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Electric and Magnetic Properties of $Ba(Co,Mn)O_{3-\delta}$ Epitaxial Thin Films

T. Inoue, T. Matsui, H. Tsuda, T. Yoshimura, N. Fujimura and K. Morii
Graduate School of Engineering, Osaka Prefecture University. 1-1 Gakuen-Cho, Sakai, Osaka 599-8531
Fax: 81-72-254-9912, e-mail: matsui@mtr.osakafu-u.ac.jp

The structural, magnetic and dielectric properties of single crystalline $Ba(Co_{1-x}Mn_x)O_{3-\delta}$ (x=0.2 and 0.7) films were investigated. The crystal structure of the films was revealed to be pseudo-cubic, while the bulk of the samples have hexagonal perovskite related crystal structures. The films were found to be highly resistive with a dielectric constant of ε=5.2 at 5 K. In contrast, the films exhibited semiconductor-like conduction behavior at room temperature. Room temperature ferromagnetic ordering can be realized in samples with a saturation magnetization of 1.20 μ_B/fu for the x=0.2 sample, in contrast to 1.41 μ_B/fu for the x=0.7 sample. A possible origin of the observed magnetic ordering may be due to the superexchange coupling of Mn^{4+} (d^3)-O^{2-}-Co^{4+} (d^5) ions with a bonding angle of 180 degrees.
Key words: magnetic and dielectric properties, superexchange coupling, epitaxial thin film, PLD

1. INTRODUCTION

Magnetoelectric materials that may possibly exhibit coupled electric, magnetic and structural order parameters in one substance have attracted considerable attention, due to their potential application to novel electronics devices. Perovskite (ABO_3) oxides have been considered one of the potential candidates for this type of material. Specifically, $BiFeO_3$, $BaFeO_3$, $BiMnO_3$ and $YMnO_3$ thin films have been intensively studied [1-6]. It was found that the many of these materials exhibit fairly good dielectric or ferroelectric properties. However, the magnetization of these materials was usually too small to consider the practical device application of these films. This is because their magnetic origin may be a weak ferromagnetism.

According to the Kanamori–Goodenough rule for superexchange magnetic coupling, the exchange interaction of (d^3)-O^{2-}-(d^5) with a bonding angle of 180 degrees should be ferromagnetic. Hence, it may be quite interesting to synthesize $AB_{1-x}B'_xO_3$ (B=$3d^5$ and B'=$3d^3$ transition metals) perovskite oxides from the viewpoint of magnetic ordering. Based on this idea, we have systematically investigated the magnetic and dielectric properties of $Ba(Co_{1-x}Mn_x)O_{3-\delta}$ (BCMO) bulk ceramics with perovskite-related crystal structures [7-9]. Presuming the charge neutrality of these materials, the Mn and Co ions in these compounds should have $3d^3$ and $3d^5$ electron configurations, respectively.

We revealed that the BCMO(x=0.15-0.25) sintered samples with 10H-type crystal structure exhibited a fairly large magnetization below 50 K. In addition, the electric resistivity of the samples abruptly increased below 50-80 K, and the samples behaved as good dielectric materials with a dielectric constant of ε=1.31. These results suggest that the BCMO (x=0.15-0.25) may be a possible candidate for potential ferromagnetic and dielectric materials. It was also found that the origin of the observed ferromagnetic ordering was supposed to be ascribed to the superexchange coupling of the Mn^{4+} (d^3)-O^{2-}-Co^{4+} (d^5) ions with a bonding angle of 180 degrees [7].

With this in consideration, it seems that it would be quite meaningful to obtain single crystalline BCMO films, not only due to their practical device application, but also due to the importance of clarifying the physical origin of their various properties. In this study, we attempted to synthesize epitaxial BCMO thin films on the (001) $SrTiO_3$ (STO) single crystal substrates through a PLD technique. This paper reports on the structural, magnetic and dielectric properties of the samples. The possible magnetic ordering is also discussed.

2. EXPERIMENTAL PROCEDURE

BCMO targets with x values from 0.2 to 0.7 were prepared from the desired amount of $BaCO_3$, Co_3O_4 and Mn_3O_4. The mixtures were calcinated at 1273K or at 1373K for 72 hr. The samples were then grounded again and pressed in a die of 15 mm in diameter. Finally, the compacts were sintered at the temperature ranging from 1373 K to 1473 K for 24 hr. to obtain the sintered targets, with fairly high relative density (>95%). The chemical composition of the targets was confirmed by an electron-probe micro-analyzer.

BCMO thin films with a thickness of 100 nm were fabricated by pulsed laser-beam deposition (PLD) on (001) STO single-crystal substrates. Nb-doped (001) STO substrates were also used for electrical measurement. The detailed deposition conditions are summarized in Table I. Structural characterization of the films was carried out by x-ray theta-2theta diffraction (XRD). Phi scans using the 4-circle XRD diffractometer for the (011) lattice planes were also performed in order to confirm the epitaxial growth of the films. A field-emission type scanning electron microscope (FE-SEM) was used to evaluate the morphology of the

Table I. Deposition condition employed.

Deposition Condition	Parameters Employed
Substrate Temperature	500~750 ℃
O_2 Gas Partial Pressure	2×10^{-6}~5×10^{-4} Torr
Laser Power (KrF)	250~300 mJ
Repetition Rate	1~10 Hz

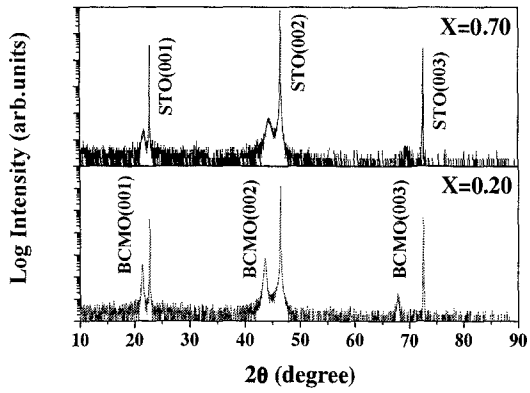

Fig. 1. XRD theta-2thata scans for the x=0.2 and 0.7 BCMO thin film samples.

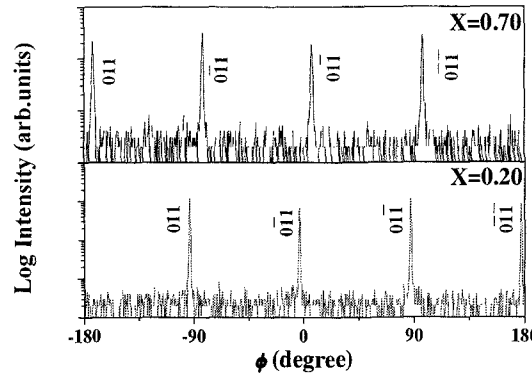

Fig. 2. XRD phi scan of the BCMO {011} reflection for the x=0.2 and 0.7 samples.

films. Magnetic properties were measured by using a superconducting quantum interference device (SQUID) over the temperature ranging from 5 to 300 K. Electrical measurements were conducted by using the configuration of Pt/BCMO/Nb-doped STO. Capacitance-Frequency (C-f) and loss-tangent were measured with an LCR meter. The temperature dependence of the resistivity of the samples was also evaluated using a four-probe technique.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization

We previously reported that $BaFeO_3$ with a hexagonal-type perovskite-related crystal structure in bulk form could grow epitaxially on (001) STO single-crystal substrates having pseudo-cubic crystal structures [10]. In that sense, we can expect that the epitaxially grown BCMO on (001) STO substrates may possibly have a pseudo-cubic perovskite-type crystal structure. The calculated lattice mismatch between the (001) STO and the pseudo-cubic BCMO(x=0.20) is 3.4%, which is a little greater than that of $BaFeO_3$ (2.7%). Based on this, we tried to grow epitaxial BCMO thin films on (001) STO substrates. If the BCMO films can grow epitaxially in cubic form, enhancement of the magnetization could be realized. This is because all the Co^{4+}-O^{2-}-Mn^{4+} bonding should have a bonding angle close to 180 degrees, which may lead to ferromagnetic superexchange coupling in accordance with the Kanamori-Goodenough rule.

We attempted to optimize the deposition parameters to obtain the epitaxial grown thin films with excellent crystallinity. Figure 1 shows the theta-2theta XRD diffraction scans for x=0.2 and 0.7 samples, which were deposited at the following optimized condition: substrate temperature of 700℃; oxygen gas partial pressure of $2x10^{-6}$ Torr; and repetition rate of 10 Hz. As Fig. 1 reveals, only diffraction peaks, which corresponded to the (00L) pseudo-cubic BMCO and STO, were observed in the scans. This simply means that the single-phase films of BCMO were successfully synthesized. Figure 2 shows the XRD phi scan for the {011} off-axis planes for BCMO in the x=0.2 and 0.7 samples. The {011} diffraction peaks of BCMO are found to appear every 90 degrees, which simply means the BCMO films were epitaxially grown having C_4 symmetry within the film plane. Since no long-range ordered diffraction peaks associated with hexagonal growth were found in any in-plane or out-of-plane theta-2theta diffraction scans, it is clear that the present BCMO samples grow epitaxially with the pseudo-cubic structure, just as is the case in BFO films. The epitaxial orientation relationship was determined to be (001)BCMO ∥ (001)STO, [100]BCMO ∥ [100]STO. Note that no superstructured XRD peaks suggesting the formation of a double perovskite structure by atomic ordering of the Co and Mn ions were observed in any theta-2theta scans. The out-of-plane lattice constantans were determined from the XRD scans to be 0.4136 and 0.4052nm for x=0.2 and 0.7 samples, respectively, while the in-plane lattice constants were 0.4043 and 0.4039 nm. This distortion may be due to the restraint of the substrates.

Figure 3 shows rocking curve diffractions for the (002) planes of the BCMO thin film samples for the x=0.2 and 0.7 samples. The FWHM for the x=0.2 sample was found to be the small value of 0.4692 degrees, which means that the crystallinity of the samples is fairly good. However, the samples with x values other than 0.2 and 0.7 did not show such a small value of FWHM. Hence, further studies are required to

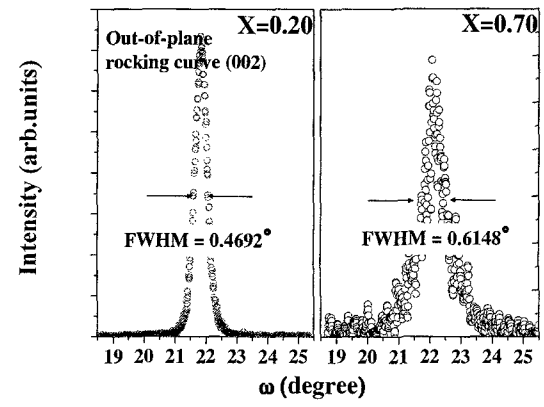

Fig. 3. Rocking curve diffractions for the (002) planes of the epitaxially grown BCMO (x=0.2 and 0.7) samples.

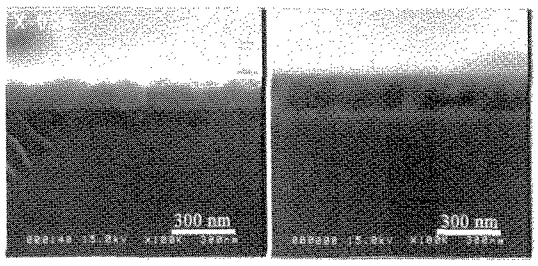

Fig. 4. Cross-sectional FE-SEM images for the epitaxially grown BCMO (x=0.2 and 0.7) thin films on (001) Nb-doped STO substrates.

know the optimized deposition condition for these samples. The FE-SEM cross-sectional images for the x=0.2 and 0.7 films are displayed in Fig. 4. The x=0.7 sample has a much flatter surface than the x=0.2 sample, in which many subgrains were found. It can be expected that the poor surface roughness for the Co-rich samples (x=0.2) may be ascribed to the relatively high vapor pressure of cobalt rather than manganese.

Consequently, single crystalline BCMO thin films with pseudo-cubic crystal structure were successfully fabricated for x=0.2 and 0.7 samples.

3.2 Dielectric Properties

Prior to discussing the dielectric properties of the thin film samples, it is necessary to recall the eclectic properties of the bulk BCMO samples. The bulk BCMO samples showed a semiconductor-like conduction behavior above 50-80 K, whereas the resistivity of the samples abruptly increased below that temperature. Thin film samples show a similar tendency, i.e., the x=0.2 and 0.7 films were revealed to be semiconductive at room temperature and to be dielectric at 5 K.

The results of the frequency dependence of the dielectric constant and dissipation factor for the samples are indicated in Fig. 5. The dielectric constant of about ε=5.2 and the relatively small dissipation factor of about 0.181 at 40 kHz was obtained for the x=0.7 sample.

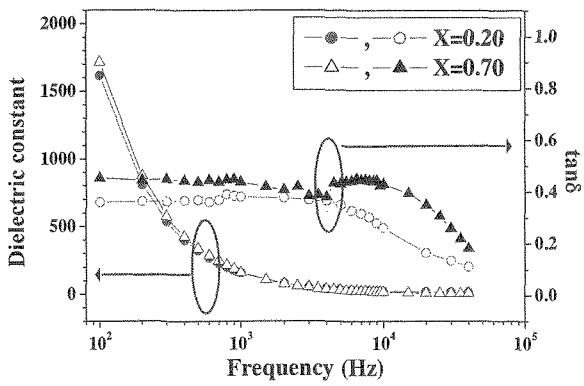

Fig. 5. Frequency dependence of dielectric constant and dissipation factor for the epitaxially grown BCMO (x=0.2 and 0.7) thin films on (001) Nb-doped STO substrates.

3.3 Magnetic Properties

Figure 6 shows the magnetization loops measured at 5 K and 300 K for the epitaxially grown BCMO thin film samples at x=0.2 and 0.7. We only indicate the portion of the spontaneous magnetization possibly due to the Co-O-Mn ferromagnetic ordering. As a result, the diamagnetic component as well as the paramagnetic component (if they exist) was neglected. As is obvious in the figure, the loops for both samples exhibit apparent hysteresis, as well as remanent magnetization even at 300 K. The saturation magnetization for the x=0.2 sample was determined to be 1.42 μ_B/fu at 5 K and 1.20 μ_B/fu at 300 K , in contrast to 1.53 μ_B/fu at 5 K and 1.41 μ_B/fu at 300 K for the x=0.7 sample. This means that the films are still ferromagnetic at around room temperature. This would be a great advantage of the BCMO epitaxial films in considering practical device application.

A possible origin of the observed magnetic ordering may be ascribed to the superexchange coupling of the Mn^{4+} (d^3)-O^{2-}-Co^{4+} (d^5) ions with a bonding angle of 180 degrees. The observed magnetization values for the x=0.2 samples were found to be considerably larger than bulk value. The difference in the crystal structures between the bulk and the film values may account for the difference. However, it is possible that magnetic inclusion may exist in the films. Further examination is required to clarify this issue.

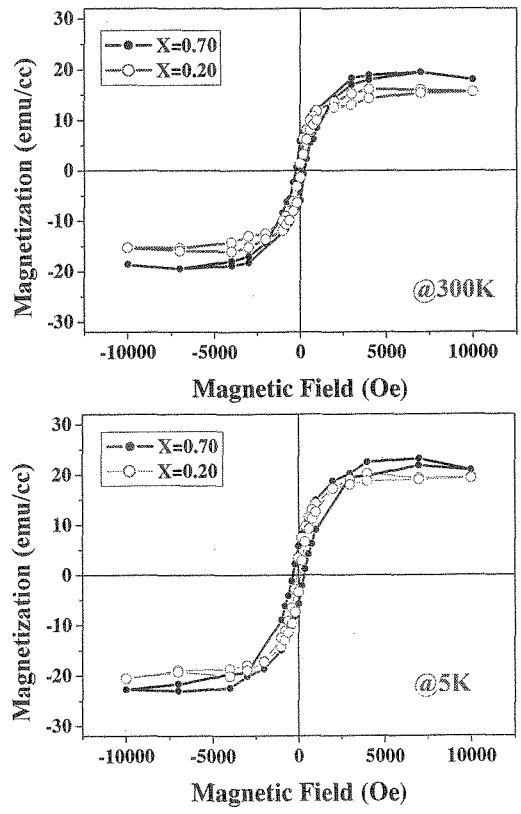

Fig. 6. Magnetization curves measured at 5 K and 300 K for the epitaxially grown BCMO (x=0.2 and 0.7) thin films on (001) STO substrates.

4. CONCLUSIONS

Ferromagnetic BCMO epitaxial thin films have been successfully synthesized on (001) STO substrates. The room temperature saturation magnetization for the x=0.2 sample was determined to be 1.20 μ_B/fu, in contrast to 1.41 μ_B/fu for the x=0.7 sample. The films were found to be highly resistive with a dielectric constant of ε=5.2 at 5 K. In contrast, the films exhibited semiconductor-like conduction behavior at room temperature.

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