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Crystallization of $SrBi_2Ta_2O_9$ Thin Films on Silicon Substrates and Their Interface Structures

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Crystallization of sol-gel derived $SrBi_2Ta_2O_9$ (SBT) thin films (thickness<100 nm) deposited on silicon substrates has been investigated by means of X-ray diffraction (XRD) and X-ray reflection (XRR). By the XRD measurements, at annealing temperatures below 700 °C the crystallization from amorphous to a fluorite-type structure (space group: *Fm3m*) was confirmed, but a Bi-layered Aurivillius phase (space group: $A2_1am$) was not recognized even after annealing for 10 hours. As annealing temperature was higher than 730 °C, the crystal structure of the thin film was transformed from the fluorite structure into the Bi-layered structure with annealing time. By atomic force microscope observations it was confirmed that grain growth occurred simultaneously with the structural transformation. This is consistent with the change in the surface roughness evaluated from the XRR analysis. Furthermore, XRR analysis indicated that an interfacial layer was formed during the annealing process. The thickness of the layer increased with annealing time.
Key words: ferroelectric thin films, $SrBi_2Ta_2O_9$ (SBT), crystallization, interface structure

1. INTRODUCTION

In recent years, ferroelectric thin films have attracted much attention for non-volatile memory applications from the viewpoint of high-speed signal processing. Strontium bismuth tantalate ($SrBi_2Ta_2O_9$: SBT) is recognized as one of the materials which are promising candidates for the memory applications because of its excellent fatigue-free property [1]. SBT thin films have been fabricated by various methods, and their structural and electrical properties have been investigated [2-7]. Also, crystal structure and phase transitions of SBT bulk ceramic have been studied and discussed [8-10]. Crystal structure of the ferroelectric SBT is orthorhombic with a space group $A2_1am$ (Bi-layered Aurivillius phase: SBT phase) [11]. It is known that the crystal of the fluorite phase (space group: *Fm3m*) or the pyrochlore phase (space group: *Fd3m*) is easily grown in the SBT thin film. The mechanism of crystallization of SBT thin film has been reported [2,12,13] and the distinction method for these phases has been developed [14,15].

In the ferroelectric memories, ferroelectric thin films have been used as a dielectric material of the storage capacitor or as a gate-insulator of the field-effect transistor (FET). A metal-ferroelectric-semiconductor (MFS) FET-type memory is recognized to have advantages compared with the storage capacitor-type memory because of the non-destructive read-out and device scaling capabilities. It is essential for the development of the MFSFET-type memory to get the insights of the crystallization mechanism, the structural properties of the SBT thin film formed on the silicon substrate and also the ferroelectric/silicon interface properties which affects seriously on the FET characteristics.

In this paper, we describe the crystallization of sol-gel derived SBT thin films (thickness<100 nm) formed on silicon substrates investigated by means of X-ray diffraction (XRD), X-ray reflection (XRR) and atomic force microscopy (AFM). Furthermore, the interface structure and the formation of the interfacial layer are also discussed from the results of XRR analysis.

2. EXPERIMETNAL

P-type Si(100) wafers were treated in diluted HF solution for 60 s after a chemical cleaning. A sol-gel precursor solution produced by Kanto Chemical co., inc. was spin-coated on the Si substrates. The coated wafers were dried at 150 °C for 30 min on a hot-plate. Subsequently, the samples were annealed at temperatures of 500-900 °C in a furnace for 30 s-100 hrs.

X-ray diffraction and reflection measurements were carried out by means of the same diffractometer (Philips: X'Pert PRO system) with the Eulerian cradle and the graded multilayer mirror for thin film analysis. Incident

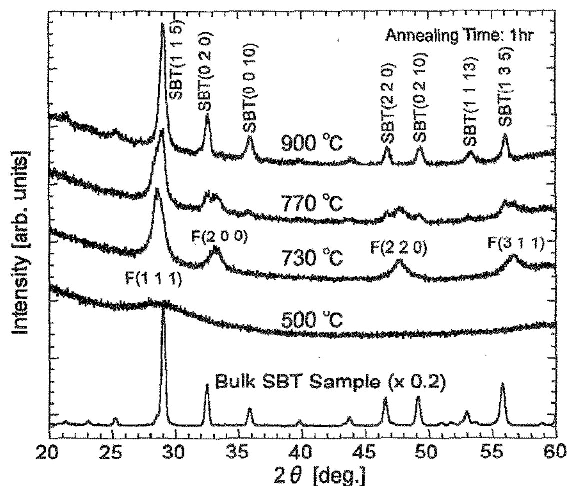

Fig. 1 Annealing temperature dependence of X-ray diffraction profile. The XRD profile for bulk SBT ceramic measured by the same diffractometer is also shown as a reference. The annealing time is 1 hour. SBT: a space group $A2_1am$. F: fluorite structure.

X-ray (CuKα) is converted from the divergent beam into a quasi-monochromatic and –parallel beam of high intensity by the mirror. A graphite monochromator was also attached before the detector. The slits before the sample and the detector were properly selected in each case of XRD or XRR measurement. In the case of XRD measurement the glancing angle of the incident beam from the surface is fixed at 5 degrees and the detector was scanned (2θ scan). Surface morphology was evaluated by AFM measurements and XRR analysis. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

X-ray diffraction profiles as a function of annealing temperature for the annealing time of 60 min are shown in Fig. 1. The profile of the bulk ceramic SBT was also shown in the figure as a reference. When the annealing temperature was 500 °C the thin film was not crystallized and solidified into amorphous phase. As the annealing temperature is higher than 730 °C the films are crystallized to the fluorite phase and/or the SBT ($A2_1am$) phase. It is found that for the higher annealing temperature the ratio of the SBT phase to the fluorite phase increases.

The annealing time dependence of XRD profile from the SBT thin film has been investigated as shown in Fig. 2. The annealing temperature was 750 °C. After 10 min annealing, only the fluorite phase was observed. The SBT phase was getting larger with time and only the SBT phase was finally observed after 5 hrs annealing.

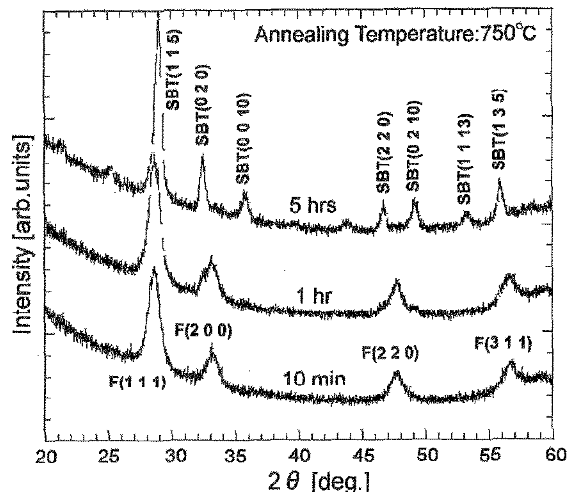

Fig. 2 Annealing time dependence of X-ray diffraction profile. The annealing temperature is 750 °C. SBT: a space group $A2_1am$. F: fluorite structure.

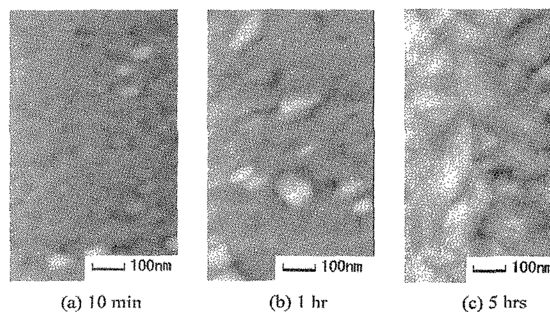

Fig. 3 AFM images of the SBT film surface after annealing for (a) 10 min, (b) 1 hour, (c) 5 hours. The annealing temperature is 750 °C.

As the annealing temperature is below 700 °C, the SBT phase was not observed even after 10 hrs annealing. Figure 3 shows the AFM images of the film surface. It is confirmed that the grains grew larger with annealing time. These results show that at first the film was crystallized from amorphous to the fluorite phase, and then the phase transformation from the fluorite to SBT phase occurs simultaneously with the grain growth.

The XRR spectra were measured as a function of annealing temperature as shown in Fig. 4. The intensity oscillation is caused by the interference between the X-rays reflected from the surface and the interface. From the period of the oscillation the film thickness is evaluated. The rate of decrease in the amplitude of the oscillation is related to the surface and interface roughness. It is found that with annealing time the film thickness was reduced and the surface roughness was increased. The simulation fitting of the XRR spectrum was carried out as shown in Fig. 5. The calculation

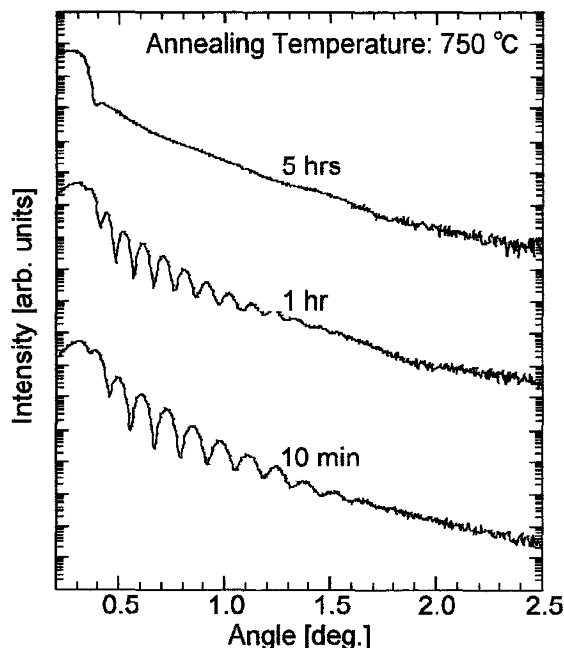

Fig. 4 Change in X-ray reflection spectrum with annealing time. The annealing temperature is 750 °C.

model was shown in the inset of Fig. 5. The changes in the surface roughness and the thickness of the interfacial layer evaluated by the fitting are shown in Fig. 6(a) and 6(b), respectively. The increase of the surface roughness qualitatively agrees with the change in the surface morphology observed by AFM (Fig. 3). The thickness of the interfacial layer rapidly increased with annealing time. The density of the interfacial layer was evaluated to be 2.1-2.5 g/cm^3. It seems that the formation of the interfacial layer is mainly owing to oxidation of the silicon.

4. CONCLUSIONS

Crystallization of sol-gel derived SBT thin films on silicon substrates has been investigated. At annealing temperatures below 700 °C the crystallization from amorphous to the fluorite phase was confirmed by the XRD measurements, but a Bi-layered Aurivillius phase (SBT phase) was not observed even after annealing for 10 hours. As the annealing temperature was higher than 730 °C, the crystal structure of the thin film was transformed from the fluorite phase into the SBT phase with annealing time. From atomic force microscope observations and XRR analysis it was confirmed that grain growth occurred simultaneously with the structural transformation. Furthermore, XRR analysis indicated that an interfacial layer was formed during the annealing

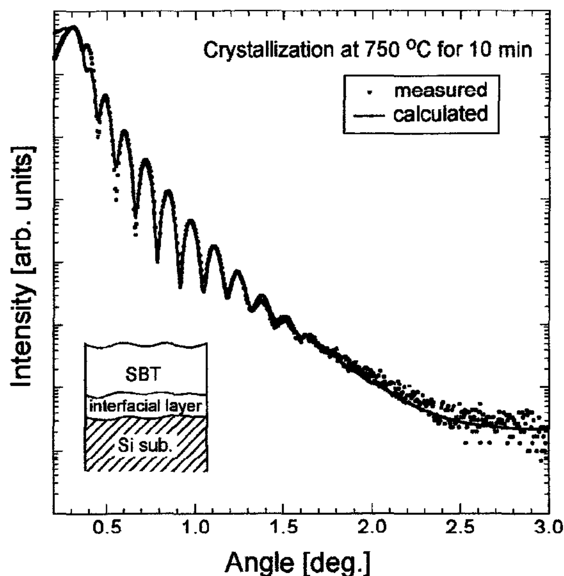

Fig. 5 Measured and calculated XRR spectra. The calculation model is also shown.

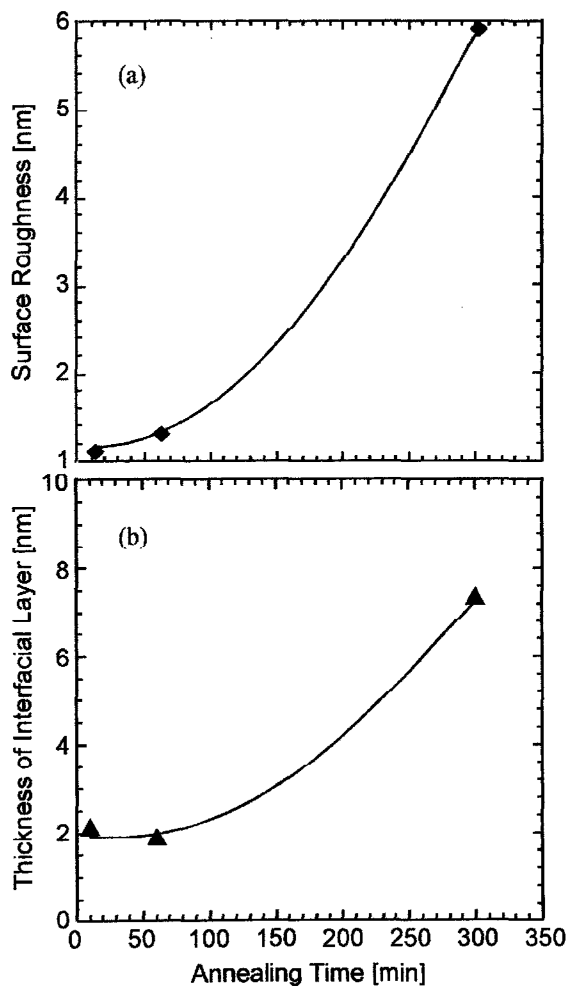

Fig. 6 Change in (a) surface roughness and (b) thickness of the interfacial layer with annealing time.

process and the thickness of the interfacial layer increased with annealing time.

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