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Structure dependent room temperature ferromagnetism in Co, Nb co-doped $BaTiO_3$ thin films prepared by RF sputtering

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ABSTRACT

Thin films of $BaTiO_3$ and Co, Nb co-doped $BaTiO_3$ on glass and Si (100) substrates were deposited by RF sputtering (at 350 ºC), and annealed. The amorphous and crystalline phases were observed for the as-deposited and annealed samples, respectively from the X-ray diffraction (XRD) studies. The magnetic behaviour of the pure and doped $BaTiO_3$ films was studied by vibrating sample magnetometry (VSM). In this study, the ferromagnetic behaviour at room temperature was observed in the Co, Nb co-doped $BaTiO_3$ of both amorphous and crystalline films. The annealed polycrystalline Co, Nb co-doped $BaTiO_3$ films have the larger saturation magnetization and coercivity than the amorphous films. The room temperature ferromagnetic responses were also observed by the Magneto-optical Kerr effect (MOKE) measurements for both as-deposited and annealed samples. Copyright © 2016 VBRI Press.

Keywords: Thin films; sputtering; phase transformation; functional; magnetic materials.

Introduction

Barium titanate ($BaTiO_3$ or BTO) as an important and typical perovskite structured material has received much attention in the past few decades due to their physical properties and potential applications in thin film capacitors, chemical sensors, dynamic random access memories (DRAMs), nonvolatile memories (NVRAM), integrated devices and optical modulators [**1-4**]. BTO is a typical ferroelectric material with useful properties such as, high dielectric constant, high permittivity and spontaneous polarization. Thin films of $BaTiO_3$ also have a great potential for electro-optic device applications [**5**]. Recently, doping of perovskite materials with 3d transition elements has led to a variety of changes in their physical properties and promising switching properties with possible applications in memristive memories [**6, 7**]. Also, the stimulation of ferromagnetism in nonmagnetic perovskite structure materials has fascinated a considerable attention by the addition of spin functionality (i.e., incorporation of transition metals like, Co, Ni, Fe, etc. to the host crystal, which leads to multi-functional materials). Multifunctional materials (multi-ferroics) are a combination of more than two functional properties, namely ferroelectric, ferroelastic and ferromagnetic. Scientifically, multiferroics play a vital role in next generation optoelectronic intelligent devices, sensors, computing, robotics and magnetic memory devices.

Barium titanate doped by the transition metals such as Ni, Co, Cr, Mn and Fe are the most promising candidates for ferromagnetism [**8**]. For instance, room temperature ferromagnetism with saturation magnetization for Co doped $BaTiO_3$ [**9**] and theoretical predictions of the magnetic moment of the Fe-doped $BaTiO_3$ films have been studied in detail to understand the magnetic behavior of the $BaTiO_3$ [**10**]. Few other researchers also observed room temperature ferromagnetism in transition metal doped $BaTiO_3$ and have explained the origin of ferromagnetism [**11-14**]. These reports prove that, the stimulation of ferromagnetism in nonmagnetic perovskite structure materials can be achieved by doping of transition metals [**15**]. The aim of the present work is to incorporate transition metals and other dopants in BTO to achieve a multi-functional material. In the present work, bi-metallic (Co and Nb) doped $BaTiO_3$ thin films were deposited by RF sputtering and followed by annealing at 900 ºC. The structural and magnetic behavior of the as-deposited and annealed films were studied and compared. The room temperature ferromagnetism in the film was observed by the study of magneto-optic Kerr measurement and VSM analysis. Hence, the reported Co and Nb co-doped $BaTiO_3$ is considered to be a promising material for the spintronic and multiferroic applications.

Experimental

The reported $BaTiO_3$ and Co, Nb co-doped $BaTiO_3$ thin films were prepared by 13.56 MHz radio frequency (RF) magnetron sputtering using a BOC Edwards TF 600 coating system. The films were sputtered in an argon atmosphere from a sintered $BaTiO_3$ ceramic target (Ø = 76.2 mm, purity 99.99 %). Three pieces of Co and Nb

pellets, respectively, were placed on the race track (erosive zone) of the $BaTiO_3$ target for doping. Prior to the sputtering process, the deposition chamber was evacuated to a base pressure of 10^{-4} Pascal by using a turbomolecular pump. Corning glasses and Si (100) wafers were used as substrates for the film coating. Before loading into the chamber, all the substrates were cleaned ultrasonically in acetone and then etched for 30 min in RF discharge in the chamber. Depositions were carried out under the following conditions: constant discharge power P_d= 400 W, argon pressure p_{Ar}= 0.6 Pa, argon flow $Ø_{Ar}$ = 5 sccm, substrate temperatures T_S = 350°C. Then, the as-deposited films were annealed in vacuum at 900 ºC in order to get crystalline films. The thicknesses of the films were found to be in the range from 600 - 700 nm from the height profile measurement.

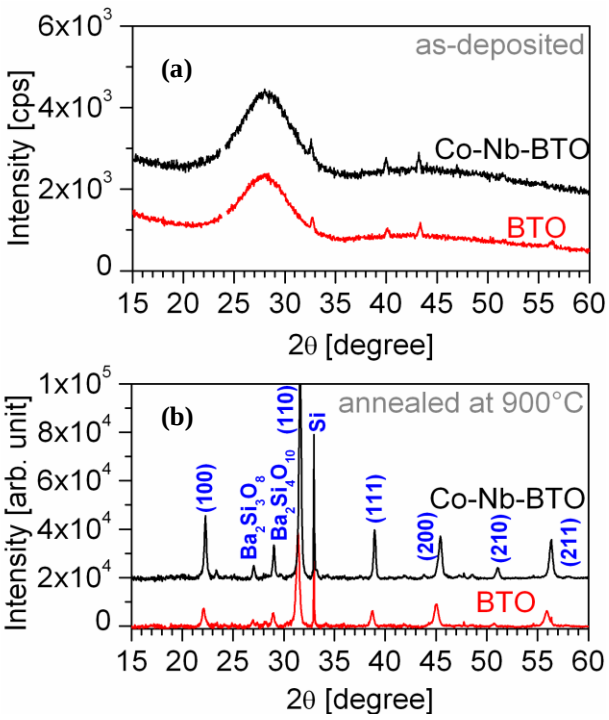

Fig. 1. X-ray diffraction patterns of, a) as-deposited and b) annealed (900 ºC) films of pure $BaTiO_3$ and Co, Nb co-doped $BaTiO_3$ on Si substrates.

The crystalline nature of the thin films was studied by the X'Pert Pro (PANalytical) X-ray diffractometer using CuK_α radiation (λ=0.154 nm). The dopant concentration and distribution of elements in the films were analysed by energy dispersive X-ray spectroscopy (EDX) using SEM (JEOL JSM-7600F) equipped with EDX (X-Max, Oxford Instruments). The magnetic properties of the both as-deposited amorphous and annealed crystalline films were studied by using vibrating sample magnetometer (VSM, Microsense EV9). The Magneto-Optic Kerr Effect (MOKE) analysis was applied for measuring the hysteresis loops, where the magneto-optic (MO) angle of Kerr rotation is depicted as a function of the applied external magnetic field generated in the film plane. As a light source, we used red laser diode at a wavelength of 670 nm, for which the films are transparent. The Kerr rotation was obtained for s-polarized incident light at the angle of incidence of 40°. Both in-plane magnetization components (longitudinal – parallel to the applied magnetic field, transversal – perpendicular to the applied magnetic field) are distinguished by simultaneous rotation of the sample and magnetic field by 90° [**16**].

Results and discussion

The X-ray diffraction patterns of the as-deposited and annealed (at 900 ºC) films are illustrated in **Fig. 1a** and **Fig. 1b**, respectively. In **Fig. 1a**, the XRD patterns of both the pure and doped films consist of a broad characteristic hump of the amorphous BTO phase. The XRD pattern shows that the as-deposited (at 350 ºC) films are amorphous with the tendency of some crystalline phase formation. The reason for the amorphous nature at such a low temperature is based on the growth method, temperature and the nature of materials. The incorporation ferromagnetic transition metal ion such as Fe, Co and Ni significantly increases the signal intensity of the background. It is also considered to be an evidence, for the presence of ferromagnetic metal ions which confirmed by the XRD analysis [**17**]. According to the standard reference JCPDS: 01-075-0212 data, the X-ray diffraction patterns of both the pure and Co, Nb co-doped BTO (annealed at 900 ºC) confirm the typical cubic perovskite structure of the $BaTiO_3$. In addition, the peak of the Co, Nb co-doped BaTiO3 is slightly shifted to higher angle than the pure $BaTiO_3$ due to internal strain. The peak position at angles 27.1º and 29.1º refers to the $Ba_2Si_3O_8$ (JCPDS: 00-006-0206) and $Ba_2Si_4O_{10}$ (JCPDS: 01-083-1446) phase formation, respectively at the interface between the Si substrate and $BaTiO_3$ film during annealing at a higher temperature at 900 ºC. Also, the peak at 33º refers to the Laue diffraction from Si substrate.

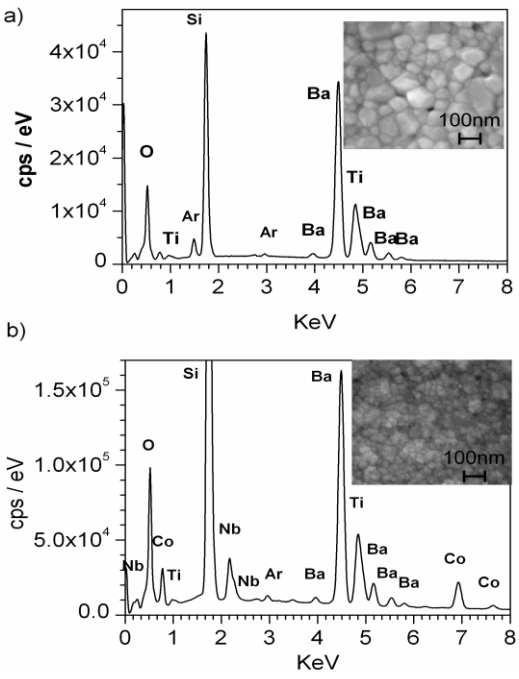

Fig. 2. EDX spectra of, a) pure $BaTiO_3$ and b) Co, Nb co-doped $BaTiO_3$ on Si substrates.

Fig. 2 shows the energy dispersive X-ray spectroscopy (EDX) from SEM, which confirms the existence and concentration of the Ba, Ti, O, Co and Nb elements in the film. The concentration of Co and Nb was found to be 6.5 and 3.5 at. %, respectively. In addition, the presence of Si, Ar and Al are observed due to substrate, trapped argon ions and pile up from the aluminium in the microscope, respectively. The inset in **Fig. 2**(**a**, **b**) are the SEM micrographs of the annealed films of the pure BTO and the Co, Nb co-doped BTO, respectively. The bulk hysteresis loop of the as-deposited and annealed films was studied by VSM analysis with an applied magnetic field of 20 kOe as shown in **Fig. 3**.

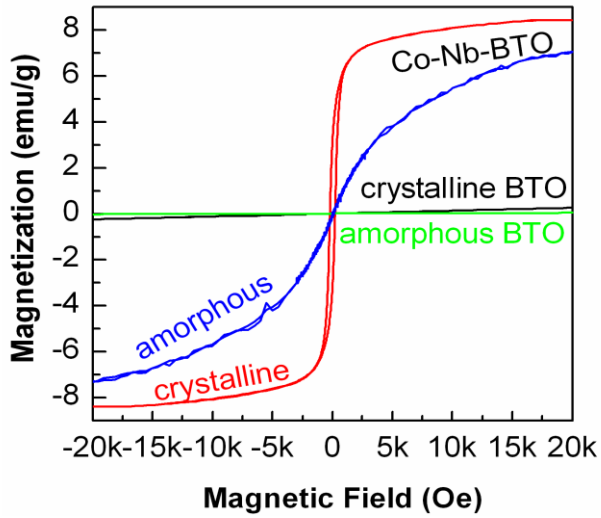

Fig. 3. VSM hysteresis of pure $BaTiO_3$ and Co, Nb co-doped $BaTiO_3$ films on Si substrates.

Table 1. Basic magnetic parameters obtained from the VSM and MOKE hysteresis loops. M_s – saturation magnetization, M_r – remnant magnetization, H_c – coercive field.

Sample	VSM			MOKE		
Co-Nb -BTO	M_s [emu/g]	M_r [emu/g]	H_c [Oe]	M_s [mrad]	M_r [mrad]	H_c [Oe]
as-deposited	7.29	0.022	3.81	0.028	0.001	12.3
annealed	8.40	3.197	206	0.299	0.155	228

It was found that the pure BTO exhibits paramagnetic behavior both in amorphous and crystalline phase, but the paramagnetism increases slightly for the crystalline BTO film. But, the amorphous and annealed films of the Co, Nb co-doped BTO exhibit ferromagnetism at room temperature. The saturation magnetization, remnant magnetization and coercive field of the as-deposited Co, Nb co-doped BTO was found to be M_s = 7.29 emu/g, M_r = 0.022 emu/g and H_c = 3.8 Oe, respectively. In another case, the coercive field and remnant magnetization of the annealed (at 900 ºC) Co, Nb co-doped BTO film increases largely. The increase of saturation magnetization, coercive field and remnant magnetization (see **Table 1**) are connected to the fact that, the anisotropy increases (increase of localized spin majority) in the poly crystalline film structure rather than in the amorphous. In the case of as-deposited Co, Nb co-doped BTO film, the magnetic moment arises due to the isolated Co ions embedded in the BTO clusters. Also, it is obvious that the pure BTO exhibits paramagnetic behaviour both in amorphous and crystalline phase, but the paramagnetism increases slightly for the crystalline BTO film.

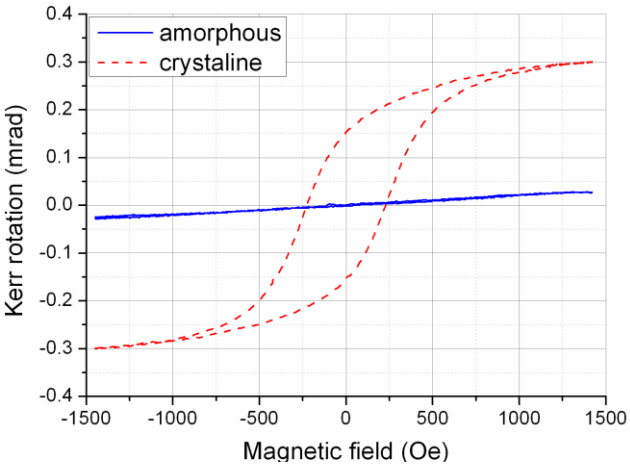

Fig. 4. MOKE hysteresis loop of the as-deposited and annealed (900 ºC) thin films of Co, Nb co-doped $BaTiO_3$ on Si substrates.

In addition, the magneto-optic Kerr effect (MOKE) measurements were performed over the as-deposited and annealed (900 ºC) films coated on silicon substrates. In the case of pure $BaTiO_3$ films, the MOKE responses were not observed and the hysteresis loop was overlapped by the noise. Whereas, the Co and Nb co-doped $BaTiO_3$ films exhibit significant magnetic responses from the MOKE measurements presented in **Fig. 4**. The plot shows the surface hysteresis loops of as-deposited (amorphous) and annealed (crystalline) Co, Nb co-doped BTO films. In the amorphous sample a weak spin-orbit interactions are responsible for low magneto-optical response (hundredths mrad), in accordance with the VSM the MOKE loop is saturated at magnetic field higher than 1500 Oe. Hysteresis loop of annealed film visibly differs in the shape. While the value of MOKE coercive field (228 Oe) is well comparable with the VSM value (206 Oe) the ratio of the remnant and saturation magnetization (MOKE = 0.52, VSM = 0.38) is higher at the MOKE experiments. Such behavior can be explained by the fact that MOKE detects the information only from the local area determined by the laser spot (diameter about 300 μm) and penetration depth (film thickness), while the VSM measures the magnetization averaged over the sample volume. Therefore, each grain exhibits its own magnetic anisotropy with (slightly) different orientation of the easy magnetization axis. We also proved the existence of the strong in-plane longitudinal magnetization component and its isotropic behavior during rotation of the sample. On the other hand, very low transversal and no polar (out-of-plane) magnetization contributions have been detected. Hence, the room temperature ferromagnetism in this material is considered to be ideal for spintronics, magneto-optic and other magneto-electric tunable applications.

Conclusion

Thin film based on BTO with saturation magnetization of 8.4 emu/g was achieved by sputtering with annealing at 900 ºC. The amorphous and cubic perovskite phases were observed in the as-deposited and annealed films,

respectively. The room temperature ferromagnetism was observed in Co, Nb co-doped $BaTiO_3$ films by using VSM and MOKE experiments. The magnetic properties of the Co, Nb co-doped $BaTiO_3$ films were enhanced by crystallization (annealing at 900 ºC). The saturation magnetization, remnant magnetization and coercive field of the Co, Nb co-doped BTO films annealed at 900 ºC was found to be M_s = 8.4 emu/g, M_r = 3.197 emu/g, and H_c = 206 Oe, respectively. Slightly different results between the MOKE and VSM measurements are due to the local sensitivity of MOKE determined by the laser spot diameter and penetration depth of incident light. The increase of magnetization in the crystalline samples is considered as the increase of anisotropic magnetic moment in the films, whereas the under-saturated magnetization observed in the amorphous film causes the isolated Co ions.

Future extension and prospective

The detailed and in-depth magnetic studies of the reported materials will be studied using functional magnetic resonance (FMR) and X-ray magnetic circular dichroism (XMCD) analyses in near future. Also, the other multifunctional properties like ferroelectric, dielectric, ferroelastic properties, etc. will be studied.

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