$ (BT), BLT has intrinsic anisotropic ferroelectric properties, which produce two major components of spontaneous polarization.[9] Therefore, the crystallographic orientations of BLT thin films have been of great concern in terms of controlling the polarization characteristics for each application. BLT thin films are strongly dependent on crystallographic orientation in terms of process conditions and substrate materials. Recent reports have pointed out the importance of annealing conditions. Kijima *et al.* reported that BLT tends to have a (00*l*) preferred orientation if it is preannealed below 400°C and a random orientation if preannealed $>$500°C in Pt/BLT/Si_3N_4/Si structure.[10] Yang *et al.* reported that random oriented BLT films could be obtained by rapid thermal annealing (RTA) at 500°C, but *c* axis oriented films were formed at a higher temperature, 600°C, in Pt/BLT/Pt.[11] However, a clear explanation for the dependency of crystallographic orientation in BLT thin films is not available. In this report, we demonstrate the orientational conversion of BLT films in relation to the intermediate rapid thermal annealing process and the microstructural properties of *c* axis oriented BLT films are also investigated.

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$Bi_{3.465}La_{0.85}Ti_3O_{12}$ thin films were spin-coated on a $SiO_2/Si_3N_4/SiO_2/Si$ substrate using an alkoxide-carboxylate precursor solution. The chemical solution was prepared with 10% excess bismuth in $Bi_{3.15}La_{0.85}Ti_3O_{12}$ and the final molar concentration was 0.06 M. The precursor solution was filtered through 0.2 μm syringe filters and then spin-deposited on $SiO_2/Si_3N_4/SiO_2$ (ONO) coated silicon substrates at 2000 rpm for 30 s. After deposition, the films were placed on a hot plate (at ~200°C) in air for 5 min to remove solvents and other organic materials. The resulting films were then preannealed by RTA at 400-550°C for 1 min. These steps were repeated and the final film thickness was set at 120 nm with a three-layer coating. Postdeposition annealing of the films was carried out in a furnace from 650 to 800°C for 30 min under an oxygen environment.

The surface morphologies and roughness were determined by scanning electron microscopy (SEM, Akashi DS-130C) and atomic force microscopy (AFM). The crystal structures were examined by high-resolution transmission electron microscopy (HRTEM, Philips, CM20T/STEM). The diffraction patterns were recorded on a Regaku X-ray diffractometer using Cu Kα radiation (30 keV) at a scanning speed of 2° (2θ)/min.

Figure 1 shows X-ray diffraction (XRD) patterns for the BLT thin films as function of RTA process temperatures. Postdeposition annealing of the films was carried out at 700°C for 30 min in an oxygen atmosphere. As shown in Fig. 1, films annealed at 700°C exhibited a well-crystallized phase and there no secondary phases were observed. However, the crystallographic orientations of the BLT films varied drastically over the 400-500°C RTA temperature range. Regardless of the RTA process, shown in Fig. 1a and b, BLT films exhibited a (117) preferred orientation if they were processed at temperatures under 400°C. Whereas, BLT films preannealed at 450°C using the RTA process showed a stronger (006) peak than a (117) peak which has the strongest intensity in the XRD pattern of BLT powder. As the RTA temperatures were increased (Fig. 1d and e), almost perfectly *c* axis-oriented BLT thin films were obtained at RTA temperatures $\geqslant$500°C. Concerning the XRD data, it is clear that the conversion of crystallographic orientation is caused by the crystallization process of BLT film itself during the RTA process. However, at this time, the exact mechanism of crystallographic orientation conversion in this RTA process temperature range is not clear.

To investigate the cause of orientation change by different RTA

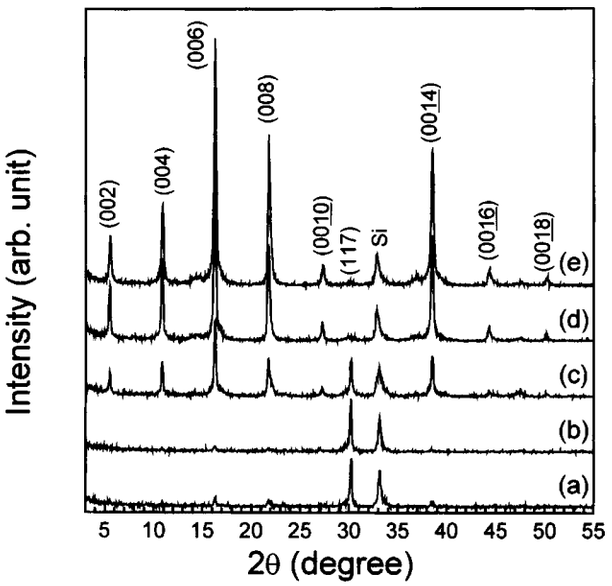

Figure 1. XRD patterns of BLT thin films as a function of RTA process temperatures: (a) no RTA, (b) 400, (c) 450, (d) 500, and (e) 550°C. Postdeposition annealing was carried out at 700°C for 30 min in an oxygen atmosphere.

temperatures, BLT thin films were prepared with one layer of coating. The thickness of these samples was about 40 nm. XRD patterns of one-layer coated BLT thin films with different RTA temperatures are displayed in Fig. 2. BLT films exhibited largely a *c* axis-oriented configuration with a strong (008) peak at rapid thermal process (RTP) temperatures >500°C. Thin BLT films were partially crystallized even at 500°C RTA. Through close examination of each peak some unknown peaks were also observed. These peaks are considered to be due to a pyrochlore phase. At an RTP temperature >500°C, BLT thin films exhibited a *c* axis orientation, but films prepared at <450°C have a random orientation with a strong (117) peak after postdeposition annealing at 700°C. The amorphous BLT

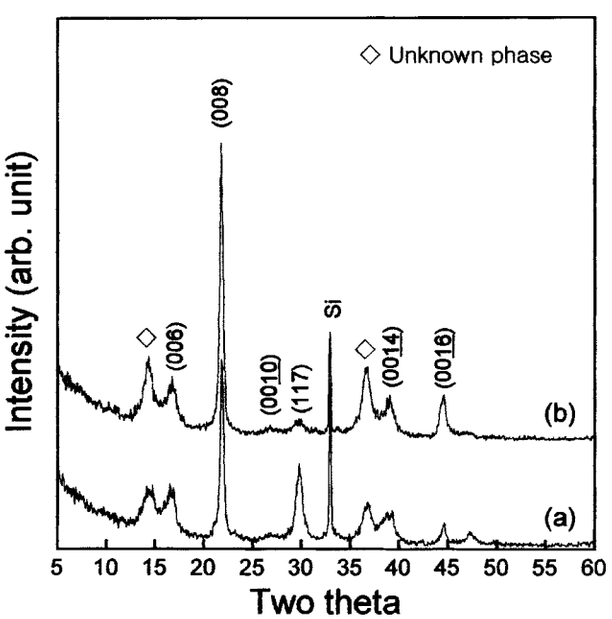

Figure 2. XRD patterns of BLT thin films with one layer at RTP temperatures of (a) 500 and (b) 550°C.

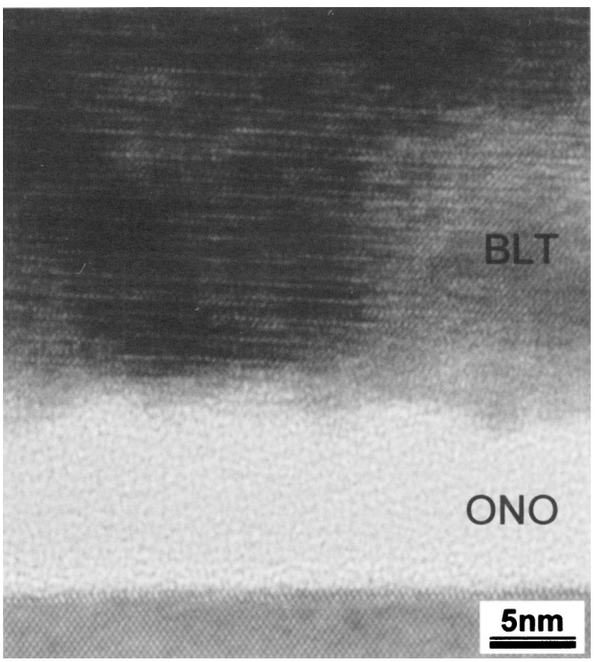

Figure 3. Cross-sectional high-resolution TEM image of BLT thin film with one layer under RTP process of 550°C.

films, after baking, form random oriented nuclei with a low activation energy under the low-temperature RTA process, and these films were crystallized, thus preserving random orientation during postdeposition annealing. However, with the high-temperature RTA process, partially crystallized BLT films with *c* axis-oriented nuclei were grown to be almost perfectly *c* axis-oriented BLT thin films during postdeposition annealing. Thus, we believe that the conditions of the first coating layer, *i.e.*, if it contains random or *c* axis-oriented nuclei, are decisive factors for high-density nucleation in subsequent layers. Furthermore, it has been reported that a *c* axis-oriented $Bi_4Ti_3O_{12}$ (BT) film can be obtained easily with a pyrochlore buffer layer. Nakamura *et al.* reported that BT films with a pyrochlore $Bi_2Ti_2O_7$ buffer layer showed a better *c* axis orientation than those prepared without a buffer layer.[12] Yamaguchi *et al.* also reported *c* axis-oriented BT films with a pyrochlore $Bi_2Ti_2O_7$ buffer layer.[13] BLT is believed to have a similar behavior, because a portion of the Bi atoms of BT are replaced with La. From these results it is clear that process conditions used for each layer coating and the initial stages of crystallization are determining factors in the crystallographic orientations of BLT thin film.

Figure 3 shows a HRTEM image of first coating BLT thin film layer after RTA processing at 550°C. The findings show that the ONO layer and BLT film are maintained as 10 and 40 nm thick layers, respectively. A flat interface was maintained between Si and ONO layers, but a thin reaction layer was found after RTP. The clear *c* axis lattice fringes of the BLT on the ONO film were observed over the large area of the TEM image. In addition, some regions where apparent amorphous and pyrochlore phases reside were locally observed, as expected from the orientation relationship shown in Fig. 2.

The morphological changes of BLT thin films on $SiO_2/Si_3N_4/SiO_2$ (ONO) substrates prepared using different RTA temperatures are shown in Fig. 4. BLT thin films annealed at 700°C by a sol-gel process show dense microstructures, especially when the RTA process is used for each layer of coatings. However, the surface images of the BLT films indicate a different morphology with increasing RTA temperatures. The BLT films without RTA processing have uniform grain sizes and the shape of each grain is

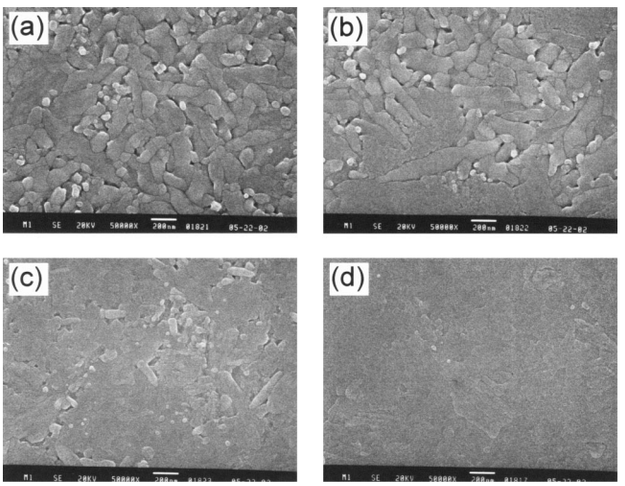

Figure 4. Morphological changes in BLT thin films on $SiO_2/Si_3N_4/SiO_2$ (ONO) substrates for different RTA temperatures: (a) no RTA, (b) 400, (c) 450, and (d) 500°C. Postdeposition annealing was carried out at 700°C for 30 min in an oxygen atmosphere.

somewhat rod-like compared to films prepared using the RTA process. The microstructures of films that were processed by RTA at >450°C exhibit a large plate-like grain morphology with smaller grains around it. As shown in Fig. 4d, the surface morphology of *c* axis-oriented BLT thin films with 550°C RTA process were observed to be perfect plate grain shape.

In summary, almost perfectly *c* axis-oriented $Bi_{3.465}La_{0.85}Ti_3O_{12}$ thin films were formed by spin coating sol-gel solutions on an ONO layer. The orientations of the BLT thin films can be controlled by intermediate rapid thermal annealing process. The *c* axis-oriented $Bi_{3.465}La_{0.85}Ti_3O_{12}$ thin films were obtained at RTA temperatures ⩾500°C. Under the high-temperature RTA process, partially *c* axis-oriented BLT films with *c* axis-oriented nuclei can be grown to be almost perfectly *c* axis-oriented BLT thin films after postdeposition annealing. The surface morphology of BLT thin films prepared at 550°C using the RTA process was observed to have a perfectly plate shaped grain. Thus, RTA conditions for the first coating layer play a major role in determining the overall crystallographic orientation of the films.

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