Transactions of the Materials Research Society of Japan 33[3] 615-618 (2008)

Formation of Preferred Orientation in $Bi_{4-x}La_xTi_3O_{12}$ Thin-Films on Si(100) During Crystallization

[1,2]Atsushi Kohno and [1]Takayuki Tajiri

[1] Department of Applied Physics, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan.
Fax: +81-92-871-6631, E-mail: kohno@fukuoka-u.ac.jp
[2] School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.
E-mail: kohno@seas.harvard.edu

La-substituted bismuth titanate (BLT) thin films formed directly on Si(100) substrates by using sol-gel methods have shown ferroelectric property and a preferred *c*-axis orientation depending on crystallization temperature. Since the spontaneous polarization and leakage current of BLT thin film strongly depend on the crystal orientation and it affects the electrical characteristics of the thin film memory devices, the investigation of orientation in the BLT film is important for the memory device development. X-ray diffraction analysis clearly showed the change in the *c*-axis orientation of the BLT film during the crystallization at 600 °C. The 00*l* diffraction from the crystal the *c*-axis of which was normal to the surface was slightly observed in the sample crystallized for 5 minutes at 600 °C, and the diffraction peak clearly appeared after 10 min and then the intensity decreased gradually. In contrast to this behavior, the in-plane *c*-axis orientation was clearly seen in the BLT crystallized only for 5 minutes and it was almost independent of the crystallization duration. The X-ray reflectivity analysis showed that the ~1 nm-thick interface layer was formed by 10 minutes at 600 °C. The in-plane *c*-axis orientation could be related to the crystal structure of silicon, and the formation of the preferred orientation might compete with the interface layer formation at the early stage of crystallization.
Key words: ferroelectric thin film, $Bi_{4-x}La_xTi_3O_{12}$ (BLT), preferred orientation, crystallization, formation of interface layer

1. INTRODUCTION

Transistor-type ferroelectric thin film memory has been attractive as a nonvolatile memory from the viewpoints of non-destructive read-out operation, device scaling capabilities, and high-density integration [1]. Electrical properties of ferroelectric thin film and ferroelectric/silicon interface seriously affect the operation of FET-type memory. Metal-ferroelectric-insulator-semiconductor (MFIS) structure has been investigated in order to make a high quality interface. On the other hand, it is attractive to deposit a ferroelectric thin film directly on a Si substrate because of the possibility of controlling the in-plane orientation of La-substituted bismuth titanate ($Bi_{4-x}La_xTi_3O_{12}$: BLT) thin film [2, 3], which is a good candidate for the ferroelectric memory due to fatigue-free and lead-free [4, 5]. The electrical properties of sub-100 nm-thick films on Si have been investigated for low-voltage memory operation and down-sizing of the FET. The Au/BLT/Si structures have shown good C-V hysteresis characteristics, and also the reduction of the interface states and fixed charges has been demonstrated by a post-annealing at 400 °C, resulting in the reduction of the oxygen vacancy [6].

The spontaneous polarization along *c*-axis is much smaller than that along *a*- and *b*- axes and also the leakage current of the BLT film is smallest along *c*-axis, and therefore the crystal orientation in the BLT thin film strongly affects the hysteresis characteristics of the MFS and also capacitor devices. Thus the investigation of the *c*-axis orientation in the BLT film is essential for the control of the device characteristics. In order to gain the insights of the crystal growth and orientation for the BLT thin films formed directly on silicon substrates by sol-gel solution coating method, in this research we have investigated the dependence of *c*-axis orientation of the BLT and the interfacial layer formation on the crystallization duration by X-ray diffraction (XRD) and X-ray reflectivity (XRR) analyses.

2. EXPERIMENTAL

Chemically cleaned p-type Si(100) wafers were treated with a diluted HF solution to obtain hydrogen terminated surfaces. Immediately after the treatment, a sol-gel precursor solution, which was produced by Kanto Chemical Co., Inc., was coated on the substrates. Simultaneously the solution-coated wafers were dried on a hot plate at 150 °C for 30 min. The films were crystallized in a furnace at 550 or 600 °C for 10 min- 2 hr. In the case of crystallization shorter than 10 min at 600 °C, the IR lamp furnace was used and the heating rate was controlled to be the same for all samples. X-ray diffraction and its pole figure measurement were carried out by using the laboratory X-ray diffractometer (X'Pert PRO system; PANalytical B.V.).

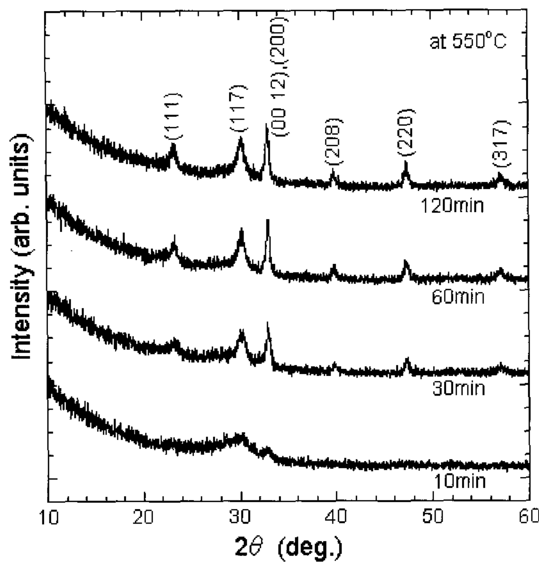

Fig. 1 X-ray diffraction profile from the BLT film as a function of crystallization duration at 550 °C.

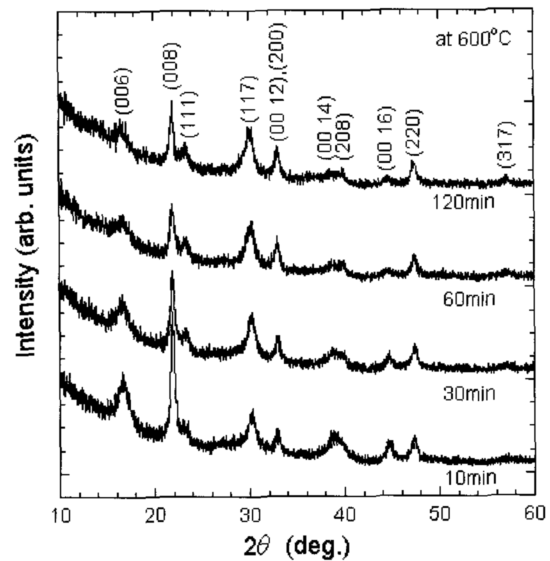

Fig. 2 X-ray diffraction profile from the BLT film as a function of crystallization duration at 600 °C.

3. RESULTS AND DISCUSSION

Since the difference in preferred orientation between the BLT thin films crystallized at 550 and 600 °C for 2hr had been confirmed [2], the time dependence of XRD pattern for the BLT films was measured at 550 and 600 °C. The XRD profiles as a function of crystallization duration are shown in Figs. 1 and 2. Here, XRD was measured as the scattering vector was fixed to the direction along the surface normal.

In the case of 550 °C the crystallization of the BLT film was observed after 30 min. The 00*l* diffraction peak, however, was not observed as shown in Fig. 1. This result means there are few crystal grains the *c*-axis of which is parallel to the surface normal. On the other hand, at 600 °C the BLT film was crystallized by 10 min and the intensity of 00*l* diffraction peaks decreased with time. Fig. 3 shows the change in the diffraction intensity during the crystallization at 600 °C. The 00*l* intensity decreased until 60 min and came to saturation, and the others tended to slight increase and saturation. These results indicate that the preferred *c*-axis orientation out of the plane might be related to the crystal grain growth.

Pole figure measurement was carried out in order to investigate the *c*-axis orientation. Fig. 4 shows the change in the intensity distribution of the 008 diffraction during crystallization at 600 °C for 5 - 60 min. The result for 120 min is not shown here because the main feature in the pole figure for 120 min was much the same as that for 60 min, though the intensity distribution might show a slight difference. As shown in Figs. 4(b)-(d), the change in the intensity around $\Psi = 0°$ (the normal to the surface) for the samples crystallized for longer than 10 min is the same as the results of Figs. 2 and 3. At 5 min the diffraction around $\Psi = 0°$ can be slightly seen in Fig. 4(a).

The broad intensity peak related to the in-plane orientation was observed even at 5 min, as shown Fig. 4.

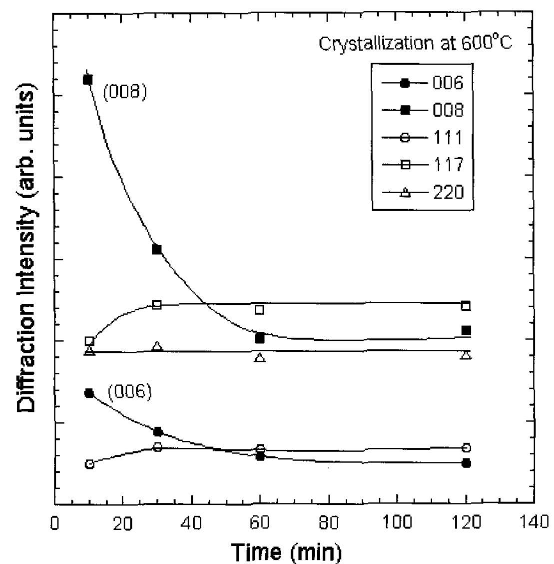

Fig. 3 The change in the diffraction intensity at 600 °C.

The distribution seems to be narrower with increase of the crystallization duration but it was not clear due to the weak intensity. The result indicates that the in-plane *c*-axis orientation was formed at an early stage of the crystallization, and hence the orientation must be related to the crystal structure of silicon and the nucleation might occur near the film/Si substrate. It is well known that the anisotropic grain growth occurs depending on the crystal orientation as secondary recrystallization [7, 8]. Therefore, the grain with in-plane *c*-axis orientation may have lower free energy and greater driving energy for the grain growth than the grains in other orientations.

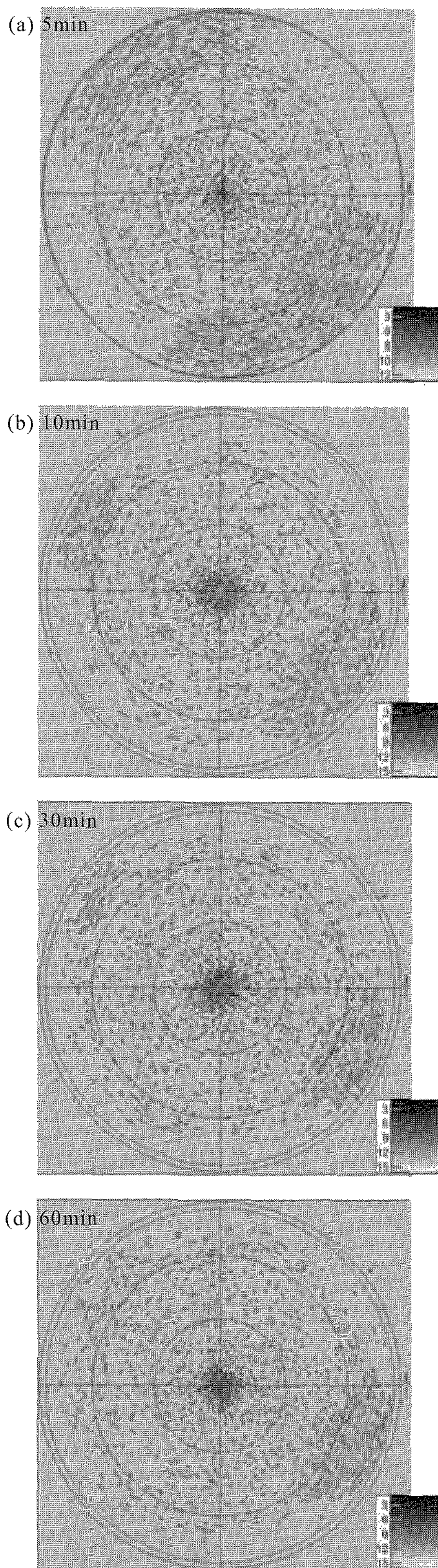

Fig. 4 The pole figures for the 008 diffraction of the BLT thin films crystallized at 600 °C for 5 min (a), 10 min (b), 30 min (c), and 60 min (d). In this measurement the 2θ was fixed at 21.9 °.

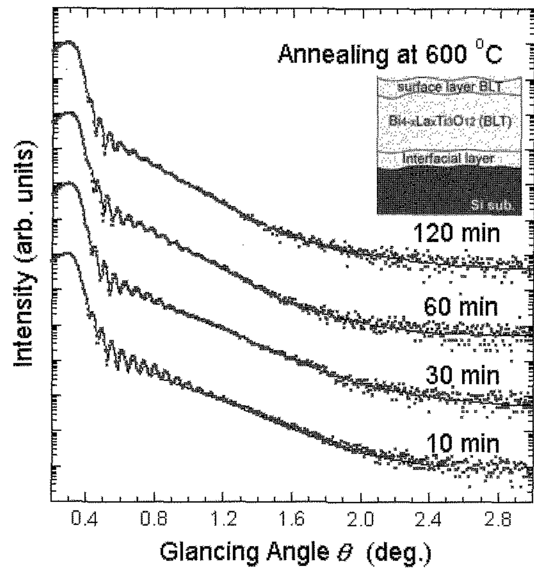

Fig. 5 X-ray reflectivity (XRR) curves from the BLT film/Si structures as a function of crystallization duration at 600 °C. The dots are for the measured and the line is for the simulated results.

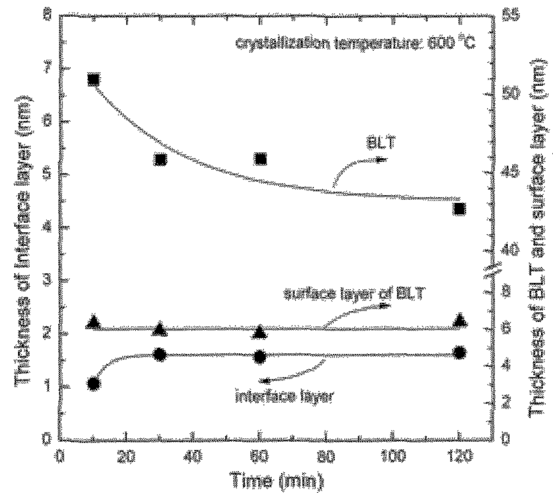

Fig. 6 The change in the thickness of the interfacial layer, BLT, and the surface layer of BLT during the crystallization at 600 °C. The thickness was determined by XRR method in Fig. 5. The symbols and lines show the XRR results and curves fitted by exponential function, respectively.

Furthermore, if the nucleation occurs preferentially near the interface, it is worth while investigating the interfacial layer formation from the viewpoint of nucleation and crystallization mechanism. The structure of BLT/Si samples was analyzed by XRR method. The change in XRR curve during the crystallization at 600 °C is shown in Fig. 5. The simulation fitting was carried out using the three layer

model shown in the inset of Fig. 5, and the best fit curves are also plotted in the figure. The oscillation amplitude was rapidly damped even at 10 min. This must be attributed to the increase of roughness due to the grain growth in the film.

The thicknesses of the BLT, interface layer, and surface layer of BLT as a function of crystallization duration are shown in Fig. 6. The BLT layer thickness decreased and tended to saturation with crystallization time. Since it was confirmed that the density of the BLT film increased with decrease of the thickness, this change suggests the densification of the BLT layer. The thickness of the surface layer didn't change significantly, though the detailed experiments are necessary for further discussion about the correlation between surface layer formation and film property. On the other hand, the thickness of the interface layer was increased until 30 min and then saturated. As the crystallization duration was 10 min the ~1 nm-thick interface layer had been already formed. The formation of the in-plane crystal orientation described above may compete with the formation of the interface layer at earlier time.

4. CONCLUSIONS

The ferroelectric BLT thin films have been successfully formed directly on Si(100) substrates by sol-gel and spin-coat techniques. The formation of the preferred *c*-axis orientation of the BLT thin film depended on the crystallization temperature. In the case of 600 °C, the diffraction from the crystal the *c*-axis of which was parallel to the surface normal increased rapidly and then decreased gradually. On the other hand, the in-plane *c*-axis orientation was observed in the BLT thin film crystallized only for 5 min at 600 °C. X-ray reflectivity analysis showed that the interface layer was formed until 10 min. The in-plane orientation in the BLT thin film must be related to the crystal structure of silicon. The formation of the preferred crystal orientation in the BLT might compete with the interface layer formation at the early stage of the crystallization.

Acknowledgements

The authors would like to thank Mr. H. Tomari and H. Ishitsu for all their helps at Fukuoka University, and also thank Dr. K. Sumitani and Dr. R. Haruki for their fruitful discussions. This work was supported in part by funds (No. 055004) from the Center Research Institute of Fukuoka University.

References

[1] H. Ishiwara, "Ferroelectric Film Devices" (Handbook of Thin Film Devices, vol. 5), ed. by D. J. Taylor, Academic Press, San Diego (2000) Chap. 3, pp. 79-88.

[2] T. Tajiri, K. Sumitani, R. Haruki, and A. Kohno, IEEE Trans. on Ultrasonic, Ferroelectrics, and Frequency Control, **54**, 2574-2578 (2007).

[3] A. Kohno, F. Ishitsu, K. Matuo and H. Tomari, Mater. Res. Soc. Symp. Proc., **784**, 497-502 (2004).

[4] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee and W. Jo, Nature, **401**, 682-684 (1999).

[5] U. Chon G. -C. Yi and H. M. Jang, Appl. Phys. Lett., **78**, 658-660 (2001).

[6] A. Kohno and H. Tomari, Mater. Res. Soc. Symp. Proc., **902E**, T03.45.1-6 (2006).

[7] J.E. Burke and D. Turnbull, "Recrystallization and grain growth," Progress in Metal Physics, Pergamon Press, London (1952), pp. 220-292.

[8] J. E. May and D. Turnbull, Trans. The Metall. Soc. AIME, **212**, 769-781 (1958).

(Recieved December 10, 2007 ; Accepted February 20, 2008)