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ScienceDirect

Physics Procedia 49 (2013) 183 – 189

Physics Procedia

Spintronic Materials: Nanostructures and Devices (SMND-2011)

Effect of Substrate Orientation on Structural and Magnetic Properties of $BiMnO_3$ Thin Films by RF Magnetron Sputtering

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Abstract

Bismuth manganese oxide ($BiMnO_3$) thin films were grown on Si (100) and Si (111) substrates by RF magnetron sputtering. The properties of grown films were analyzed by X-ray diffraction (XRD), Energy dispersive analysis of X-ray Spectrum (EDX), Atomic force microscopy (AFM) and Vibrating sample magnetometer (VSM). The XRD result reveals that $BiMnO_3$ (BMO) thin films on both the substrates are polycrystalline in nature with monoclinic structure, however the films on Si (100) showed better crystalline quality than those deposited on Si (111). It has been observed from the room temperature VSM studies that BMO / Si (100) system has high saturation magnetization of 3.7 x 10^{-4} emu/cm^3 compared to the BMO / Si (111).

Selection and peer-review under responsibility of the Department of Physics, School of Science and Humanities, Kongu Engineering College

Keywords: Thin films; $BiMnO_3$; Sputtering; Multiferroic; Ferromagnetism.

1. Introduction

Metal oxides have been the focus of many research groups because of its wide range of structures, properties and exciting phenomena that are manifested in these materials [1, 2]. Some of the metal oxides are perovskite structure, which have the chemical formula ABO_3 (Example: $SrTiO_3$, $BiFeO_3$, $BiMnO_3$) made up of corner sharing octahedral with the A-cation coordinated with twelve oxygen ions and the B-cation with six. Selection of the appropriate A- and B-site cations can dramatically impact structural, electronic, magnetic, polar and other properties. The electronic structure and coordination chemistry of the cationic species control the wide range of physical phenomena manifested in these materials [3].

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Selection and peer-review under responsibility of the Department of Physics, School of Science and Humanities, Kongu Engineering College
doi:10.1016/j.phpro.2013.10.025

Very few materials exist in nature which exhibits both ferroelectric (FE) and ferromagnetic (FM) ordering in the same phase with coupling between the two orders and these materials are termed as multiferroics. As a result, they have spontaneous magnetization that can be switched by an applied magnetic field and spontaneous polarization that can be switched by an applied electric field. [4-9]. This effect can be potentially exploited to allow the construction of novel spintronic devices such as tunneling magneto resistance (TMR) sensors, spin valves, multistate memories, recording and other applications [6, 9, 10]. For device applications, the maximization of controllable multiferroic properties is necessary at or above room temperature. Bismuth manganese oxide (BMO) is one of the few materials recently shown to be simultaneously ferromagnetic and ferroelectric and highly distorted perovskite structured material [5, 6, 8, 9, 11-19]. However, bulk BMO has serious problems such as low Curie temperature for the ferromagnetic property (T_C = 105 K) and high leakage current at room temperature. To overcome such difficulties, we reported the successful synthesis of BMO thin films by RF magnetron sputtering with optimized growth conditions that led to the ferromagnetism in BMO films at room temperature.

2. Experimental

Single crystal silicon wafers doped with phosphorous (n-type) and cleaved parallel to (100) and (111) planes were used as substrate material for BMO thin film deposition by RF magnetron sputtering. The substrates were cleaned by successive rinses in ultrasonic baths of distilled water, ethanol and acetone and then blown with dry air before being loaded into the chamber. The target with a nominal composition of $BiMnO_3$ has been prepared by conventional solid state reaction route. The required stoichiometric ratio of highly pure bismuth oxide (Bi_2O_3) and manganese oxide (MnO_2) powders were mixed, ground and pre-reacted in atmospheric air at 973 K for 4h. To obtain a denser target, Poly Vinyl Alcohol (PVA) was added with the reacted powder and made into a disc of 2” diameter using hydraulic press. Then the pellet was sintered at 973 K for 6h. The PVA was evaporated at 773 K. Thus, prepared target and substrate were loaded into the chamber. The deposition process started with pre-sputtering (about 10 min) to avoid chamber pollution and target poisoning. The sputtering was carried out under the following operating conditions (Table 1).

Table 1. Summary of sputtering conditions

Operating Parameters	Observed Values
Target to substrate distance	~ 5 cm
Sputtering gas	100 vol.% Ar
Base pressure	1×10^{-6} mbar
Working pressure	0.01mbar
Substrate	n-Si (100), n-Si (111)
Substrate temperature	873K
RF power	60W
Deposition time	45 min

3. Results and Discussion

3.1. X-Ray diffraction Analysis (XRD)

The structural properties of BMO films deposited on Si (100) and Si (111) substrates were studied by XRD using CuK_{α} radiation at room temperature. Fig.1 shows the XRD pattern of the as prepared BMO films. The XRD peaks were indexed by comparing the data with standard JCPDS file (#894544). It reveals that the films are polycrystalline in nature with monoclinic structure and C2 space group. The peaks with low full width at half maximum (FWHM) indicating the good crystallinity with larger grains and free from the formation of any other secondary phases. Further, the film grown on Si (100) is highly crystalline and better quality (less strain) than the film grown on Si (111). It might be due to lower value of lattice mismatch of Si (100) substrate and film.

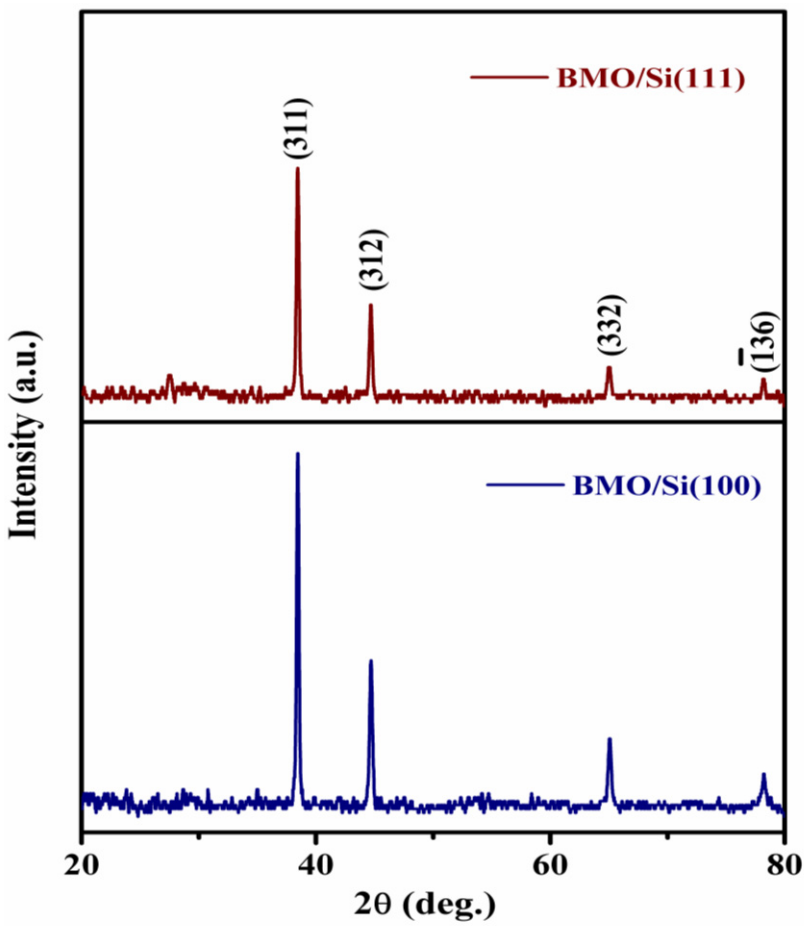

Fig. 1 XRD pattern of BMO thin films

The average crystallite size (D), dislocation density (ρ) and lattice strain (η) of the prepared films were estimated from the following formulae. The estimated values are given in Table 2.

$$D = \frac{K\lambda}{\beta\cos\theta}\ (m) \tag{1}$$

$$\rho = \frac{1}{t^2}\ (lines/m^2) \tag{2}$$

$$\eta = \left[\frac{\lambda}{t\cos\theta} - \beta\frac{\pi}{180}\right]\frac{1}{\tan\theta} \tag{3}$$

Table 2. The Geometric parameters of BMO films

Samples	Crystallite size (nm)	Dislocation density (lines/m^2)	Strain
BMO/ Si (100)	44	5.146×10^{14}	0.001
BMO/ Si (111)	36	7.627×10^{14}	0.002

3.2. Energy dispersive X-ray Analysis (EDX)

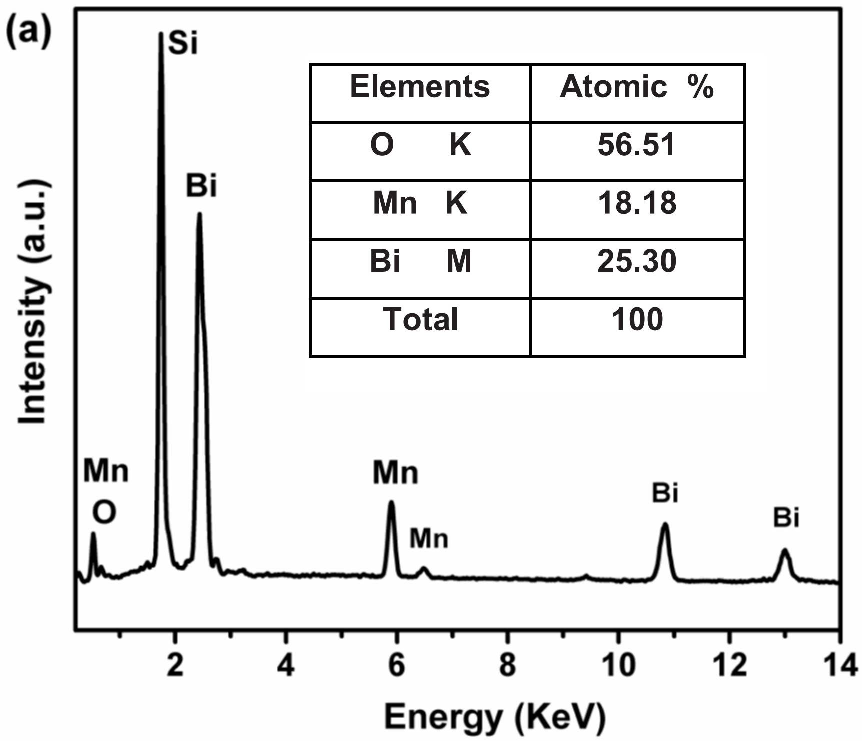

Fig. 2 EDAX spectrum of BMO/Si (100) system

Quantitative elemental composition of the films were analysed using EDX indicate the formation of BMO film on Si (100) substrate with good stoichiometry (Fig. 2). The absence of other elemental peaks in EDX spectra implies that the prepared samples are in better quality. The result shows the ratio of chemical elements Bi : Mn is approximately 1.4 : 1. This discrepancy in ratio of Bi and Mn elements are possibly due to the lesser desorption of Bi ions during the film growth process.

3.3. Atomic Force Microscopy Analysis (AFM)

The surface topography of the films have been studied using AFM (Fig. 3). The rms roughness over a scan area (row x column: 256 x 256) of the BMO film deposited on Si (100) and Si (111) are observed as 3.55 nm and 0.8 nm respectively. The top view of this film looks like a uniform grains with roughly estimated thickness of 28 nm and 22 nm respectively.

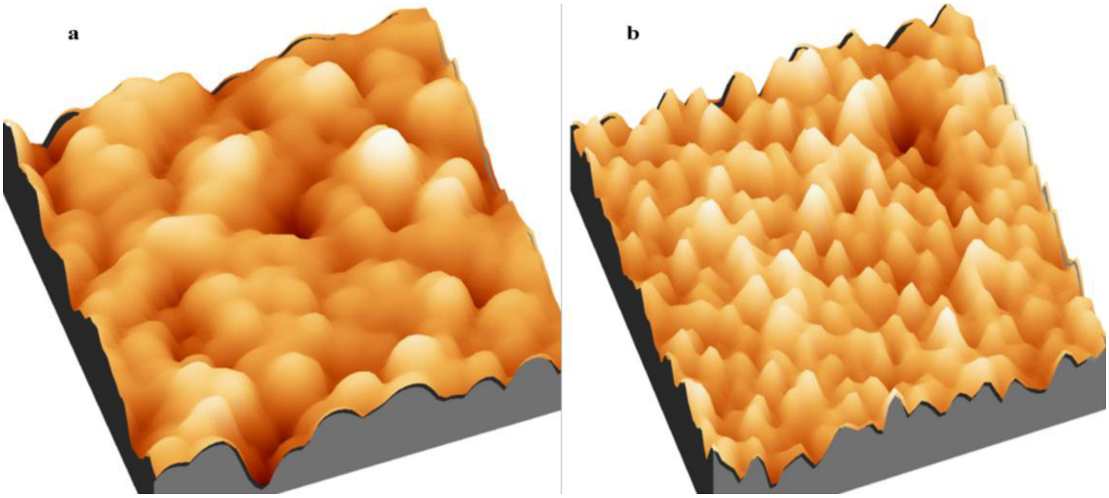

Fig. 3 (a) AFM image of BMO/Si (100) film; (b) AFM image of BMO/Si (111) film

3.4 Vibrating Sample Magnetometer Analysis (VSM)

Magnetic properties of BMO thin films have been studied using vibrating sample magnetometer at room temperature (Fig.4). The magnetic field up to 1T has been applied parallel to the surface of the film. Hysteresis loop shows that both the films have FM nature and illustrates that the curve reaches M_{sat} and with immediate decrease, which is due to the presence of paramagnetic contribution of silicon substrate. Table 3 shows ferromagnetic properties of the films such as saturation magnetization (M_{sat}), remnant magnetization ($M_{rem.}$) and coercivity ($H_{coer.}$). However, BMO/Si (100) system exhibits good ferromagnetic behaviour than BMO / Si (111) system. This is possibly due to higher crystallinity of BMO / Si (100) film because of the less lattice misfit. Further, the low magnetization behaviour could be explained by the presence of Bi vacancies that locally disturb the complex orbital ordering that is essential for the long range ferromagnetic order in BMO [18]. VSM results also have good agreement with XRD and AFM results.

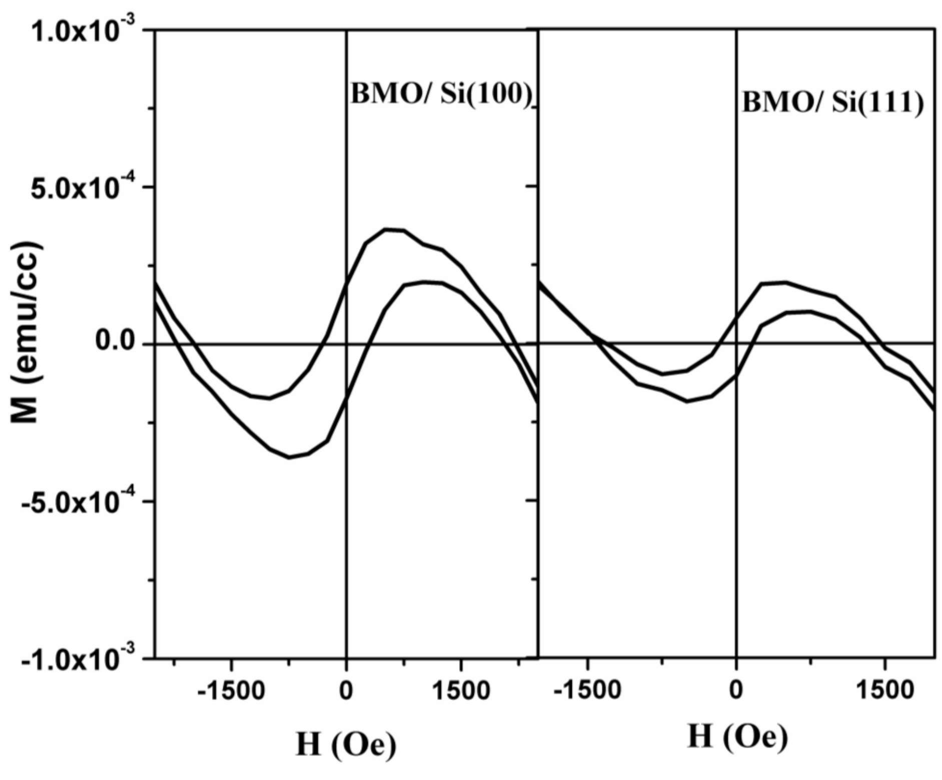

Fig. 4. M-H curve of BMO thin films at RT

Table 3. Magnetic properties of BMO films at room temperature

Samples	$M_{sat.}$ (emu/cc)	$M_{rem.}$ (emu/cc)	$H_{coer.}$ (Oe)
BMO/ Si (100)	3.7 x 10^{-4}	1.9 x 10^{-4}	323
BMO/ Si (111)	2 x 10^{-4}	7.8 x 10^{-5}	165

4. Conclusion

$BiMnO_3$ thin films were deposited on the Si (100) and Si (111) substrates by RF magnetron sputtering at a substrate temperature of 700 °C. Structural, elemental and topographical properties of the films were analyzed by XRD, EDX and AFM. From the XRD, it has been found that the film grown on Si (100) have better crystallinity compared to Si (111). Moreover, VSM studies illustrate that the BMO / Si (100) film exhibited a better ferromagnetic behavior compared to the film on Si (111). From these analyses, it has been concluded that the BMO film grown on Si (100) substrate is an active candidate for storage applications.

Acknowledgement

The authors wish to acknowledge University Grant Commission (UGC), New Delhi, India for providing the financial support through the project [F.No.38-107/2009 (SR)].

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