ANALYSIS OF MULTIFERROIC PROPERTIES IN BIMNO3 EPITAXIAL THIN FILMS

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Resumen

En este trabajo, películas delgadas de $BiMnO_3$ fueron depositadas utilizando la técnica r.f. magnetrón sputtering (13.56 MHz) sobre sustratos de SrTiO3 (100): Nb 0.1% y $Pt/TiO_2/SiO_2/Si$. La estructura de las películas delgadas fue analizada usando difracción de rayos X, indicando este análisis que las películas eran monoclínicas con dos orientaciones dominantes relacionadas con el sustrato. La primera es (111) $BiMnO_3$ ║ (100) $SrTiO_3$; la segunda es (222) $BiMnO_3$ ║ (200) $SrTiO_3$. La rugosidad de las películas fue caracterizada por medio de AFM; valores cuantitativos de la rugosidad y del tamaño de grano están en un rango entre 300Å y 0.3 µm. Mediciones eléctricas fueron hechas vía R vs. T desde 450 K hasta 15 K empleando un electrómetro programable Keithley modelo 167. La caracterización magnética se llevó a cabo para la magnetización Vs. Temperatura y para ciclos de histéresis a diferentes temperaturas en un magnetómetro de muestra vibrante. Se observó un momento magnético de saturación de $3.2\mu_B$ por ión de Mn a 5 K (más pequeño que en bloque, 3.6 μ_B), que decrece al aumentar la temperatura. La caracterización ferroeléctrica se realizó a bajas temperaturas y a 300 K utilizando un sistema de enfriamiento, un controlador de temperatura Cryodine modelo 22C de la serie LTS cryo systems, el software VISION y un sistema de análisis RT66 de la Radiant Technologies Inc. Se obtuvieron ciclos de histéresis (Polarización vs. Voltaje), mostrando polarizaciones de saturación de 22 nC/cm^2, 36 nC/cm^2, and 7 nC/cm^2 a 105 K, 122 K, y300 K.

Palabras claves: *Películas delgadas epitaxiales, propiedades magneto-eléctricas. Materiales multiferroicos.*

Abstract

In this work, BiMnO3 thin films were deposited by r.f. magnetron sputtering (13.56 MHz) on single-crystal $SrTiO_3$ (100) : Nb 0.1% and $Pt/TiO_2/SiO_2$ substrates. X-ray diffraction was used to analyze the crystal structure of the thin films, indicating that the films were monoclinic with two dominant orientation relationships along the substrate. The first is (111) $BiMnO_3$ ║ (100) $SrTiO_3$; the second is (222) $BiMnO_3$ ║ (200) $SrTiO_3$. Film roughness was characterized by AFM; quantitative values of roughness and grain size are in the range between 300Å and 0.3 µm. Electrical measurements via R vs. T were measured from 450 K to 15 K by using a Keithley Model 167 Programmable Electrometer. Magnetic characterization was carried out by using a Vibrating Sample Magnetometer for magnetization vs. temperature and for hysteresis loops at different temperatures. The saturation magnetic moment of 3.2µB per Mn ion (still fairly smaller than that of the bulk, 3.6µB) was observed at 5 K, decreasing with increasing temperature. Ferroelectric characterization was carried out at low temperatures and at 300 K by using a cooling system, a temperature controller Cryodine model 22C from the LTS cryo systems series, the VISION software and an RT66 test system from Radiant Technologies Inc. Hysteresis loops (Polarization vs. Voltage) were obtained, showing saturation polarizations of 22 nC/cm^2, 36 nC/cm^2, and 7 nC/cm^2 at 105 K, 122 K, and 300 K.

Keywords: *Epitaxial thin films, magneto-electric properties, multiferroic materials.*

1. INTRODUCTION

The term multiferroic has been coined to describe materials in which two or all three ferroic properties, ferroelectricity, ferromagnetism, and ferroelasticity coexist in the same phase [1]. It means 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 stresses. These compounds have gained renewed and ever increasing research interest in the last three years [2]. Especially, for those in which magnetic and ferroelectric orderings exist simultaneously, called magneto-electric materials, it is possible to find a coupling between the magnetic and ferroelectric properties through the magneto-electric effect that is the induction of an electric polarization by using a magnetic field or vice versa. Those substances have stirred up scientific, as well as research interest given the huge potential of applications they can offer based on the mutual control of magnetic and electric orderings. Additionally, the physics behind magneto-electric materials is fascinating and interesting [3]. Unfortunately, the number of ferroelectromagnets is sparse and reduced dramatically to some few cases, due to the incompatibility between magnetism and ferroelectricity. Most ferromagnetic oxides have a symmetry center and they do not allow electric polarization, while most ferroelectric oxides consist of transition metal ions without the seed of magnetism, that is, active electrons *d*. Hence, few multiferroics have been reported until now [4], although the history of studies on magneto-electric materials goes back to the 1950s years with Smolenski *et al* [5,6]. Recently, there has been a lot of interest in the simple perovskite $BiMnO_3$ as a multiferroic material. Moreira dos Santos *et al* reported on the synthesis of $BiMnO_3$ thin films, which show the coexistence of ferromagnetic and ferroelectric properties [7], as well as W. Eerenstein *et al*. [8]. Recent theoretical calculations also suggest the likelyhood of both ferromagnetic and ferroelectric characteristics, because of the covalent bonding between the bismuth and oxygen atoms [9]. These properties make this material potentially interesting for technological applications and to study magneto-electrical interactions. An interesting characteristic of $BiMnO_3$ is that it can only be synthesized in bulk-like by looking at high pressures of at least 6 GPa and high temperatures around 1100 K [10], making it a hard material for research. One way to facilitate research of such a compound would be its stabilization as a high-quality thin film. We successfully deposited thin films of $BiMnO_3$ onto a (100) face of the cubic perovskite $SrTiO_3$ and $Pt/TiO_2/SiO_2/Si$ substrates by using r.f. magnetron sputtering technique. Detailed growth conditions are reported in the next paragraph, and we conducted structural, magnetic, and electrical characterization of these thin films.

2. EXPERIMENTAL DETAILS

Thin films of $BiMnO_3$ were deposited by employing the r.f. magnetron sputtering technique onto a (100) $SrTiO_3$ (STO): Nb 0.1% and $Pt/TiO_2/SiO_2/Si$ substrates in an O_2 atmosphere. Ceramic targets were prepared by a solid-state reaction from a stoichiometric mixture of Bi_2O_3 and MnO_2. This mixture was pre-reacted in atmospheric air at 700 ºC for one day. To obtain a denser target, polyvinyl butyral (PVB) was added to the reacted powder in a 2.0% in weight. It was later removed by 5 h of annealing at 500 ºC in air. Then, the pellet was sintered at 785 ºC, in a hermetic furnace in air atmosphere for 12 h to obtain a compact dark-grey pellet with a density in the order of 80% of the theoretical one with a one-inch diameter. The deposition process starts with a long period of pre-sputtering (about one day) to avoid chamber pollution and target poisoning; then, beginning by heating the substrate to the desired temperature, 850 ºC, at the system base pressure 6.4×10^{-4} mbar; depositing the film for one hour using an optimized oxygen pressure of 5×10^{-2} mbar; then carrying out a thermal treatment in an oxygen atmosphere for about fifteen minutes and, finally, cooling the substrate to room temperature in the deposition gas atmosphere.

We surveyed the crystalline structure with X-ray diffraction (XRD) using a Philips X'pert difracctometer with Cu $K\alpha$ radiation at room temperature. Atomic force microscopy (AFM) measurements were performed on a 5 x 5 μm^2 area to investigate surface roughness. We measured resistance vs. temperature from 450 to 15 K by using a Keithley Model 167 Programmable Electrometer. The polarization measurements of $BiMnO_3$ thin films onto a single-crystal (100) oriented $SrTiO_3$: Nb 0.1% 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 measurement was a Cryodyne 22C model with LTS series. The system for collecting data used for ferroelectric measurement was the precision LC analyzer with the VISION software from Radiant Technologies. Ferroelectric hysteresis loop measurements were conducted on the $BiMnO_3$ thin films of in a range between 100 and 400 K. We used a mask to deposit on the films by evaporation circular top electrodes with diameters between 0.1 and 0.5 mm. We performed ferromagnetic measurements employing a Vibrating Sample Magnetometer (VSM) at 5, 10, 20, 40, 60, 80, 100, and 120 K.

3. RESULTS AND DISCUSSION

X-ray diffration (XRD) patterns corresponding to a thin film of $BiMnO_3$ deposited onto a STO (100)-oriented substrate using the r.f. magnetron sputtering technique is depicted in Fig. 1. The diffraction peaks have been indexed taking account the basis of the perovskite lattice, revealing a perovskite type structure with the (111) and (222) orientation on (100) substrate, We did not observe diffraction peaks due to impurity phases. The shape of the peaks suggest good growth along the (a00) orientations showing that they grow in a single orientation.

We looked for the best parameters to deposit the samples finding that pressure is very important in getting epitaxial growth with the r.f. magnetron sputtering technique and the properties of the sputter deposited films can be dependent on the gas pressure since film stress can vary dramatically with pressure. The inset in Fig. 1 displays the topography of the surface; the AFM images suggest that the films form via the island growth mechanism with homogeneous growth and that there is good alignment between the film and the substrate. This film was grown by using a substrate temperature of 850 ºC. The grains seem randomly oriented. Values of the roughness were calculated from a statistical treatment of the images obtaining for the surface roughness 300Å and for the grain size 3µm. The thickness of the film was 100 nm.

Figure 2 displays the plot of resistance vs. temperature from 450 to 15 K. We can observe how $BiMnO_3$ is a highly insulating composite and how this state is very robust. At taking temperature down to 150 K, we appreciate that the resistance increases very sharply. About T = 135 K, we can see the starting of ferromagnetic order and then a drop in resistance around 125 K, indicating that the material is undergoing a transition T_c at this temperature. This value is higher than the value obtained in bulk-like (105 K) and another measurement made in thin film-like using the PLD technique [7, 10]. This is due to the high quality of the epitaxial thin film because of the goodness of the r.f. magnetron sputtering method. The film reaches an approximate resistance of 1.9×10^{11} Ω, consistent with another measurement [3]. This value is large enough for the BMO thin film to be taken as a good insulator. It could be regarded with Mn-O-Mn bond angles, which are fairly apart from 180º (distributed between 160º and 140º). Typical ferroelectric hysteresis loops for a thin film are depicted in figures 3 and 4. The former has the following values for P_s, P_r, and F_c: P_s of 36 nC/cm^2, 28 nC/cm^2 and 2.1 Kv/cm; the plot in Fig. 4 also displays ferroelectric behavior. Based on the above results, we suggest that the magnetic phase of $BiMnO_3$ (T < 125 K) is ferroelectric. The P-E hysteresis loop persists up to ~ 400 K, but it was difficult to have good measurements at higher temperatures due to the increasing conductivity of the sample.

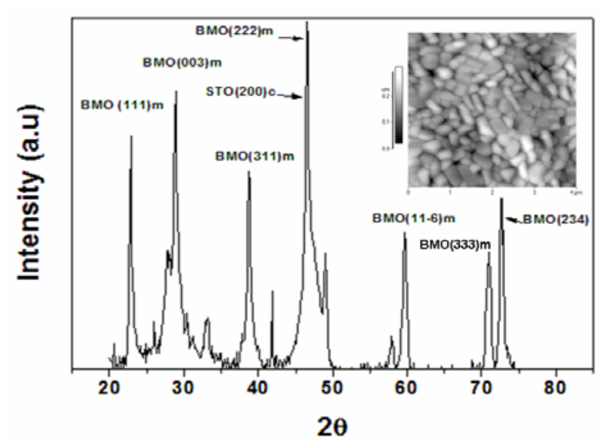

Figure 1. XRD and Atomic force microscopy (AFM) of a BiMnO3 thin film on a SRTiO3 (100) substrate. Inset shows the AFM image of a 100nm thin film, note the grain size near 0.3µm.

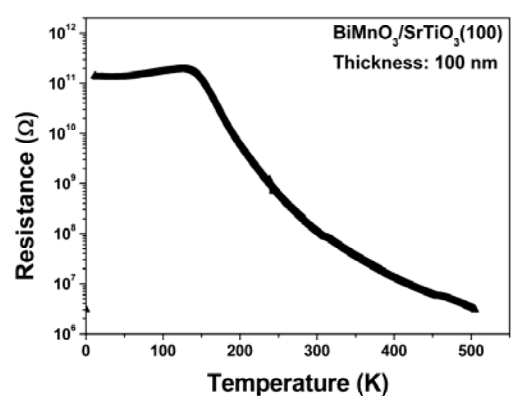

Figure 2. Resistance (R) in zero applied magnetic field as a function of temperature for a BMO thin film grown onto STO (100) substrate. Below 150 K, the resistance increases very sharply. Around T = 135 K, we can see the onset of ferromagnetic order.

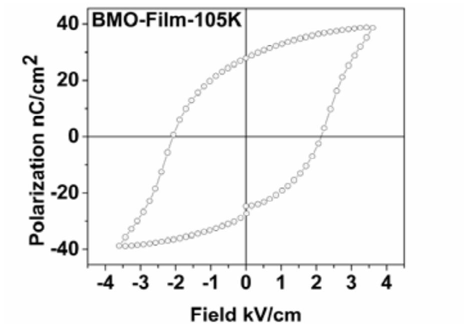

Figure 3. P-V hysteresis loop of a BMO thin film on a $Pt/TiO_2/SiO_2/Si$ substrate at 105 K.

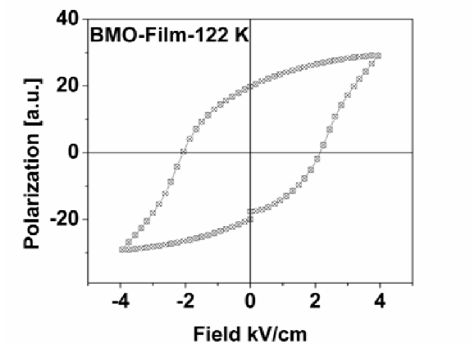

Figure 4. P-V hysteresis loop of a BMO thin film on a $SrTiO_3$ (100) substrate at 122 K.

We can appreciate well-defined M-H hysteresis loops at different temperatures in Fig.s 5 and 6. Zero-field cooling (ZFC) and field cooling (FC) plots as a function of temperature were measured during warming in 10000 Oe after cooling in zero field and applied field of 10 kOe, respectively, by using a VSM.

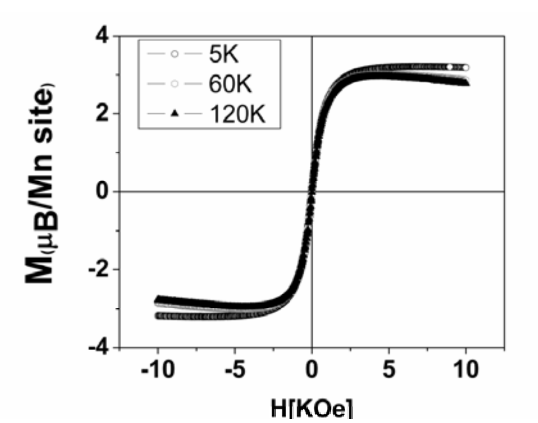

Figure 5. Magnetic hysteresis loops at different temperatures of $BiMnO_3/SrTiO_3(100)$ thin films.

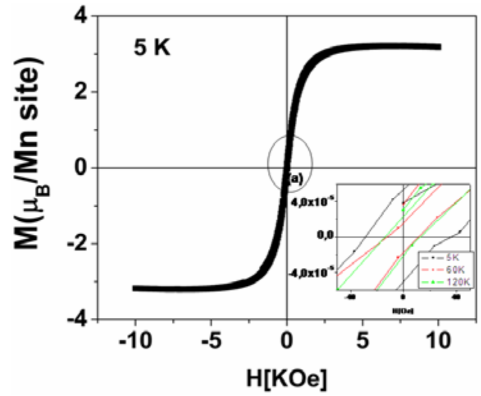

Figure 6 Magnetic hysteresis loop for a $BiMnO_3/SrTiO_3(100)$ thin film at 5 K. The zoom displays the region enclosed in the circle.

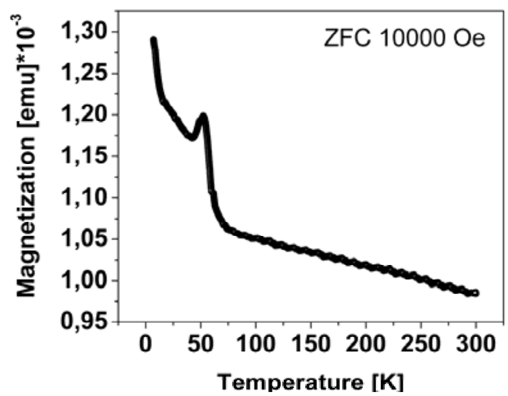

Figure 7. ZFC temperature dependence of the magnetization for a $BiMnO_3/SrTiO_3$ (100) thin film in a field of 10000 Oe.

We do not see any substantial difference between the two curves. Around 50 K, there is a sharp peak showing ferromagnetic transition consistent with another survey of a thin films deposited onto a $LaAlO_3$ and a $Pt/TiO_2/SiO_2/Si$ substrates and using the Pulsed Laser Deposition (PLD) technique [11]. We do not observe another abrupt change in the curves. We suppose that this peak in the curve can be attributed to a non-stoichiometric composition, strain or size effect that produce a magnetic interaction between grains.

4. CONCLUSION

We successfully grew $BiMnO_3$ thin films via r.f. magnetron sputtering on $SrTiO_3$ (100) : Nb 0.1% single-crystal and $Pt/TiO_2/SiO_2/Si$ substrates. We have corroborated the effectiveness of the r.f. magnetron sputtering method and learned how to control parameters to obtain good-quality thin films that allow us to get good results. X-ray Diffraction data indicate the epitaxial growth of the $BiMnO_3$ thin films on (100) $SrTiO_3$.

Variable pressure X-ray diffraction patterns clearly show a possible dependence of the oxygen pressure, indicating that microstructure, magnetic, and ferroelectric properties can be very sensitive to this parameter and must be kept in mind to get epitaxiality.

We could verify that $BiMnO_3$ is a highly insulating compound in film-like and, remarkably, the insulating state is very robust at low temperatures and has ferroelectric behavior. Thin films on (100)-oriented $SrTiO_3$: Nb 0.1% and $Pt/TiO_2/SiO_2/Si$ substrates show the same behavior down to 100 K.

The ferromagnetism of $BiMnO_3$ was verified both via magnetization vs. applied field and magnetization vs. temperature in an epitaxial thin film sample, grown on a $SrTiO_3$ (100) substrate. We observed two transitions around 50 and 125 K and we obtained a magnetic moment of 3.2 μ_B.

5. ACKNOWLEDGMENT

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