Analysis of multiferroic properties in BiMnO₃ thin films

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Abstract. Textured BiMnO₃ [111] thin films on SrTiO₃ (100) and Pt/TiO₂/SiO₂ substrates were grown via r.f. magnetron sputtering (13.56 MHz). The XRD spectra confirmed a monoclinic structure and high-quality textured films for the BiMnO₃ films. The films grown on SrTiO₃ (100) showed higher crystalline quality than those developed on Pt/TiO₂/SiO₂. Through optimized oxygen pressure of 5×10⁻² mbar during the r.f. sputtering deposition, the crystalline orientation of the BiMnO₃ film was improved with respect to the previously reported value of 2×10⁻¹ mbar. The values of spontaneous polarization (Pₛ), remnant polarization (P_r), and coercive field (F_c) from ferroelectric hysteresis loops (P–E) at different temperatures were also obtained. Samples with higher crystalline order revealed better dielectric properties (high Pₛ and P_r values and a low F_c). For films on both types of substrates, the ferroelectric behavior was found to persist up to 400K. Measurements at higher temperatures were difficult to obtain given the increased conductivity of the films. Magnetic hysteresis loops from 5K to 120K were obtained for BiMnO₃ films grown on SrTiO₃ and Pt/TiO₂/SiO₂ substrates. The results suggested that the coexistence of the magnetic and electric phases persists up to 120K.

1. Introduction

The term multiferroic has been coined to describe materials in which two or all three ferroic properties, namely, ferroelectricity, ferromagnetism, and ferroelasticity coexist in the same phase [1]. This indicates that these materials have spontaneous polarization, magnetization, and strain and that these order parameters can be regulated by the application of electric fields and/or magnetic fields, and/or by using mechanical stress. These compounds have gained renewed and ever-increasing research interest in the last three years [2]. Particularly, for magnetoelectric materials, it is possible to find a coupling between the magnetic and ferroelectric properties through the magnetoelectric effect. Those substances have stirred scientific, as well as research interest, given the numerous potential applications they can offer based on the mutual control of magnetic and electric orderings. The number of ferroelectromagnets is sparse and is reduced dramatically to a few cases, owing to the incompatibility between magnetism and ferroelectricity. Most ferromagnetic oxides have a symmetrical center and do not allow electric polarization, while most ferroelectric oxides consist of transition metal ions without the seed of magnetism, i.e., active electrons, d. Hence, only a few multiferroics have been reported to date [3]; although the history of studies on magnetoelectric materials dates to the 1950s with Smolenski et al. [4,5]. Recently, there has been renewed interest in the simple perovskite BiMnO₃ as a multiferroic material. Moreira dos Santos et al. reported on the
synthesis of BiMnO$_3$ thin films, demonstrating the coexistence of ferromagnetic and ferroelectric properties [6]. This was also reported by Eerenstein et al. [7]. Recent theoretical calculations also suggest the likelihood of both ferromagnetic and ferroelectric characteristics, because of the covalent bonding between the bismuth and oxygen atoms [8]. These properties make this material potentially interesting for technological applications and in studying magnetoelectric interactions. An interesting characteristic of BiMnO$_3$ is that it can only be synthesized in bulk at high pressures of at least 6 GPa and high temperatures around 1100K [9], making it a difficult material for research. One way to facilitate research of such a compound would be its stabilization as a high-quality thin film. Through optimized oxygen pressure of $5 \times 10^{-2}$ mbar during the r.f. sputtering deposition, the crystalline orientation of the BiMnO$_3$/SrTiO$_3$ film can be improved with respect to the earlier value of $2 \times 10^{-1}$ mbar reported in another paper published by the authors [10]. In this study, we conducted structural, magnetic, and ferroelectric characterization of BiMnO$_3$/SrTiO$_3$ and BiMnO$_3$/Pt/TiO$_2$/SiO$_2$/Si films.

2. Experimental Details

BiMnO$_3$ thin films were deposited by employing the r.f. magnetron sputtering technique onto SrTiO$_3$ (100): Nb 0.1% and Pt/TiO$_2$/SiO$_2$/Si substrates in O$_2$ atmosphere. Ceramic targets were prepared by a solid-state reaction from a stoichiometric mixture of Bi$_2$O$_3$ and MnO$_2$. This mixture was pre-reacted in atmospheric air at 973K for 24 h. To obtain a denser target, polyvinyl butyral (PVB) was added to the reacted powder of 2.0% concentration in weight. The PVB was later removed after 5 h of annealing at 773K in air. Subsequently, the pellet was sintered at 1060K in a hermetic furnace in atmospheric air for 12 h to obtain a compact dark-gray pellet with a density in the order of 80% of the theoretical value with a 1-inch diameter. The deposition process commences with a long period of pre-sputtering (about one day) to avoid chamber pollution and target poisoning: beginning by heating the substrate to the desired temperature of 1120K at the system base pressure of $6.4 \times 10^{-4}$ mbar, depositing the film for 1 h by using an optimized oxygen pressure of $5 \times 10^{-2}$ and $5 \times 10^{-3}$ mbar for SrTiO$_3$ and Pt/TiO$_2$/SiO$_2$/Si substrates, respectively, carrying out a thermal treatment in an oxygen atmosphere for about 15 min and cooling the substrate to room temperature in the deposition gas atmosphere. The thickness of the films was estimated from the deposition rate at 100 nm.

A PANalytical X’Pert PRO X-ray diffraction system was used with Cu $K_\alpha$ radiation at room temperature. Polarization measurements of BiMnO$_3$ thin films on SrTiO$_3$ and Pt/TiO$_2$/SiO$_2$/Si substrates were conducted by using an RT66 test system (Radiant Technologies). The cooling system and temperature controller used for ferroelectric measurements was a Cryodyne 22C model with LTS series. The system to collect data used for ferroelectric measurements was the precision LC analyzer with the VISION software from Radiant Technologies. Ferroelectric hysteresis loop measurements were conducted on the BiMnO$_3$ thin films in a temperature range between 100K and 400K. We used a mask to deposit circular top electrodes with diameters between 0.1 and 0.5 mm on the films. For the 1-mm thick target pellets, the dielectric losses or dissipation factor, $tan \delta$, as conductivity, were measured as a function of temperature from room temperature to 870K. An HP 428A LCR was used at 10 selected values of frequencies between 20 Hz and 1 MHz.

3. Results and Discussion

X-ray diffraction was used to analyze the crystal structure of the thin films, indicating a monoclinic structure, where the (-113) peak was reported as the 100% peak (PDF 01-0071-5450). This indicates high-quality textured BiMnO$_3$/SrTiO$_3$ [111] films (Figure 1a). For BiMnO$_3$/Pt/TiO$_2$/SiO$_2$/Si (Figure 1b), the XRD showed that the intensity of the (222) peak is 3 times higher than the (-113) peak, suggesting light textured growth along the [111] orientation.
Typical ferroelectric hysteresis loops (P–E) of the thin films are given in Figures 2 and 3. Values for spontaneous polarization ($P_s$), remnant polarization ($P_r$), and coercive field ($F_c$) are presented in Table 1. As expected, the bulk material presents larger values of $F_c$ and smaller values of $P_s$ and $P_r$ than the film samples. The sample with higher crystalline order (BiMnO$_3$/TiSrO$_3$) has better dielectric properties (high $P_s$ and $P_r$ values and a low $F_c$). For both films on TiSrO$_3$ and Pt/TiO$_2$/SiO$_2$/Si substrates, the $P_s$ and $P_r$ values are improved by reducing temperature. For bulk material, no remarkable effect of temperature was observed. The P–E hysteresis loop persists up to 400K, but it is difficult to have good measurements at higher temperatures, given the increasing conductivity of the sample.

### Table 1. Characteristic values for BiMnO$_3$

| Sample          | T(K) | $P_s$ (µC/cm$^2$±0.01) | $P_r$ (µC/cm$^2$±0.01) | $F_c$ (kV/cm±0.02) |
|-----------------|------|------------------------|------------------------|-------------------|
| BiMnO$_3$       |      |                        |                        |                   |
| Bulk            | 220  | 0.25                   | 0.12                   | 4.42              |
| Bulk            | 300  | 0.23                   | 0.11                   | 4.65              |
| On Pt/TiO$_2$/SiO$_2$/Si | 105  | 1.51                   | 1.07                   | 2.24              |
| On SrTiO$_3$    | 122  | 2.21                   | 1.50                   | 2.12              |
| On SrTiO$_3$    | 300  | 0.70                   | 0.50                   | 4.21              |

Magnetic hysteresis loops for BiMnO$_3$ on SrTiO$_3$ and Pt/TiO$_2$/SiO$_2$/Si at 5K are shown in Figure 4. From magnetization, $M$, vs. applied field, $H$, curves, the values of $M_s$ and $H_c$ were obtained. These values, along with the values corresponding to BiMnO$_3$ developed at $P = 2 \times 10^{-1}$ mbar [10], are given in Table 2. The $M_s$ and $H_c$ are influenced by the crystalline quality of the films, i.e., the value of $M_s$ increases when the crystalline qualities increase; while the value of $H_c$ decreases with low crystalline qualities of the film. Magnetic hysteresis loops from 5 to 120K were obtained for BiMnO$_3$ films developed on SrTiO$_3$ and Pt/TiO$_2$/SiO$_2$ substrates (Fig. 4).
Figure 2. P-E hysteresis loop at 300K of BiMnO$_3$/SrTiO$_3$ film.

Figure 3. P-E hysteresis loop at 105K of BiMnO$_3$/Pt/TiO$_2$/SiO$_2$/Si film.

Table 2. Magnetic properties of BiMnO$_3$ at 5K

| Sample                  | Oxygen Pressure (mbar) | $M_s$ (μB/Mn site) | $H_c$ (Oe) |
|-------------------------|------------------------|-------------------|------------|
| BiMnO$_3$               |                        |                   |            |
| [10]$^{[10]}$BiMnO$_3$/SrTiO$_3$ | 2×10$^{-1}$           | 2.78              | 50         |
| BiMnO$_3$/SrTiO$_3$     | 5×10$^{-2}$            | 2.85              | 28         |
| BiMnO$_3$/Pt/TiO$_2$/SiO$_2$/Si | 5×10$^{-3}$           | 2.75              | 38         |

Figure 4. Magnetization (M vs H) hysteresis loops at 5K and 120K on BiMnO$_3$/SrTiO$_3$ grown in oxygen pressure of 5×10$^{-2}$ mbar. Inset displays $H_c \sim 28$ Oe.

Figure 5 shows conductivity as being independent of frequency below 673K. For middle frequencies (5000-10000 Hz), conductivity enhances strongly from 720 K; and for a frequency of 1000 Hz, the conductivity increases in the range of 720–820K and then decreases. However, for small frequencies, we did not observe any remarkable changes in the conductivity. This complex behavior of BMO
suggests that this material starts to break down if it is heated at the temperature range of 770K–920K, and that the path to decomposition is very complex with several metastable phases. In Figure 6, the dissipation factor, tan(δ) vs. temperature, shows possible ferroelectric–paraelectric transition around 630K. The magnitude of tan(δ) diminishes when the frequency is increased. We also observed a shift to higher temperatures when the frequency was increased. This may be attributed to the fact that conductivity increases when the temperature is increased.

![Figure 5. Conductivity vs. Temperature for a BiMnO₃ bulk sample.](image1)

![Figure 6. Dissipation factor (tan δ) vs. temperature for a BiMnO₃ bulk sample.](image2)

4. Conclusions

By optimizing the oxygen partial pressure in an r.f. sputtering deposition, we have obtained high-quality textured BiMnO₃ thin films on SrTiO₃ and Pt/TiO₂/SiO₂. A ferroelectric-paraelectric transition around 630K for the BiMnO₃ bulk has also been indicated. For both samples, films and bulk, the Ps and Pr values have been improved by reducing the temperature, while no remarkable effect of temperature was observed on the bulk material. The Ms and Hc were observed to be influenced by the crystalline quality of the films, i.e., the Ms increases when the crystalline qualities increase, while the Hc decreases with low crystalline quality of the film. Furthermore, magnetic hysteresis loops from 5K to 120K were obtained for BiMnO₃ films grown on SrTiO₃ and Pt/TiO₂/SiO₂ substrates. Thus, the results obtained suggest that the coexistence of the magnetic and electric phases persists up to 120K.

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