Growth of $[\text{CaFeO}_x/\text{BiFeO}_3]$ superlattice by Pulsed Laser Deposition Method Using High Density Target Prepared by Pechini Method

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Superlattice composed of alternative growth of 7 units CaFeO_x (CFO) and 5 units BiFeO_3 (BFO) for 14 times was grown on 7 units grown LaFeO_3 (LFO) / $\text{SrTiO}_3(001)$ substrate. The 7 units LFO was used as calibration layer for CFO/BFO superlattice because an intensity oscillation of a RHEED specular spot of LFO 135.4 units single layer maintained until the end of the growth, and the estimation thickness from initial RHEED oscillation period was consistent with the XRD result. Smooth surface and streaky RHEED pattern were observed in the superlattice. From the result of 2θ -XRD, we can clearly see the satellite peaks from -4 to +4, indicating the superstructure with smooth interface. Superstructure unit was calculated at 4.750 nm with an average lattice parameter of 0.3848 nm. Those values were consistent with the result of low angle x-ray reflection with the error less than 0.45%. The initial deposited LFO film thickness was 2.817 nm (7.10 units). Superstructure unit was composed of 2.564 nm (6.942 units) of CFO and 2.165 nm (5.319 units) of BFO, and totally 4.729 nm.

Key words: LaFeO_3 , CaFeO_x , BiFeO_3 , Superlattice, PLD, multiferroic

1. INTRODUCTION

As well known in the SrTiO_3 (STO) / LaAlO_3 (LAO) multilayer when LAO is deposited on TiO_2 terminated STO substrate, n-type conduction at the interface is induced[1-3]. At a low temperature, a superconductivity appeared and ferromagnetic ordering is indicated as well. In the STO perovskite structure, SrO , TiO_2 charge neutral layers are stacking sequentially, while in the LAO pseudo perovskite structure, positive charge state of LaO and negative charge state of AlO_2 layers are stacked. One of the reasons why the n-type conduction appears is net transfer of electron through the interface to reduce the electric potential caused by the polar / non-polar interface, polar discontinuity[4-7].

We expect an induced ferromagnetic ordering near the interface in the CaFeO_3 (CFO) / BiFeO_3 (BFO) superlattices. In this superlattice the iron atom was substituted for Al in LAO and Ti in STO multilayer. The Fe^{3+} has five electrons in 3d orbital showing the largest spin values. Since the magnetic ordering of BFO is antiferromagnetic, the induced ferromagnetic ordering is expected due to the electron transfer. When the electron transfers, we expect that the superexchange interaction between iron ions in BFO changes from antiferromagnetic to ferromagnetic according to the Kanomori-Goodenough rule[8,9]. In this research, single layer growth of LFO, CFO, and BFO was demonstrated, and CFO/BFO superlattice was synthesized.

2. EXPERIMENTAL

The STO(100) substrates were ultrasonically cleaned

in acetone and ethanol. The cleaned substrate was soaked in pure water for 30 min in ultrasonic bath. The substrate surface was etched by a commercial BHF (Daikin Industries, Ltd., pH=5.0) for 45 sec, immediately rinsed by pure water. The etched substrate was annealed at 920°C for 6 h in air.

All films were deposited by PLD method using KrF excimer laser with high-pressure RHEED equipment. Used targets were pretty-high-dense LaFeO_3 (LFO) (95.48%) and CFO (96.38%) prepared by using Pechini powder, see ref. [10]. BFO target was calcined by conventional solid state reaction method. All targets were finally calcined at Toshima MFG. Co. Ltd. The typical deposition conditions are described as follows. A heater temperature, energy density, spot size at a target, repetition rate, oxygen partial pressure, and the distance between substrate and target were 670°C, 2.56J/cm², 1.91 mm², 4Hz, 0.20 mbar, 50 mm, respectively. In order to obtain accurately controlled CFO/BFO superlattice in each thickness, the growth rate of the LFO film was referred by depositing initial seven LFO layer. The CFO/BFO superlattice was deposited on seven LFO layers / STO substrate.

3. RESULTS & DISCUSSION

3.1 Lanthanum iron oxide film

Figure 1 shows intensity oscillation of a specular spot generated by RHEED (left vertical axis) and growth rate (right vertical axis) calculated from the oscillation peak interval. The RHEED oscillation was maintained until the end of growth. The average growth rate was

0.0671 unit/sec, the standard deviation of which was 3.98%. We estimate growth time to obtain 133 units from the period of initial 10 oscillations. After all the grown film thickness, fitted XRD result at low angle oscillation, was 135.4 units. The difference D , defined as eq.(1), was only 1.8%.

$$D = \frac{u_{\text{result}} - u_{\text{estimation}}}{u_{\text{estimation}}} \times 100 \quad (\%) \quad (1)$$

We have confidence in using LFO film growth as a calibration layer for CFO/BFO superlattice due to the observation of the clear RHEED oscillation and consistent number of thickness between estimation and result. The surface of the LFO film showed a step-terrace structure with almost same step height to that of STO substrate. From those results, the LFO film epitaxially grew with layer-by-layer manner.

Figure 1, RHEED intensity and growth rate are described as a function of time. An appearance of the RHEED oscillation revealed a layer-by-layer growth. The growth rate was quite stable during growth.

3.2 Calcium iron oxides film

Figure 2 shows the XRD spectra of CFO film with an inset figure at low angle oscillation. The open circles were come from the STO substrate. The CFO indices were assigned assuming the CFO was pseudo-perovskite structure. Bragg diffractions of CFO(00 n) ($n=1\sim4$) were clearly observed, in addition, extra peaks, indicated by open triangle, were also observed at the intermediate position between CFO(00 n) peaks, indicating the double periodicity. The peaks were expected to be caused by the growth of $\text{Ca}_2\text{Fe}_2\text{O}_5$. The result of the RHEED oscillation was correspondent to the double periodicity by detecting transfer from a layer-by-layer growth to a so-called two-layers-by-two-layers growth after three or four monolayers were deposited. Therefore initial three of four CFO layers were expected to be CaFeO_3 following the $\text{Ca}_2\text{Fe}_2\text{O}_5$ growth. Details were discussed in our previous report, see ref. [11]. From the result of the low angle oscillation, the grown CFO thickness was fitted to be 127.6 units, the difference D of which was only 0.48%. Estimation thickness was 127 units from the initial RHEED oscillation period. The accurate control of growth rate was achieved as well. The RHEED oscillation can be seen until 31 units grew. The full width at half maximum (FWHM) of a rocking

curve was 0.11° for CFO(002), indicating the fine crystallinity. The surface did not show the step-terraces structure, but quite smooth without any droplets and large particles.

Figure 3 shows scanning electron microscope (SEM) images of (a) LFO and (b) CFO targets after PLD deposition. The surface was quite smooth, by which constant growth rate was obtained as shown in Fig.1 and Fig.2.

Figure 2, XRD spectrum of CFO films with low angle diffraction in the inset. Open circles are the peaks of STO substrates. Bragg diffractions of CFO were observed with intermediate peaks indicated by open triangles because of $\text{Ca}_2\text{Fe}_2\text{O}_5$ growth. From the oscillation in the inset figure, the film thickness was calculated at 127.6 units.

Figure 3, The SEM images of (a) LFO and (b) CFO targets after deposition are illustrated. Quite flat surfaces were obtained, indicating the stable ablation during growth.

3.3 Bismuth iron oxides film

Figure 4 shows XRD result with the magnified image around BFO(001). The indices were assigned assuming that the grown BFO film was pseudo-perovskite structure. Laue oscillation was obviously seen around BFO(001). The FWHM of the rocking curve for BFO(001) was 0.077° , indicating the quite good crystallinity. In the same manner, the film thickness was estimated at 175.7 units from the initial RHEED oscillation period, however the result was 153.5 units (using total thickness of 62.48 nm and lattice constant of 0.40705 nm). The D value was as high as -13% probably due to a melting pillar structure of the BFO target, which were prepared by the SS method. The RHEED oscillation was gone after seven units growth. Since the structure of a bulk BFO is rhombohedral with 3.98% lattice mismatch to the STO substrate, it is difficult to obtain thick epitaxial BFO film.

Actually, there is a report, where the BFO film grows first as a tetragonal and following the monoclinic growth with boundary around 50 nm[12]. However, since the thickness of each BFO layer was approximately 5 units in the CFO/BFO superlattice, the film is expected to grow as tetragonal.

Figure 4, The XRD spectrum of BFO films with the inset figure around BFO(001). Laue oscillation was clearly observed. Open circles are from substrate.

3.4 Superlattice of CFO/ BFO

From the results of the LFO, CFO, and BFO single layer growth, we concluded that the estimation of the deposition rate from the RHEED oscillation of LFO is the best for accurate control of thickness of CFO and BFO layers when the CFO/BFO superlattice is prepared, because the RHEED oscillation of LFO (layer-by-layer growth was maintained until the end of growth, growth rate was quite constant, and LFO surface showed still step-terraces structure. The ratio of growth rate of LFO to CFO and BFO was investigated in advance for superlattice growth.

Figure 5 shows the RHEED oscillation and growth rate of initial seven units of LFO at repetition rate of 2Hz. The rate was calculated from the last stable three oscillations. In the case of CFO, and BFO the 248 and 189 pulses are required for seven unit and five unit growth, respectively.

Figure 5, The RHEED intensity (solid line) of a specular spot at initial seven LFO units growth. Period between neighboring peaks is an inverse of growth rate (open circle).

Figure 6 shows (a) surface morphology and (b) RHEED pattern after deposition of [7-units CFO / 5-units BFO]₁₄ / 7-units LFO on STO substrate. It was faint but step-terraces structure was observed at the surface of the superlattice with the step height of approximately 0.5 nm. The streaky RHEED pattern demonstrated two dimensional flat surface of the superlattice.

Figure 6, (a) Surface morphology and (b) RHEED pattern of [7units-CFO / 5-units BFO]₁₄ / 7-units LFO on STO substrate. The step-terraces structure was observed, but it was faint. Incident electron beam was along the STO[100] direction.

Figure 7 shows XRD spectrum of CFO/BFO superlattice. Open circle indicates substrate peaks. Satellite peaks were observed from -4 to +4, indicating the creation of superstructure with a smooth interface. In addition, Laue oscillation was also observed. Lattice parameter of [7units CFO / 5-units BFO] unit was estimated at 4.750 nm from the intervals of satellite peaks. The average lattice constant was 0.3848 nm calculated from the Bragg diffraction indicated by zero.

Figure 7, XRD 2θ-θ spectrum of the [7units-CFO / 5-units BFO]₁₄ / 7-units LFO. Appearance of Laue oscillation and satellite peaks indicate that the superstructure with smooth interface grew on the whole substrate.

Figure 8 shows low angle x-ray reflection to investigate the lattice parameter by fitting. The short (small intensity) and long (large intensity) period oscillations were caused by the film thickness and superstructure period, respectively. The initial deposited LFO film thickness was 2.817 nm, corresponding to the 7.10 units using the lattice parameter 0.39673 nm of LFO single layer film. Superstructure unit was composed of 2.564 nm of CFO

and 2.165 nm of BFO, and totally 4.729 nm was repeated for 14 times. The number of unit of CFO and BFO was calculated at 6.942 units and 5.319 units, respectively. The average lattice constant of this superlattice can be also calculated at 0.3856 nm using 0.36933 nm of CFO and 0.40705 nm of BFO. The calculated value of one unit superstructure length and average lattice constant by fitting the low angle x-ray reflection was -0.44 % and 0.23 % comparing with those of the results of XRD 2θ - θ spectrum.

Figure 8, Low angle x-ray reflection is shown to examine each thickness of LFO, CFO, and BFO. By fitting to low and high frequency oscillation, each films thickness was calculated at 2.817, 2.564, and 2.165 nm in initial LFO, CFO and BFO of superstructure.

4. CONCLUSION

We expect an induced ferromagnetic ordering near the interface in the CFO / BFO superlattices. When the electron transfers through the interface, the superexchange interaction between iron ions in BFO is expected to change from antiferromagnetic to ferromagnetic according to the Kanomori-Goodenough rule.

All films were grown by PLD method using KrF excimer laser with high-pressure RHEED equipment. Used targets were pretty-high-dense LFO (95.48%) and CFO (96.38%) prepared by using Pechini powder. BFO target was calcined by conventional solid state reaction method.

The estimation of the deposition rate from the RHEED oscillation of LFO is the best for accurate control of thickness of CFO and BFO layers when the CFO/BFO superlattice is prepared, because the RHEED oscillation of LFO (layer-by-layer growth was maintained until the end of 135.4 units growth, growth rate was quite constant, and LFO surface showed still step-terraces structure. The ratio of growth rate of LFO to CFO and BFO was investigated in advance for superlattice growth. In the case of CFO growth, the CaFeO_3 grew for initial 3 or 4 units and following $\text{Ca}_2\text{Fe}_2\text{O}_5$, demonstrated by the intermediate peaks of CFO pseudo-perovskite Bragg diffractions in the XRD and the transfer from layer-by-layer RHEED oscillation to the double periodicity oscillation, so-called two-layers-by-two-layers growth. Therefore initial

three of four CFO layers were expected to be CaFeO_3 . The difference between estimation thickness and calculation thickness of LFO, CFO and BFO from the results of low angle x-ray reflection was 1.8, 0.48, and -13% probably due to the target structure.

From the growth rate of initial 7 units LFO, required pulses of 7 units CFO and 5 units BFO was calculated at 248 and 189 pulses. In the 2θ - θ XRD result, satellite peaks were observed from -4 to +4, indicating the presence of superstructure with smooth interface. From the x-ray oscillation at low angle, lattice parameter of [7units CFO / 5-units BFO] unit composed of 2.564 nm of CFO and 2.165 nm of BFO, and totally 4.729 nm. The number of unit of CFO and BFO was calculated at 6.942 units and 5.319 units, respectively. The average lattice constant was 0.3856 nm.

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