Integration of Ferroelectric Ca$_2$Bi$_4$Ti$_5$O$_{18}$ Thin Films on Pt-Passivated Si via Spin-Coating Technique

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Ca$_2$Bi$_4$Ti$_5$O$_{18}$ (CBTi245) thin films were deposited by spin-coating a precursor solution of metal alkoxides on Pt-passivated Si substrates. Thickness of the as-deposited amorphous layer affected the nucleation site, microstructure and electrical properties. The onset of crystallization of thin films to a pyrochlore phase was below 550°C via rapid thermal annealing in oxygen. A perovskite phase developed by further annealing at temperatures of 650°C or higher. The CBTi245 thin films which were prepared by multi-coating and multi-crystallizing of the 20 nm-thick amorphous layer showed random orientation, a columnar-like structure, and P-E hysteresis loops.

Key-words : Ferroelectric thin film, Aurivillius compound, Alkoxide precursor, Spin-on deposition, Crystallization behavior, Microstructure, Ferroelectric property

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1. Introduction

Ca$_2$Bi$_4$Ti$_5$O$_{18}$ (CBTi245) is a member of the Aurivillius family, (Bi$_2$O$_3$)$_{2+X}$(An$_{2n+1}$B$_n$O$_{3n+2}$)$^2$-, in which A represents mono-, di-, trivalent ions or a mixture thereof, B represents tetra-, penta- or hexavalent ions, and n represents numbers of oxygen octahedron along c-axis in the perovskite layer. Bulk ceramics or single crystals of Pb$_2$Bi$_4$Ti$_5$O$_{18}$ (PBTi245), Ba$_2$Bi$_4$Ti$_5$O$_{18}$ (BBTi245) and Sr$_2$Bi$_4$Ti$_5$O$_{18}$ (SBTi245), which have an the n value of 5 and have the same structure as CBTi245, have been studied for their dielectric and ferroelectric properties. Also, thin films of these three compounds were synthesized by the sol-gel and pulsed laser deposition method, and were characterized for application to ferroelectric random access memories because of their high resistance to fatigue. Since these compounds have large anisotropic crystal structure, control of the electrical properties relating to the crystal structure is inevitable especially for the thin film form. Additionally, the potential for application to FeRAM is addressed.

2. Experimental

2.1 Integration of ferroelectric thin films

A precursor solution for CBTi245 thin films was prepared by the following method. Calcium metal was dissolved in ethanol (C$_2$H$_5$OH) by reaction at 78°C. Separately, bismuthtetriethoxide (Bi(OC$_2$H$_5$)$_3$) and titaniumtetraisopropoxide (Ti(Oi-C$_3$H$_7$)$_4$) in the molar ratio of 4:5 were dissolved together in methoxyethanol (CH$_3$OC$_2$H$_5$OH) at 124°C. The two solutions were mixed and then heated at 78°C for 2 h. Next, deionized water, diluted in CH$_3$OC$_2$H$_5$OH was added to the mixture solution in the molar ratio of 1:36 (H$_2$O:alkoxy group). The solution was stirred at room temperature for 1 h after hydrolysis. The concentration of the hydrolyzed alkoxide solution was 0.01 M. The volume ratio of C$_2$H$_5$OH to CH$_3$OC$_2$H$_5$OH was about 1:4. The atomic ratio of calcium, bismuth and titanium was stoichiometric 2:4:5. Pt-passivated silicon (Pt(111)/TiO$_x$/SiO$_2$/Si(100)) was used as the substrate material. CBTi245 thin films were deposited on the substrate by spin coating the hydrolyzed alkoxide solution. Each layer was deposited at 2 steps of 1000 rpm for 3 s and 3000 rpm for 30 s. The layer was dried at 150°C and then calcined at 350°C for 10 min in air. Thickness of the as-deposited amorphous layer followed by crystallization was increased to be about 20 or 40 nm by repeating the spin coating and calcining. Then, the amorphous thin layers crystallized by rapid thermal annealing in an oxygen flow. The ramp rate was 100°C/s and the heating period at desired temperatures was 10 or 20 min. Thickness of the crystalline thin film increased by stacking the thin crystalline layers, which were prepared by repeating the spin coating, calcining and rapid thermal annealing. Net heating period and full thickness...
were adjusted to be constant at 80 min and about 160 nm, respectively.

2.2 Characterization

The crystal phase and crystallinity of the thin films were identified by X-ray diffraction (XRD) measurements using Cu Kα radiation. The acceleration voltage and current were 40 kV and 40 mA, respectively. Microstructure and surface morphology of the thin films were observed using a transmission electron microscopy (TEM) and an atomic force microscopy (AFM). Film thickness was determined by an ellipsometer. Prior to electrical measurements, circular Pt electrodes of 500 μm diameter were deposited by r.f. sputtering followed by annealing at the same temperatures as crystallization or at 650°C when the crystallization temperature was higher than 650°C for 10 min in oxygen flow. Dielectric and ferroelectric properties were measured at room temperature using a multi-frequency impedance analyzer (HP 4275A) and a ferroelectric test system (Radiant Technologies, RT6000S) at room temperature, respectively.

3. Results and discussion

3.1 Crystallization behavior

Figures 1(a) and 1(b) show XRD profiles of 20 or 40 nm-layer stacked CBTi245 thin films with annealing temperature. The onset of crystallization of the thin films was below 550°C and independent of the thickness of as-deposited amorphous thin layer. The 550 and 600°C-annealed thin films were a pyrochlore phase. In comparison, the CBTi245 thin films annealed at 650°C or higher were mixtures of pyrochlore and perovskite phases. The perovskite phase developed and the pyrochlore phase diminished with annealing temperature. However, the 750°C-annealed thin film still contained a trace amount of the pyrochlore phase. Both the thin films showed random orientation. The crystallinity and relative intensities of each diffraction lines changed with the thickness of as-deposited amorphous thin layers. The intensities of all crystalline diffraction lines attributing to the thin films other than the substrate and the relative intensities of 00l diffraction lines to other diffraction lines were rather lower with respect to the 40nm-layer stacked CBTi245 thin films. Compared with the appearance, the higher relative intensities of 00l lines were obtained for the 20 nm-layer stacked CBTi245 thin films. The little higher degrees of the c-axis orientation may be stem from the effects of the crystallinity of the Pt bottom electrode and also the differences in the thermal expansion coefficients of the thin film and Si substrate. The lower relative intensities of 00l diffraction lines for the 40 nm-layer stacked CBTi245 thin films indicate the films are little affected the crystallinity of the Pt bottom electrode.

3.2 Surface morphology and cross section microstructure

Figures 2(a) and 2(b) show AFM images of surface topography of 20 and 40 nm-layer stacked CBTi245 thin films, respectively. The 20 nm-layer stacked and 600 or 650°C-annealed thin film consisted of uniform rectangular square-shaped grains. Some grains developed at temperature of 700 and 750°C, while the unique appearance remained. In contrast, the 40 nm-layer stacked thin films consisted of inhomogeneous grains, which had a broader size distribution. The remarkable difference in the surface morphology was found to relate to the crystallographic orientation as discussed above and may originate in the nucleation sites and growth mechanisms.

By a cross-sectional TEM photograph of the 20 nm-layer stacked and 750°C-annealed CBTi245 thin film (Fig. 3(a)), it was confirmed that it had a columnar-like structure, and neither void nor interface layer was present between the thin film and Pt layer. Each grain was closely packed in the thin film. In contrast, it was observed that several grains were stacked in the direction perpendicular to the film surface in the case of the 40 nm-layer stacked and 750°C-annealed CBTi245 thin film (Fig. 3(b)). The size and shape of the grains were not uniform, and some voids seem to exist between the grains or in the interface region although no interface layer was observed. The results indicate that the nucleation site depended on the thickness of the as-deposit-
ed amorphous layer followed by crystallization. The stacking of thinner layer such as the 20 nm-thick layer resulted in the preferable nucleation and growth at the surface of bottom crystalline layers, and thereby the columnar-like uniform grains formed. However, a number of random nucleation inevitably proceeded in the thicker layer such as the 40 nm-thick layer and resulted in the inhomogeneous microstructure. The critical thickness, which induces uncontrolled and random nucleation without influences of the bottom layer, may be in the range of 20 to 40 nm and be almost identical to the crystallite size. Electron diffraction patterns (Figs. 3(a) and (b)) indicated that the grains were CBTi245 perovskite phase and showed random orientation. Not all but only a few grains simultaneously showed a ring pattern. It clearly revealed that the grains contained a microcrystalline phase, which was identified as a trace amount of the pyrochlore phase. The microcrystalline pyrochlore phase seems to be included as small subgrains in the few grains.

3.3 Dielectric and ferroelectric properties

Figure 4 shows changes of the dielectric constant $\varepsilon$ and loss factor (tan $\delta$) of CBTi245 thin films at 100 kHz with annealing temperature. The $\varepsilon$ of the 20 nm-layer stacked thin films increased with annealing temperature and the increase became to be slight at temperatures higher than 650°C. The loss factor (tan $\delta$) did not change significantly. The $\varepsilon$ and tan $\delta$ of the thin films annealed at 650°C or higher were almost constant in the frequency range of 10 kHz to 1 MHz, and the values of the 650°C-annealed thin film were 330 and 0.028, respectively, at 100 kHz. In contrast, the $\varepsilon$ of the 40 nm-layer stacked thin films increased linearly with annealing temperature up to 700°C and was much lower than that of the 20 nm-layer stacked thin films. The $\varepsilon$ and tan $\delta$ of the 700°C-annealed thin film were 230 and 0.030, respectively, at 100 kHz. As the dielectric properties of the thin films depended on the crystallinity and microstructural development, the temperature dependence in wider range and lower $\varepsilon$ values for the 40 nm-layer stacked thin films was considered to strongly relate to slow enhancement of crystallinity and slow growth of grains. Thin film annealed at 600°C did not show ferroelectric hysteresis loop, while thin films annealed at 650°C or higher exhibited $P-E$ hysteresis loops. The shape and slope of the
loops depended on the annealing temperature and thickness of as-deposited thin layer. Figure 5 shows comparisons of hysteresis loops of 750°C-annealed CBTi245 thin films at 8 V. The expanded and sloped loop obtained for the 40 nm-layer stacked CBTi245 thin film is due to the lower crystallinity, lower dielectric constant and lower electrical resistance. The characteristics strongly related to the microstructure. The 20 nm-layer stacked thin film showed better hysteresis properties. The remanent polarization ($P_r$) and coercive electric field ($E_c$) of the 750°C-annealed thin films were 5.3 µC/cm² and 101 kV/cm, respectively, at 8 V.

The endurance behaviors of the thin films were preliminarily examined. The voltage and width of an applied bipolar pulse sequence were 6 V and $10^{-4}$ s, respectively. The frequency was 500 kHz. The polarization did not change after $10^{11}$ switching cycles with respect to the 20 nm-layer stacked and 650°C-annealed thin film, however, the polarization began to decrease after $7.2 \times 10^8$ switching cycles with respect to the 750°C-annealed thin film (Fig. 6(a)).12 The rather poor result of the 750°C-annealed thin film may be due to grain boundaries as electrically leak paths. Although the 40 nm-layer stacked and 650°C-annealed thin films exhibited a marginal behavior, the 700 and 750°C-annealed thin films had rather poor behaviors. The poor behavior for the 40 nm-layer stacked thin films is considered to relate to the properties of interface layer between the stacked grains. The charge may be easy to trap in the depletion layer at surface of the stacked grains and thereby the domains must be pinned.

4. Conclusions

Novel CBTi245 thin films were prepared on Pt-passivated Si substrates by using the precursor solution of complex metal alkoxides. The thickness of as-deposited amorphous layer affected the nucleation site, cross-sectional microstructure and electrical properties. The layered-perovskite phase developed in the temperature range of 650°C to 750°C via rapid thermal annealing in oxygen. The thin films pre-
pared by multi-coating and multi-crystallizing of 20 nm-thick amorphous layer showed random orientation, well-developed columnar-like structure, and better $P-E$ hysteresis properties. The thin films exhibited the minimal fatigue behaviors.

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References