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Irradiation Effects on Microstructure and Dielectric Properties of $Ba[(Mg_{0.32}Co_{0.02})Nb_{0.66}]O_3$ [BMCN] Thin Films

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$Ba[(Mg_{0.32}Co_{0.02})Nb_{0.66}]O_3$ [BMCN] thin films prepared on Pt-Si, MgO, Silicon and ITO coated glass substrates by Pulsed Laser Deposition Technique are investigated. Relative growth parameters suggest that ITO coated glass substrate has good potential for growing films with near Nano size columnar grains. In comparison to bulk, dielectric constant and dielectric loss increases in BMCN films. This undesirable rise in dielectric loss can be drastically reduced by a factor of more than 1/100th times through Ag^{15+} ion irradiation at 1×10^{12} ions/cm^2 dose.

Keywords: Microstructure and dielectric properties, Thin films, SHI irradiation.

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1. INTRODUCTION

In recent years, modern electronic device industry, area of microwave communication is increasingly looking for nonlinear dielectric materials in thin film form. They permit miniaturize microwave devices such as duplex filters, down converters and voltage-controlled oscillators as well as it also helps in developing new frequency tunable microwave devices. The complex oxide $Ba(B'_{1/3}B''_{2/3})O_3$ constitutes a special family of perovskite. This series of compounds were first prepared by Roy and Galasso in the 1950s, and found to possess a 1:2 ordered superstructure for B' and B" atoms in a Hexagonal lattice. Attempts were made by previous investigators to correlate an increase of its Q values with an increase of Hexagonal ordering in these ceramics. Majority of earlier research work on these compounds are carried out with bulk materials [1-6]. However, materials in thin film form are of importance in the integration of related microwave components into microelectronic systems. Further, the dielectric properties of ferroelectric thin films are pronouncedly different from that of bulk. The Lead based perovskite systems are well suited for the applications but due to its toxicity and fatigue ness a lot of research is undergoing towards the environment friendly compositions with Barium, Bismuth, Strontium or Calcium based layered perovskites structures [7, 8]. The appropriate substrate to the dielectric oxides drastically improves the fatigue property of ferroelectric/dielectric thin films. At present most of the films are grown on the relatively expensive single crystals in order to get the epitaxial growth. In recent times efforts are on to grow the non epitaxial films of the desired structure by choosing the appropriate parameters. Si, MgO or ITO are the cost-effective substrates [9]. Recently, we have reported $Sr[(Mg_{0.32}Co_{0.02})Nb_{0.66}]O_3$ [SMCN] non-polar thin films, on ITO coated glass substrate which exhibits promising enhancement in low frequency dielectric constant values and lower (T_m) compared to bulk [10]. The SMCN films showed two step activation energy around 70 °C, which is technologically useful for switching device applications.

SHI irradiation provides several interesting and useful aspects in understanding the damage and material modifications [11]. The effect of the energetic ion beam depends on ion energy, fluence and ion species. It is evident that the electronic energy loss, S_e, due to inelastic collision is able to generate the point/clusters defects, if the S_e is less than the threshold value of the electronic energy loss. But it produces columnar or amorphization of materials, if S_e is higher than the S_{th} [12]. In addition, it is known that SHI produces the strain/stress in the oxides films [13, 14].

In the present study, we have prepared thin films of polar dielectric materials BMCN and studied its growth characteristics on different substrates. The irradiation effects of the 200 MeV Ag^{15+} and 100 MeV O^{7+} ion beams on BMCN films dielectric properties are reported here.

2. EXPERMENTAL DETAILS

Single Phase $Ba[(Mg_{0.32}Co_{0.02})Nb_{0.66}]O_3$ [BMCN] targets were prepared by standard solid state reaction technique. These targets are used to prepare BMCN thin films by Pulsed Laser Deposition (PLD) technique using a pulsed KrF excimer laser (248 nm, in wavelength, with a beam fluence of about 220 mJ/cm^2 and a repetition rate 10 Hz). The bulk target were mounted in a deposition chamber which was subsequently evacuated to a base pressure of $\sim 5 \times 10^{-5}$ Torr. The pressure of the flowing ambient oxygen was 200 mTorr. The films were deposited on various substrates such as

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Pt-Si, Si (111), MgO (001) and ITO coated glass substrates at varing substrate temperatures. The BMCN films on Si, Pt-Si and MgO were deposited at 450 °C substrate temperature while on ITO coated glass substrate at 300 °C. The BMCN thin films were characterized by 3 kW X-ray generator with Cu target θ-2θ Goniometer with LiF monochromater in diffracted beam arm. The thickness of all the films is around 100-200 nm as measured by stylus Profilometer. The well characterized film were irradiated at room temperature with 200 MeV Ag^{15+} and 100 MeV O^{7+} ions at fluence of 1×10^{11}, 1×10^{12}, 1×10^{13} ions/cm^2 using a 15 UD tandem accelerator at the Nuclear Science Centre, New Delhi, India. The beam current was kept around 0.5-1 pnA for Ag^{15+}, and O^{7+} to avoid heating. The ion beam was focused to a spot of ~ 1 mm diameter and scanned over the entire area of the thin film using a magnetic scanner. The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. The thin film morphology on a wide range of scan lengths (500 μm to 1 μm) was investigated by atomic force microscopy (AFM) using Nan scope-E from Digital Instruments, USA. A 100 μm Si_3N_4 cantilever with a spring constant of ~ 0.57 N/m is used and the images were taken in contact mode. Dielectric constant measurement were measured using a Agilent 4285 A (LCR) bridge which has a frequency range of 75 kHz to 30 MHz and operated in the temperature range 100 K to 450 K.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

Figure 1 shows the XRD pattern of BMCN films deposited on different substrates along with the bulk. No impurity phase is detected in the films. It confirms the single phase nature of the films and matches well with the bulk targets. The substrates Si, MgO and ITO coated glass substrates are single crystals with cubic lattice and films have hexagonal symmetry- noting also that the different Symmetries do not preclude epitaxy to occur.

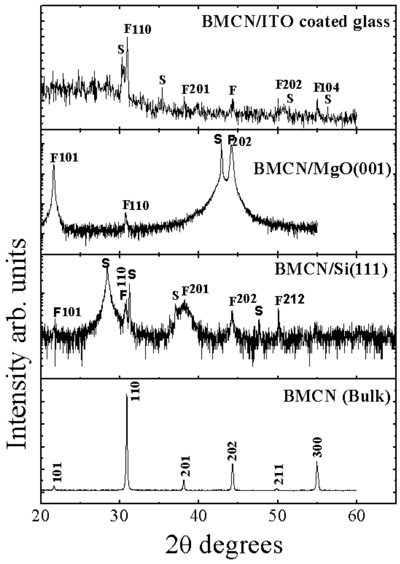


Fig. 1 – X-ray diffraction pattern of unirradiated BMCN bulk, Si, MgO and ITO coated glass substrates

The lattice parameters calculated from the standard Powder X Program [15] shows that there is a marginal increase in the lattice constant values of films compared to bulk. The XRD peaks shift by a small increment towards lower 2θ side in the case of films grown on Si and MgO substrates while on ITO substrates, peaks shift towards higher 2θ side.

We calculated the grain size (D) of the film for (110) peak using the Debye-Scherrer formula given by [16]

$$D = \frac{0.94 \cdot \lambda}{B \cos\theta} \tag{1}$$

Here λ is the wavelength of the x-ray source and B the full width at half maximum (FWHM) of an individual peak at 2θ (where θ is the Bragg angle).

The lattice strain (T) in the material causes broadening of diffraction peak, which can be represented by the relationship

$$T \tan\theta = \left(\frac{\lambda}{D \cos\theta}\right) - B \tag{2}$$

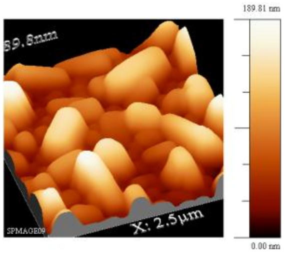
These calculated parameters are tabulated in Table 1. It is clear from Table 1 that the film deposited on ITO coated on glass substrate, has maximum FWHM values (lowest D). We observe maximum strain in the film deposited on ITO. Previous literature study reveals that strain/stress has pronounced effects on the electrical properties of the films.

Table 1 – XRD peak and AFM analysis of BMCN films on Si, MgO and ITO coated glass substrates

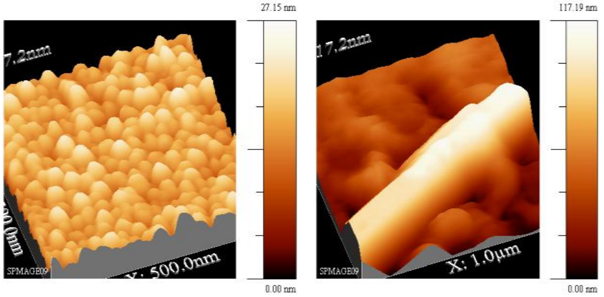
Compositions	Grai Size (nm)	Strain	Lattice Constant (nm)	Rough ness (nm)	Irradiated Rough ness (nm)
BMCN-Bulk	425	1.1×10^{-3}	$a = 0.578$ $c = 0.707$	-	-
BMCN-MgO	459	7.5×10^{-4}	$a = 0.581$ $c = 0.708$	27.81	10.50
BMCN-Si	344	9.0×10^{-4}	$a = 0.581$ $c = 0.708$	2.89	4.07
BMCN-ITO	74	4.7×10^{-3}	$a = 0.579$ $c = 0.708$	2.56	6.68

3.2 Microstrucutal analysis

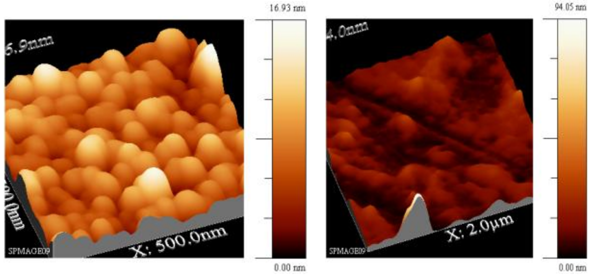
Figure 2 shows the AFM images growth characteristics of the BMCN films on different substrates. We observe uniform columnar grain formation on Si, Pt-Si and ITO films, while on MgO we do not notice any grains formation. Average tip size on each substrates are found to be ~ 100 nm (Pt-Si), 20-25 nm in Si and ~ 50 nm in case of ITO coated on glass substrate films. From the XRD analysis it is observed that films grown on ITO has higher strain compared to others and its grain size roughly matches with the AFM images. MgO substrates show poor grain formation. Though Pt-Si shows large grains but with arbitrary orientation and absence of any columnar packing of grains. Further, Si substrate shows good grain growth but with moderate strain and roughness. Analysis of growth characteristics from AFM and XRD measurement reveal that films grown on ITO are relatively better compared to Si, MgO or Pt-Si for electrical parameters studies and device application. Further, on irradiating BMCN films with Si and MgO substrate (Fig. 2b' and c') we observe large scale amorphization, variations in roughness and track formation. BMCN films on ITO substrate though show some agglomeration but columnar grain growth is still maintained even after irradiation by Ag^{15+} (1E12) fluence.



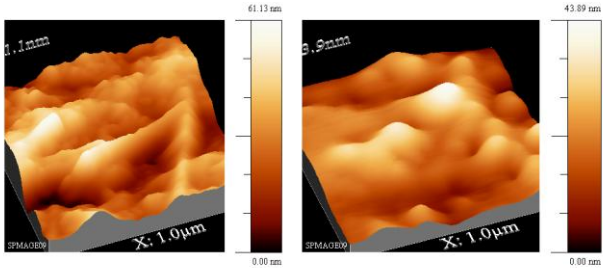
(a) Pt-Si



(b) Si (c) MgO



(d) ITO coated (b')
Si–Irradiatedglass substrate



(c') MgO- Irradiated (d') ITO Irradiated

Fig. 2 – AFM images of BMCN films on different substrates before and after irradiation by Ag^{15+} (1E12) fluence

3.3 Dielectric measurements

Figure 3 shows the temperature dependence of the dielectric constant of unirradiated, Ag^{15+} and O^{7+} irradiated films at 300 KHz frequency. Growth parameters can be directly tested on the dielectric response of the films. Further, SHI irradiation can help in modulating lattice strain which can alter dielectric loss as well as dielectric constant of the film. In the present study the dielectric constant (ε'), dielectric loss (tanδ) and T_ε(TCK) are investigated as a function of temperature for BMCN films. The samples irradiation results are reported only for the highest fluence. We observe linear temperature dependence of dielectric constant for unirradiated and irradiated samples. The unirradiated film shows abrupt rise in the magnitude of dielectric constant compared to that of bulk which on correlating with our XRD results indicate that the drastic rise in dielectric constant in the film is mainly due to strain rather than lattice mismatch as there is marginal increase in the value of lattice constant of film compared to bulk.

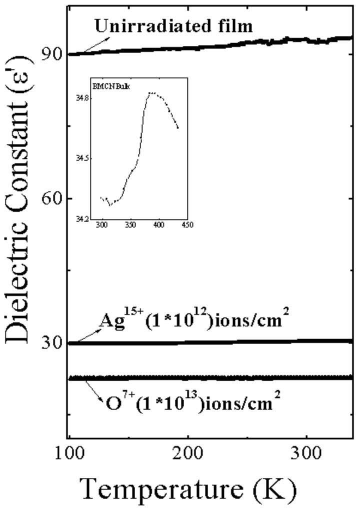


Fig. 3 – Temperature dependence of dielectric constant of BMCN sample in range 100 K-350 K at 300 KHz for unirradiated, and Ag15 + and O7 + irradiated films

The present studies indicate that in these materials irradiating the films with either of the beams exhibit reduction in the magnitude of dielectric constant. Values decrease much more drastically for O^{7+} irradiated films compared to Ag^{15+}. The drastic fall in values is dictated by the type of defects created in the films along the latent tracks. Normally silver ion beam produces points/columnar defects while O^{7+} beams produces amorphization of materials during its passage.

By the study of evolution of ε' as a function of temperature it is possible to calculate the temperature coefficient of dielectric constant, T_ε, defined as:

$$T_\varepsilon = \left(\frac{\tan\alpha}{\varepsilon_{20}}\right)\times 10^6 \left(\frac{ppm}{^\circ C}\right) \qquad (3)$$

where $\tan\alpha$ is the slope of the $\varepsilon(T)$ curve ($\tan\alpha = \Delta\varepsilon/\Delta T$) and ε_{20} is the value of ε at 20 °C (a conventional reference value). For the BMCN compounds the ε (T) has a linear dependence along the entire range. The calculated values of T_ε for all studied compounds are in the range of +300-3 ppm/ °C. From the table II we find that by irradiating with O^{7+} beam at highest fluence of 1×10^{13} ions/cm^2, the absolute value of T_ε decreases to a very low value, nearly zero temperature coefficients. In comparison to unirradiated and Ag^{15+} irradiated films a drastic fall in the value of TCK is observed in oxygen irradiated films.

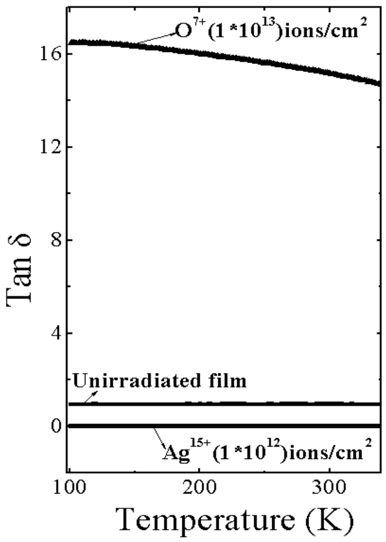


Fig. 4 – Variation of tanδ vs. temperature at 300 kHz for pristine, Ag^{15+} and O^{7+} irradiated films

Figure 4 represents the dielectric loss parameter (tanδ) for pristine, Ag^{15+} and O^{7+} irradiated films at 300 kHz with temperature. We observe nearly temperature independent dielectric loss for unirradiated and Ag^{15+} irradiated films while for O^{7+} irradiated film it shows drastic rise. Ag^{15+} ion irradiation reduces the dielectric loss to the order of 10^{-3}

4. CONCLUSIONS

The BMCN thin films deposited on different substrates shows that the growth formation on the ITO coated on the glass substrates films is relatively better. We observe marginal shift in the lattice parameters, but large tensile strain in ITO films is the reason behind the larger values of dielectric constant in film compared to bulk. After irradiation there is marginal degradation of dielectric constant values but we observe minimal losses in Ag^{15+} irradiated films compared to O^{7+}. Comparing the overall effects of irradiation on films dielectric response, it is inferred that Ag^{15+} irradiation is more helpful then O^{7+} irradiation. This is mainly due to the fact that Ag^{15+} irradiation is more effective in reducing lattice strain induced dielectric losses due to type of defects it created, though marginal loss of dielectric constant as well as TCK do take place. The values still lie in the useful range of parameters for microwave device applications.

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