Microelectronics Journal 39 (2008) 1308–1310

Microelectronics Journal

www.elsevier.com/locate/mejo

Occurrence of ferroelectricity in epitaxial $BiMnO_3$ thin films

M. Grizalez[a,d,*], E. Martinez[b], J. Caicedo[d], J. Heiras[c], P. Prieto[d]

[a] *Physics and Mathematics Program, Universidad de la Amazonia, Florencia Caquetá, Colombia*

[b] *Centro de Investigación en Materiales, DIP-CUCEI, Universidad de Guadalajara, Apartado Postal 2 - 638, 44281, Guadalajara, Jalisco, México*

[c] *Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Ensenada, B.C, México*

[d] *Excellence Center for Novel Materials, Universidad del Valle, Cali, Colombia*

Available online 25 June 2008

Abstract

In this paper, we report evidence of ferroelectricity in perovskite manganite ($BiMnO_3$) thin films synthesized via r.f. magnetron sputtering method on a single-crystal (1 0 0)-oriented $SrTiO_3$:Nb 0.1% and $Pt/TiO_2/SiO_2/Si$ substrates. X-ray diffraction measurements were used to analyse the crystal structure of the thin films, revealing epitaxial growth for $BiMnO_3$ films with their (1 1 1) and (2 2 2) planes parallel to the (0 0 1) and (0 0 2) planes of the $SrTiO_3$ substrate. AFM measurements were performed to investigate surface morphology; quantitative values of roughness and grain size are in the range between 300 and 500 nm. Ferroelectric characterization was conducted at low temperatures and at 300 K. Hysteresis loops (polarization vs. voltage) were obtained, showing saturation polarizations of 40 nC/cm^2, and 25 nC/cm^2 at 105, 122, and 300 K. Resistance vs. temperature measurements were performed, which indicated this to be very robust insulating material.

PACS: 64.60.−i; 64.70.Kb; 61.10.Nz

Keywords: Multiferroic materials; Ferroelectricity; Epitaxial thin films

1. Introduction

There is much interest in multiferroic materials [1,2] showing simultaneous ferromagnetism, ferroelectricity, and ferroelasticity, given their potential applications in magnetoelectrics and spintronics, in addition to the inherent interest in the underlying physics of the coexistence of ferroelectricity and ferromagnetism. The remarkable magnetoelectric properties of $BiMnO_3$ have attracted considerable attention during the last three years. Its magnetic structure was recently described as resulting from a particular ordering of the occupied d_z^2 orbitals [3]. The ferromagnetism of this material, along with recent experimentally verified ferroelectric behaviour [4], makes this compound potentially interesting for technological applications and for the study of magnetoelectric interactions. An intriguing peculiarity of $BiMnO_3$ lies in that it can only be synthesized in bulk form by resorting to high pressures of at least 6 GPa and high temperatures around 1100 K [5], making it quite an inaccessible material for research. One way to facilitate research of such a compound would be its stabilization as a high-quality thin film [6]. We successfully synthesized $BiMnO_3$ thin films under ordinary growth conditions reported elsewhere. The optimization of growth conditions have led to BMO with a low temperature resistance as high as $1.9 \times 1011\,\Omega$. This fact has permitted us to conduct measurements of the ferroelectric properties of this compound.

2. Experimental details

The $BiMnO_3$ thin films were deposited onto a single-crystal (1 0 0)-oriented $SrTiO_3$:Nb 0.1% and $Pt/TiO_2/SiO_2/$ Si substrates via magnetron r.f. sputtering in an O_2 atmosphere, starting from a Bi-rich ceramic target. The target was sintered from a stoichiometric mixture of Bi_2O_3 and MnO_2. The crystalline structure was analysed with X-ray diffraction (XRD), while film surfaces were studied

*Corresponding author at: Physics and Mathematics Program, Universidad de la Amazonia, Florencia Caquetá, Colombia.

E-mail address: mgrizales@calima.univalle.edu.co (M. Grizalez).

0026-2692/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.mejo.2008.01.023

in tapping mode with a Digital Instruments Nanoscope III atomic force microscope (AFM). Ferroelectric properties were assessed using an RT66 test system (Radiant Technologies). The RT measurements were obtained with a Keithly 642 electrometer.

3. Results and discussions

The XRD pattern corresponding to the thin film $BiMnO_3$ compound obtained via r.f. magnetron sputtering method is displayed in Fig. 1(a). The dominant features in the scans are the substrate peaks. Additionally, the spectra show strong reflections stemming from the BMO layer close to the substrate peak, revealing highly textured growth mode. The diffraction peaks were indexed on the basis of the perovskite lattice. They reveal that films have a monoclinic-type structure with the (1 1 1) and (2 2 2) orientations on the (1 0 0) STO substrate. Those are sharp and narrow peaks indicating large grain size, suggesting good growth along the (0 0 a) orientations.

AFM measurements were performed on a $5 \times 5\,\mu m^2$ area to investigate surface roughness. Fig. 1(b) shows surface topography; quantitative roughness values can be extracted from a statistical treatment of images. Surface roughness

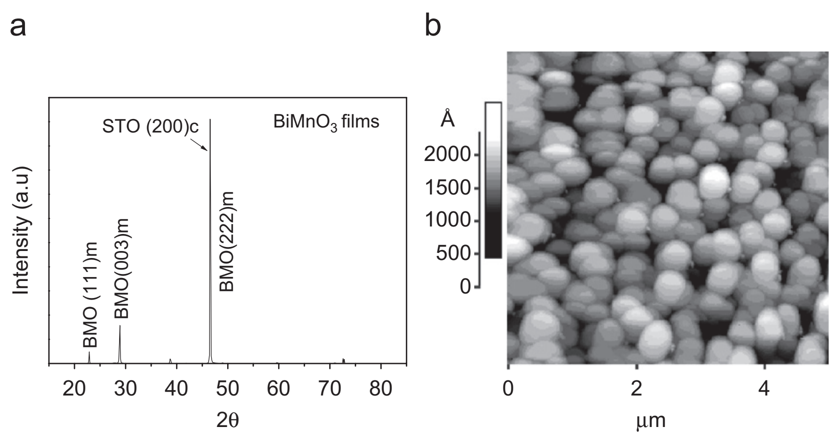

Fig. 1. (a) X-ray diffraction pattern of $BiMnO_3$ thin films grown on $SrTiO_3$ (1 0 0) substrates. (b) AFM of a $BiMnO_3$ thin film on an $SrTiO_3$ (1 0 0) substrate. Note that grain size is near 500 nm.

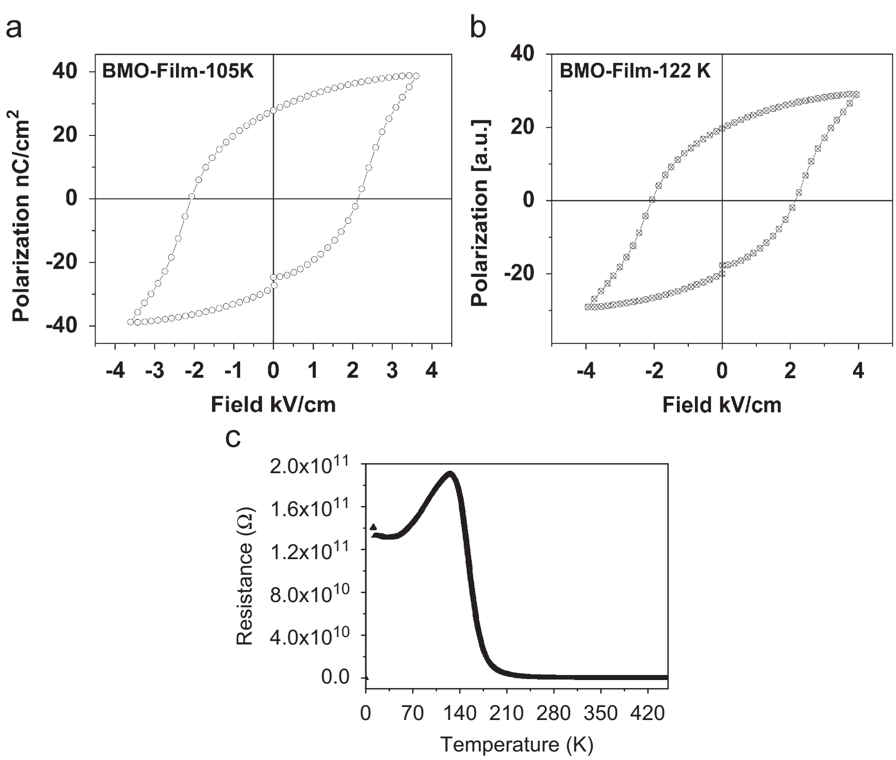

Fig. 2. (a) P–V hysteresis loop of a BMO thin film on a $Pt/TiO_2/SiO_2/Si$ substrate at 105 K. (b) A P–V hysteresis loop of a BMO thin film on an $SrTiO_3$ (1 0 0) substrate at 122 K. (c) Resistance (R) in zero magnetic applied field as a function of (T) for a BMO thin film grown on STO.

and grain size of about 250 Å and 0.5 μm, respectively, were obtained. Figs. 2(a) and (b) show hysteresis loops of BMO thin films on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ substrates. The former displays a spontaneous polarization P_s of $40\,nC/cm^2$, and a remanent polarization of $30\,nC/cm^2$, respectively, with cohersive voltage V_c of about 2.07 V; the latter displays a P_s of $2.21\,\mu C/cm^2$, a P_r of $1.50\,\mu C/cm^2$, and V_c of 2.08 V. Fig. 2(c) shows temperature dependence of the resistance of a BMO film on STO. As noted, $BiMnO_3$ is a highly insulating compound and, remarkably, the insulating state is very robust. When temperature decreases to 150 K, resistance increases very sharply.

4. Conclusions

We successfully grew BMO thin films via r.f. magnetron sputtering on STO single-crystal and $Pt/TiO_2/SiO_2/Si$ substrates. The ferroelectricity of BMO was verified through polarization vs. voltage. The P–V hysteresis loop persisted up to $\sim$400 K, but good measurements at higher temperatures were difficult due to the increasing conductivity of the films. We also studied this material as an insulator, noting very robust insulating state. Our results, thus, show the potential of complex ferroelectric insulating oxides for novel application possibilities.

Acknowledgements

This work was supported by the Excellence Center for Novel Materials, CENM at Universidad del Valle, Cali Colombia, the Centro de Ciencias de la Materia Condensada, CCMC, at UNAM, Ensenada, B.C., México (DGAPA Proy. In114207), and Universidad de la Amazonia, Florencia Caquetá, Colombia.

References

[1] H. Schmid, Ferroelectrics 162 (665) (1994) 317.
[2] N.A. Hill, J. Phys. Chem. B 104 (2000) 6694.
[3] A. Moreira dos Santos, A.K. Cheetham, T. Atou, Y. Syono, Y. Yamaguchi, K. Ohoyama, H. Chiba, C.N.R. Rao, Phys. Rev. B 66 (2002) 064425.
[4] A. Moreira dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, C.N.R. Rao, Solid State Commun. 122 (2002) 49.
[5] F. Sugawara, S. Iida, J. Phys. Soc. Jpn. 20 (1965) 1529.
[6] M. Grizalez, E. Delgado, M.E. Gomez, P. Prieto, Phys. Stat. Sol. (c) 4 (11) (2007) 4203–4208.