Crystal Structure and Magnetic Properties of $CaMnO_3$ Thin Film and Related Superlattices

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Abstract : $CaMnO_3$ (CMO) thin film and [CMO (7 units)/ $BiFeMnO_3$ (BFMO) (7 units)]$_{14}$ superlattices were grown on Nb doped $SrTiO_3$ (NSTO) (100) substrates by pulsed laser deposition (PLD) method. Crystal structure was characterized by x-ray diffraction (XRD) method. Magnetic properties were measured by a physical property measurement system (PPMS, Quantum Design). The existence of the satellite peaks in XRD spectra confirmed the successful preparation of superlattices. Meanwhile, the calculated in-plain lattice parameters were slightly larger than that of the substrate, which indicated existence of lattice mismatch. According the M-H measurement data CMO has the residual magnetization only at the temperature as low as 10K, and the residual magnetization becomes lower when the temperature increases. However [CMO (7 units)/ BFMO (7 units)]$_{14}$ superlattices can remain the residual magnetization at 300K, which is higher than room temperature.

1. Introduction

As electric device developing in direction of miniaturization and multi-functional, much effort has been made in order to realize multi-functional materials which encapsulates properties of electricity, magnetism, light and heat together. Among them, multiferroic materials represented by magnetoelectric materials have been paid close attention by many researchers. But in single phase materials, the magnetoelectric couple is weak and Curie temperature is too low. So composite materials have become new hot spot among researchers. Multiferroic composite nano-films can be used to make miniature electronic devices, high-density information storage and so on.

It is widely reported that the remarkable properties can be achieved in the multilayers and superlattices using the magnetic interaction at the interface. The superlattices are composed of alternating stacks of $Ca_{2+}Mn_{4+}O_3^{6-}$ and $RE_{3+}M_{3+}O_3^{6-}$ (RE=Bi, La, M=Fe). Considering the electron transfer from M_{3+} ($3d^5$) for Fe^{3+} to Mn_{4+} ($3d^3$) similarly observed in the LAO/STO heterostructure, a ferromagnetic superexchange can be expected around the interface owing to the interaction of Fe^{3+} ($3d^5$)-O-Fe^{4+}/Mn^{3+} ($3d^4$).

2. Experimental

$CaMnO_3$ (CMO) thin film and [CMO (7 units)/BFMO (7 units)]$_{14}$ superlattices were grown on Nb doped $SrTiO_3$ (NSTO) (100) substrates. The NSTO (100) substrates were ultrasonic cleaned in acetone and ethanol. The cleaned substrates were soaked in pure water for 30min. The surfaces of substrates were etched by Buffered HF (BHF) (Daikin Industries, Ltd, pH=5.0) for 45 seconds, immediately rinsed by pure water. The etched NSTO (100) substrates were annealed at 920ºC for 6 h in air. All films were grown by the PLD method with excimer laser of KrF 248 nm. Typical ablation conditions were introduced in detail in references [1]. All films were post-annealed in oxygen atmosphere of 0.1 MPa and the temperature change rate was 10 ºC/min

3. Results and discussion

3.1 Crystal structure

3.1.1 CMO on NSTO (100)

Fig. 1 shows the reciprocal space mappings (RSMs) around (a) NSTO (002), (b) NSTO (103), and (c) NSTO (113). There was no change in the position and the intensity of the peaks in all RSM results when rotating the substrate along the ϕ direction. From the result of (a), both film peak and substrate peaks were observed, which indicated that the CMO thin film grew with the tilting angle of 0.15° from the substrate crystal plane. All peaks appeared in (b) and (c) as well. The crystal structure is expected to be orthorhombic from the results of RSM.

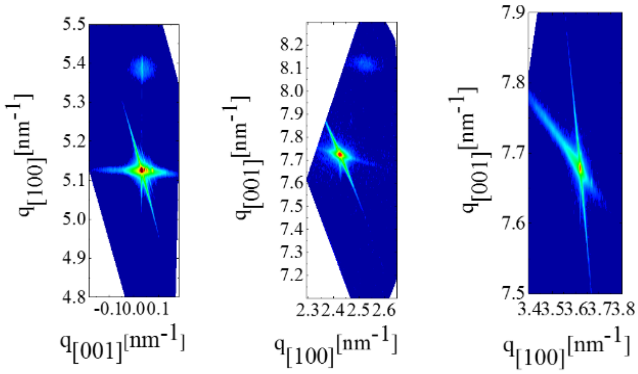

Fig. 1 RSMs results around (a) NSTO (002), (b) NSTO (103), and (c) NSTO (113).

According to the results of the RSM, we expect that the structure of CMO thin film was orthorhombic at an initial stage of the crystal growth due to the stress from mismatch between film and substrate.

3.1.2 [CMO/BFMO] on NSTO (100)

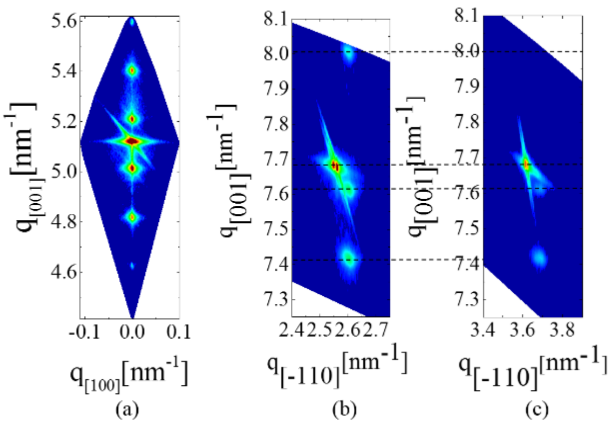

Fig. 2 RSMs results of [CMO/BFMO] superlattices around (a) NSTO (002), (b) NSTO (103) and (c).

Fig. 2 shows the RSMs results of [CMO/BFMO] superlattices around (a) NSTO (002), (b) NSTO (103) and (c) NSTO (113). It is clearly shown in (a) that satellite peaks exist which indicates the successful preparation of superlattices. Meanwhile the calculated in-plain lattice parameter was slightly larger than that of the substrate, which indicates lattice mismatch exists [CMO/BFMO] superlattices.

3.2 Magnetic properties

3.2.1 CMO on NSTO (100)

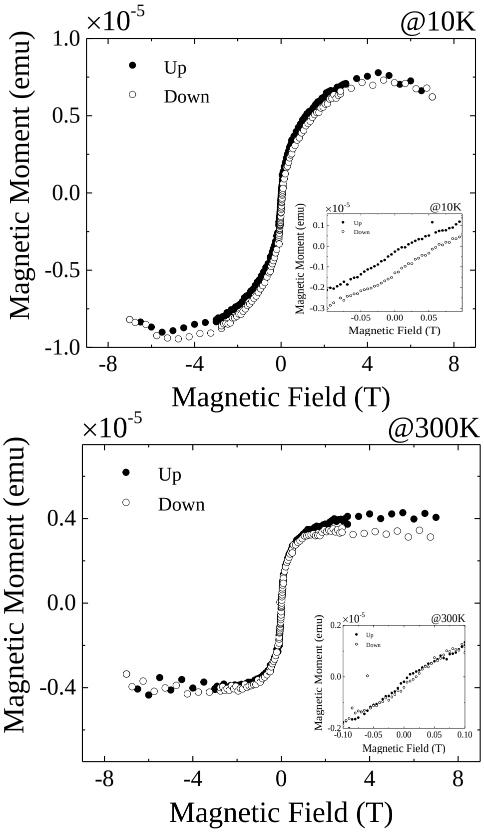

Fig. 3 M-H curves of CMO film.

The magnetic properties were also investigated. In ferromagnetic perovskite oxides, magnetic hysteresis (M-H) loop is expected to exist.

Fig. 3 shows M-H curves of CMO thin film at 10 K and 300 K temperature which were measured by a physical property measurement system (PPMS, Quantum Design). In this figure, solid dots mean the process of increasing magnetic field and hollow dots mean the process of reducing magnetic field.

It is clear that CMO thin film has the residual magnetization at 10 K temperature, but the residual magnetization becomes lower when the temperature increases.

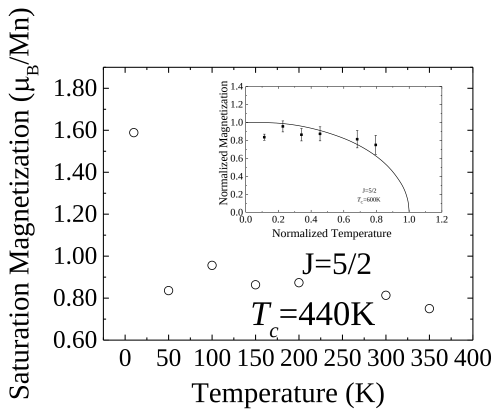

Fig. 4 M-T fitting curve of CMO thin film.

Fig. 4 presents the relationship of saturation magnetization and temperature of CMO thin film. The saturation magnetization at 10 K, 150 K and 300 K is 1.56×10^{-5}, 5.46×10^{-6}, 7.97×10^{-6} [emu], respectively. The saturation magnetization reduces while the temperature increases. And Curie temperature T_c is fitted to be about 440 K.

3.2.2 [CMO/BFMO] on NSTO (100)

Fig. 5 presents M-H curves of [CMO/BFMO] superlattices at 10K and 300K temperature. It is clear that [CMO/BFMO] superlattices can remain the residual magnetization at room temperature (300 K).

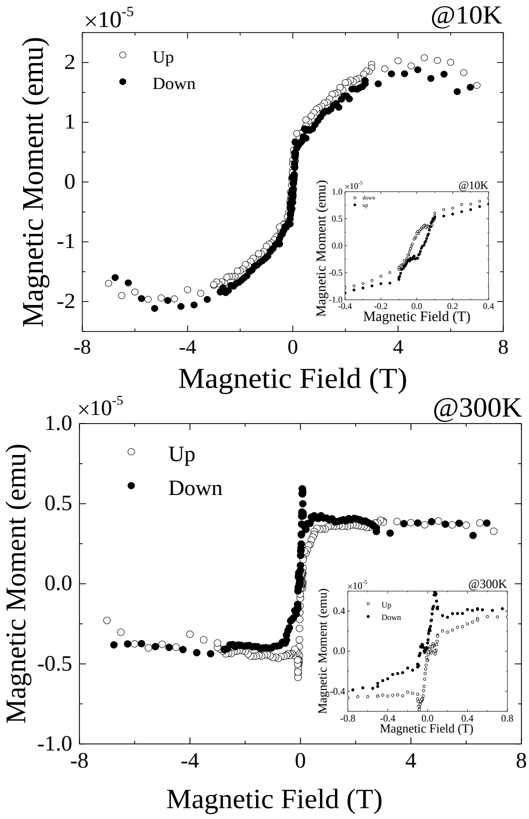

Fig. 5 M-H curve of [CMO/BFMO] superlattices

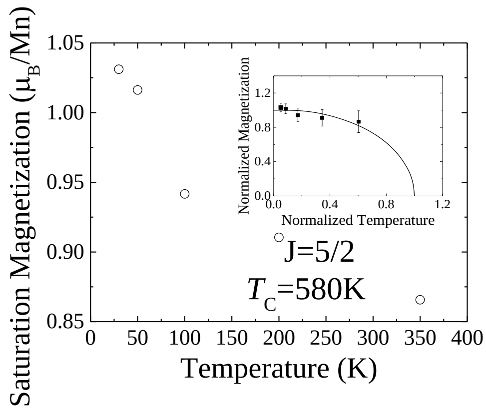

Fig. 6 M-T fitting curve of [CMO/BFMO] superlattices.

Fig. 6 presents the relationship of saturation magnetization and temperature of [CMO/BFMO] superlattices. The saturation magnetization at 10 K, 150 K and 300 K is 2.28×10^{-5}, 6.31×10^{-6}, 1.43×10^{-6} [emu], respectively. And Curie temperature T_c is fitted to be about 580 K.

4. Summary

The CMO thin film and [CMO/BFMO] superlattices were grown on NSTO (100) substrates using the PLD method. Represented by RSMs results, film peak and satellite peaks exist. This indicates the successful preparation of thin film and superlattices. Meanwhile, the calculated in-plain lattice parameters were slightly larger than that of the substrate, which indicates lattice mismatch exists. The magnetic properties showed that [CMO/BFMO] superlattices had a higher Curie temperature T_c (580 K) than that of CMO thin film (440 K).

5. Reference

[1] Y. Watabe, N. Iwata, T. Oikawa, T. Hashimoto, M. Huijben, G. Rijnders and H. Yamamoto, *Jpn. J. Appl. Phys*, 53, 05FB12 (2014).