Preparation of the Ferromagnetic Perovskite $Bi_{1-x}Sr_xMnO_3$ Thin Film

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Perovskite manganite $BiMnO_3$ thin films were synthesized by a pulsed laser deposition method on $SrTiO_3$ single crystal substrates. When (110) $NdGaO_3$ or (100) MgO single crystals were used for the substrates, the $BiMnO_3$ could not be grown. The $BiMnO_3$ thin films showed a ferromagnetic transition at 105 K, being consistent with the previous reports for the bulk of the $BiMnO_3$ prepared under high pressure. The magnetization reached to 2.8 μ_B, which was somewhat smaller than the value of the bulk crystal (3.6 μ_B). The effect of Sr substitution for the Bi site was also investigated.
Key words: ferromagnetism, thin films, epitaxy, exchange and superexchange

1. INTRODUCTION

The perovskite manganite $(La,AE)MnO_3$ (AE = alkaline earth) [1,2] has attracted great interest because of characteristic magnetic and transport properties represented by the colossal magnetoresistance (CMR) [3-5]. $LaMnO_3$ can be synthesized under ambient pressure, and shows an antiferromagnetism [6]. Although Bi^{3+} (1.24 Å) and La^{3+} (1.22 Å) have similar ionic radii, the perovskite manganite $BiMnO_3$ is known to be stabilized only under high pressure, and shows a large ferromagnetic moment below the Curie temperature (T_C=105 K) without the AE substitution [7-9]. From the structural analysis by neutron diffraction experiments, triclinic distortion of the $BiMnO_3$ due to highly polarized Bi^{3+} ions with $6s^2$ lone pair was revealed. This distortion should account for the stabilization of the ferromagnetism [10].

In this work, we investigated film growth of the $BiMnO_3$ by a pulsed laser deposition method considering substrate materials. The thickness dependency of the crystal structure and magnetic properties are discussed based on the lattice parameters and magnetization measurements. The effect of Sr substitution for the Bi site was also investigated.

2. EXPERIMENTAL

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The thin films of the $BiMnO_3$ were deposited by a pulsed laser deposition on the (100) and (110) $SrTiO_3$ (STO), (110) $NdGaO_3$ (NGO) and (100) MgO single crystal substrates. An ArF excimer laser (λ = 193 nm) with the repetition rate of 1 Hz was employed. The substrates temperature of 400 ~ 600 °C and oxygen pressure of 5.0×10^{-2} ~ 5.0 Pa were kept during the growth. The ceramic target was prepared by a solid state reaction from stoichiometric Bi_2O_3, $SrCO_3$ and Mn_2O_3. For $BiMnO_3$, the mixture of Bi_2O_3 and Mn_2O_3 was prefired in air at 700 °C and finally fired in air at 800 °C. The ceramic target and the prepared thin films were examined by X-ray diffraction (XRD) θ-2θ scans using Cu $K\alpha$ radiation. The lattice parameter of the out-of-plane was calculated from the observed d-spacings. The thickness of the films was measured with the step measurement system, Dektak II. The magnetization measurements were performed with a SQUID magnetometer (Quantum Design) with an applied field parallel to the film.

3. RESULTS AND DISCUSSION

The XRD pattern of a ceramic target is shown in Fig.1 (a). The ceramic target was a mixture of $Bi_2Mn_4O_{10}$ and Bi_2O_3. The perovskite type $BiMnO_3$ was not included in this target. In Fig.1 (b) and (c), typical XRD patterns of the deposited thin films on the NGO and MgO substrates are shown, respectively. The peak at around 28 degree is attributable to the $Bi_2Mn_4O_{10}$. indicating the $BiMnO_3$ was not grown on the NGO or
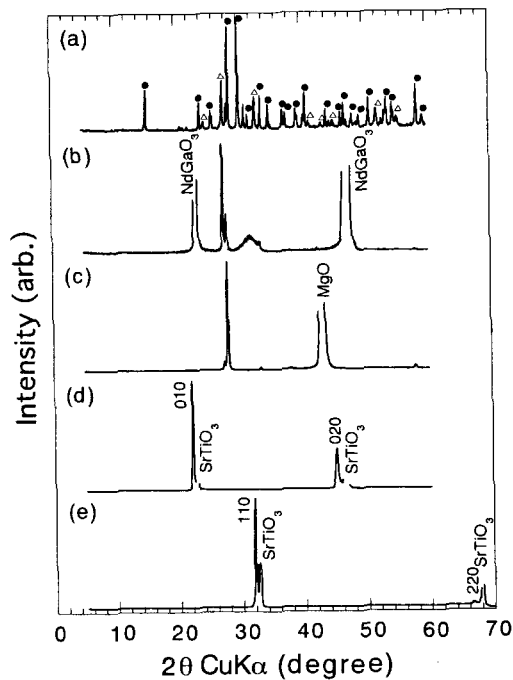
Fig.1. XRD patterns at room temperature for: (a) a ceramic target; (b) the deposition thin film on the (110) NdGaO$_3$; (c) the deposition thin film on the (100) MgO; (d) the BiMnO$_3$ thin film grown on the (100) SrTiO$_3$; (e) the BiMnO$_3$ thin film grown on the (110) SrTiO$_3$ substrates. The closed circles and the open triangles indicate peaks corresponding to Bi$_2$Mn$_4$O$_{10}$ and Bi$_2$O$_3$, respectively.

Fig.2. The thickness dependency of the lattice parameter b, which is perpendicular to the substrate, of the BiMnO$_3$ thin films grown on the (100) SrTiO$_3$ substrate. A broken line shows the lattice parameter b of the BiMnO$_3$ bulk synthesized under high pressure.

MgO substrates under any conditions. Fig.1 (d) and (e) show the typical XRD patterns of the BiMnO$_3$ thin films grown on the (100) and (110) STO, respectively. The substrates temperature of 450 °C and oxygen pressure of 5.0 × 10^{-2} Pa were chosen and kept during the growth. The diffraction peaks were indexed on the basis of the perovskite lattice reported in the previous studies [7-9], revealing that both films have the perovskite type structure with the (010) and (110) orientation on the (100) and (110) STO substrates, respectively. No diffraction peaks due to impurity phases were observed. From a comparison of lattice parameters, the lattice mismatch between BiMnO$_3$ and various substrates was estimated to be -0.77 % with the STO, -1.8 % with the NGO and 6.8 % with the MgO. On the NGO and MgO substrates, the growth of the perovskite BiMnO$_3$ was difficult due to the large lattice mismatch. Even though the BiMnO$_3$ is a metastable phase under ambient condition (only stabilized under high pressure and high temperature), the lattice matching is still considered to be important for the film growth.

The change of the lattice parameter b of the films grown on the (100) STO is shown in Fig.2. In the case of thin films, b was larger than that of the bulk, and decreased to the value in the bulk as the film thickness was increased. The change in b became small when the film thickness was larger than about 50 nm. These
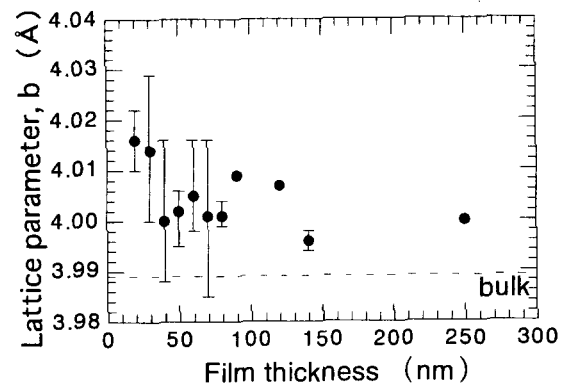
results indicate that the influence of the substrate is not negligible, but is a thicker film relieved from it.

The temperature dependence of the magnetization measured at 1 T for the BiMnO$_3$ thin films grown on the (100) and the (110) STO with various thickness is shown in Fig.3. The BiMnO$_3$ thin films showed the
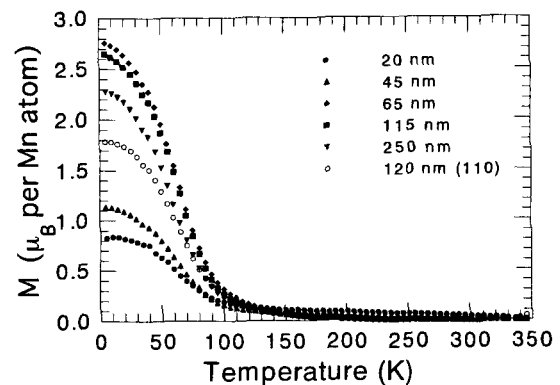

Fig.3. Temperature variation of the magnetization of the BiMnO$_3$ thin films with various thickness grown on the (100) and the (110) SrTiO$_3$ substrate measured at 1 T.

ferromagnetic transition at about 105 K, being consistent with the previous report for the bulk BiMnO$_3$ prepared under high pressure [7-9]. The magnetic moments measured at 1 T and 5 K, increased almost linearly as the film thickness increased when the thickness was less than 50 nm. However, the maximum value of 2.8 μ_B was still fairly smaller than that of the bulk (3.6 μ_B) [9]. The magnetization might be influenced by the change of the structure, because the lattice parameter varies with the film thickness below 50 nm. Also, the triclinic distortion of the BiMnO$_3$ might be relaxed in the thin film owing to stress at the interface with the STO substrate. Possibly, the

ferromagnetism of the $BiMnO_3$ thin film would be disturbed with the change in the crystal structure. On the other hand, the magnetic moment slightly decreased with the increase of the film thickness greater than 100 nm. The $BiMnO_3$ should be difficult to be synthesized when the film was thicker, because the substrate effect became weaker than a thinner film. Inhomogenity of the crystal caused by separation of the impurity phases could degrade the ferromagnetism of the material. The magnetic moment of the thin film grown on the (110) STO measured at 5 K and 1 T was smaller than that of the films grown on the (100) STO. This difference suggests an anisotropy of the magnetization in the $BiMnO_3$. It is pointed out by the neutron diffraction study that the spins easily aligned in the ac-plane [11]. The observed results are consistent with the easy axis of the magnetization because the measurement was carried with an applied field parallel to the film.

The magnetization curves measured at 5 K for the $BiMnO_3$ thin films grown on the (100) STO is shown in Fig.4. A hysteresis was observed in a field lower than
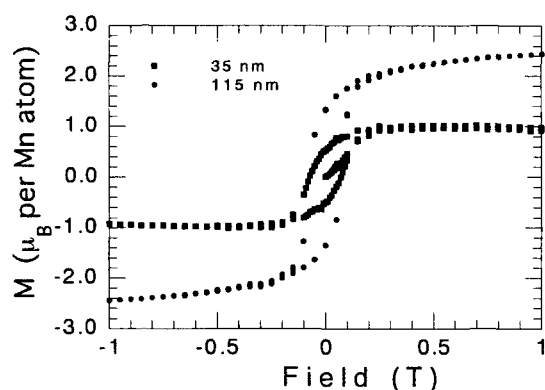

Fig.4. Magnetization curve of the $BiMnO_3$ thin films grown on the (100) $SrTiO_3$ substrate measured at 5 K.

0.2 T. This is in contrast to the very small hysteresis observed in the magnetization of the bulk $BiMnO_3$ [9]. When the thickness was 115 nm, a small gradual increase in the magnetization was observed above 0.5 T, which is similar to the result of the bulk $BiMnO_3$. However, when the thickness was 35 nm, the magnetization was saturated at 0.2 T. This difference is seemed to be due to a influence of the substrate. The magnetization curve was also measured at 5 K for the $BiMnO_3$ thin film on the (110) STO. The shape of the magnetization curve was not different from that of the film on the (100) STO.

The dependence of the magnetic property of the $Bi_{1-x}Sr_xMnO_3$ thin film on the Sr content, x, for the Bi site was also investigated. Fig.5 shows the temperature dependence of the magnetization measured at 1 T for the $Bi_{1-x}Sr_xMnO_3$ thin films for the composition of $0 \leq x$
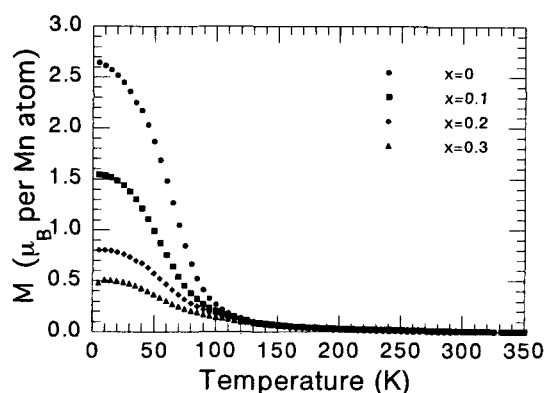

Fig.5. Temperature variation of the magnetization of the $Bi_{1-x}Sr_xMnO_3$ thin films grown on the (100) $SrTiO_3$ substrate measured at 1 T.

≤ 0.3. The films were grown on the (100) STO with the thickness of 120 nm. All the film for $0 \leq x \leq 0.3$ showed almost the same ferromagnetic transition at about 105 K, while the magnetic moment decreased as the Sr content, x, increased. The magnetization curves measured at 5 K for the $Bi_{1-x}Sr_xMnO_3$ thin films are superimposed in Fig.6. The hysteresis became more remarkable with
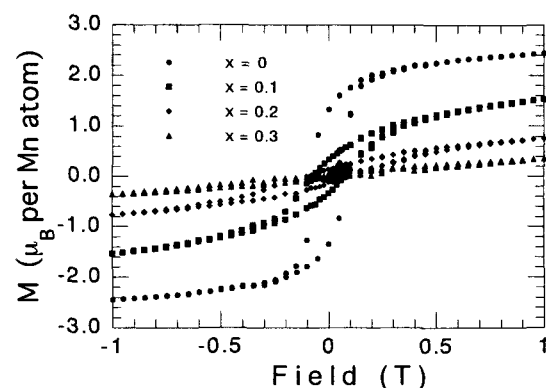

Fig.6. Magnetization curves of the $Bi_{1-x}Sr_xMnO_3$ thin films grown on the (100) $SrTiO_3$ substrates measured at 5 K.

increasing x, and the magnetization became hardly to saturate. These phenomena are consistent with the previous report for the bulk $Bi_{1-x}Sr_xMnO_3$ [9].

4. CONCLUSION

We successfully synthesized the $BiMnO_3$ thin film by the pulsed laser deposition on the STO single crystal substrates. The $BiMnO_3$ was not grown on the NGO or MgO substrates under any conditions. The lattice parameter of the $BiMnO_3$ thin film was different from the bulk value due to the stress effect of the substrate. The $BiMnO_3$ thin film showed the same ferromagnetic transition at about 105 K, however, the smaller magnetic moment, compared to the bulk. The magnetization of the $BiMnO_3$ thin film grown on the

(110) STO substrate was smaller than that of the film on the (100) STO. The effect of the Sr substitution for the Bi site was consistent with the behavior observed in the bulk.

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