$BiFeO_3$ THIN FILMS – STRUCTURAL AND DIELECTRIC PROPERTIES

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ABSTRACT: *Bismuth iron oxide ($BiFeO_3$) belongs to the class of multiferroic materials that exhibit the simultaneous presence of ferromagnetic and ferroelectric properties at room temperature. But, synthesis of phase pure $BiFeO_3$ is extremely difficult due to volatile nature of Bi_2O_3. In addition, the temperature reported for synthesis of pure phase $BiFeO_3$ is reported in the range of 400-700˚C. We here report synthesis of phase pure bismuth iron oxide thin films using sol-gel method at a low temperature of 300˚C. The films are studied under as-deposited and 200˚C and 300˚C anneal conditions. X-ray Diffraction results indicate the formation of pure phase $BiFeO_3$ at 300˚C. Under as-deposited conditions, bismuth impurity phase is observed and this phase persists as the films are annealed at 200˚C. Crystallite size increases from 26.5 nm to 38.69 nm with increase in annealing temperature. Dielectric constant shows dispersion in low frequency region and becomes constant at high frequencies. The dielectric constant increases from 6.75 to 125 as the films are annealed at 200˚C and 300˚C with low dielectric loss of 0.00277*

1. INTRODUCTION

Multiferroic materials are compounds that exhibit antiferroic or ferroic (e.g. ferromagnetic, ferroelastic) properties [1, 2]. Amongst such materials, the one that exhibit simultaneous presence of ferromagnetic / antiferromagnetic and ferroelectric / antiferroelectric properties are known as magnetoelectric materials. In such materials magnetization can be induced by application of external electric field and vice versa [3]. The coupling between ferromagnetic and ferroelectric properties makes them a potential candidate for data storage and spintronic devices [3, 4].

But, there are only few materials that show both ferromagnetic and ferroelectric properties at or above room temperature. Among various multiferroic materials, bismuth iron oxide ($BiFeO_3$) is promising because of its high ferroelectric and magnetic ordering temperatures. $BiFeO_3$ has rhombohedrally distorted perovskite structure. The lattice parameters of rhombohedral unit cell are a=5.56Å and α=59.35˚ [5, 6]. The equivalent hexagonal lattice parameters are a=5.59Å and c=13.869Å. $BiFeO_3$ belongs to R3c space group [5]. $BiFeO_3$ shows G-type antiferromagnetic ordering with Neel temperature of 370˚C. It also exhibits ferroelectric properties with Curie temperature of 810˚C [7, 8].

Despite the advantages of $BiFeO_3$, mixing and heating of stoichiometric ratio of bismuth (Bi) and iron (Fe) does not result in pure $BiFeO_3$ phase. Non-stoichiometric phases like $Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$ are more likely to be formed as compared to the desired $BiFeO_3$ phase. These phases have adverse effect on insulating properties thus result in high leakage current. This, in turn, deteriorates the ferroelectric properties.

For overcoming this difficulty, we here report the structural and dielectric properties of bismuth iron oxide thin films prepared using sol-gel method. The films were studied under as-deposited and 200˚C and 300˚C annealed conditions.

2. EXPERIMENTAL DETAILS

Bismuth iron oxide thin films were prepared using sol-gel method. Bismuth nitrate ($Bi(NO_3)_3.5H_2O$) and iron nitrate ($Fe(NO_3)_3.9H_2O$) were used as precursors. Bismuth nitrate and iron nitrate were separately dissolved in ethylene glycol and stirred at room temperature. The two solutions were mixed together and heated on hot plate to obtain bismuth iron oxide sol. The details of sol-gel synthesis are reported earlier [9, 10]. The sols were spin coated on copper substrate and annealed at 200˚C and 300˚C for 60min. Prior to use, 1cm×1cm copper substrates were etched using diluted HCl and then placed in ultrasonic bath in acetone and isopropyl alcohol for 10 mins and 15mins respectively [11, 12].

The films were characterized structurally using Bruker D8 Advance X-ray Diffractometer. Dielectric studies were carried out using 6500B Precision Impedance Analyzer.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of bismuth iron oxide thin films prepared using sol-gel method under as-deposited, 200˚C and 300˚C annealed conditions. The presence of diffraction peaks corresponding to planes (024), (122) and (315) indicate the presence of $BiFeO_3$ under as-deposited conditions. The presence of diffraction peaks at 2θ˚=60.8˚ and 71.8˚ corresponding to planes (422) and (610) respectively indicate that bismuth rich phase is present in the films under as-deposited conditions. So, the films were annealed at 200˚C for 60mins. It can be seen in Fig. 1(b) that the contribution from bismuth rich phase decreases. But annealing at 200˚C does not completely eliminate the bismuth rich phase. Annealing at 300˚C completely eliminated the bismuth rich phase thus resulting in formation of phase pure $BiFeO_3$.

Crystallite size (t), strain ($\Delta d/d$) and dislocation density (δ) [13, 14] of bismuth iron oxide thin films were calculated using Eqs. (1)-(3).

$$t = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

$$Strain = \frac{\Delta d}{d} = \frac{d_{\exp} - d_{pdf}}{d_{pdf}} \quad (2)$$

$$\delta = \frac{1}{t^2} \quad (3)$$

Where, λ is the wavelength (1.5406Å), B is the Full Width at Half Maximum (FWHM), d_{exp} is the d-spacing calculated

Table 1: Structural properties of bismuth iron oxide thin films

Sample conditions	Crystallite size (nm)	Dislocation density (10^{14} lines/m^2)	Strain (10^{-3})	Lattice constant (Å)		Unit cell volume (Å^3)	X-ray density (g/cm^3)	Porosity (%)
				a	c			
As-deposited	26.54	14.19705	18.236	5.48167	14.025	364.9611	8.530465	8.525
200˚C anneal	32.58	9.421018	12.697	5.50437	13.999	367.3078	8.475964	5.362
300˚C anneal	38.69	6.680401	5.256	5.58	13.965	376.554	8.267839	2.697

from XRD pattern and d_{pdf} is the d-spacing taken from JCPDS card.

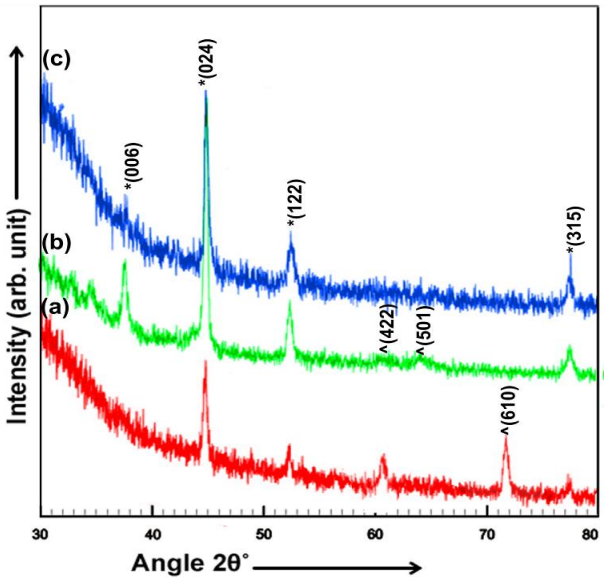

Fig. 1 XRD patterns for bismuth iron oxide thin films (a) as-deposited (b) 200˚C annealed and (c) 300˚C annealed

Lattice parameters (*a*, *c*), X-ray density (ρ) and porosity of bismuth iron oxide thin films were calculated using Eqs. (4)-(6) [13].

$$\sin^2\theta = \frac{\lambda^2}{3a^2}\left(h^2 + k^2 + hk\right) + \frac{\lambda^2 l^2}{4c^2} \qquad (4)$$

$$\rho = \frac{1.66042\Sigma A}{V} \qquad (5)$$

$$Porosity(\%) = \left[1 - \frac{\rho_{\exp}}{\rho_{std}}\right] \times 100 \qquad (6)$$

Where, *(hkl)* represent the miller indices, ΣA is the sum of atomic weights of the atoms in the unit cell, *V* is the volume of unit cell (V=0.866a^2c), ρ_{exp} is the experimental density (calculated using Eq. (5)), ρ_{std} is bulk density of bismuth iron oxide.

Structural properties of bismuth iron oxide thin films are listed in Table 1. Crystallite size increases from 26.5 nm to 38.69 nm as the annealing temperature was increased to 300˚C. This increase in crystallite size is attributed to Ostwald ripening mechanism. The decrease in dislocation density from 14×10^{14} to 7×10^{14} lines/m^2 is attributed to decrease in number of grain boundaries as the crystallite size had increased. In addition, the crystallite size in thin films also depends on: 1) Strain. Decrease in strain was observed as grain size increased. 2) Neighboring grains that have different energies due to curvature of energetic grain boundaries. Lattice parameters and unit cell volume of the films annealed at 300˚C are equal to those reported in literature indicative of phase pure $BiFeO_3$. High density (8.3-8.5g/cm^3) and low porosity (2.7-8.5%) of the films is indicative of compact structure of the films.

For studying the dielectric properties of $BiFeO_3$ thin films impedance analyzer was used in parallel plate configuration. The parallel capacitance and parallel resistance were measured and then using Eq. 7 and Eq. 8 the dielectric constant ε and dielectric loss (tangent loss tan δ) were calculated.

$$\varepsilon = \frac{C \times d}{\varepsilon_O \times A} \qquad (7)$$

$$\tan\delta = \frac{1}{2\pi\varepsilon\varepsilon_O\rho} \qquad (8)$$

Where, *C* is the capacitance, *d* is thickness of the specimen, *A* the area of the device, ε_o is the permittivity of free space and ρ is the resistivity of the thin films. Dielectric constant shows dispersion in low frequency region and becomes constant at high frequencies. Dispersion arises because the space charge carriers that are present in the sample require some time to get aligned in the direction of the externally applied field. However, with the increase in frequency of field the space charge carriers don't get enough time to get aligned in the direction of field before the field is switched again so at high frequencies they take no part in polarization and in turn give steady dielectric constant. The dielectric constant increased from 5.7 under as-deposited conditions to 6.75 and then to 125 (at 1kHz) as the films were annealed at 200˚C and 300˚C. The increase in dielectric constant is attributed to phase purity of bismuth iron oxide thin films as the annealing temperature was increased.

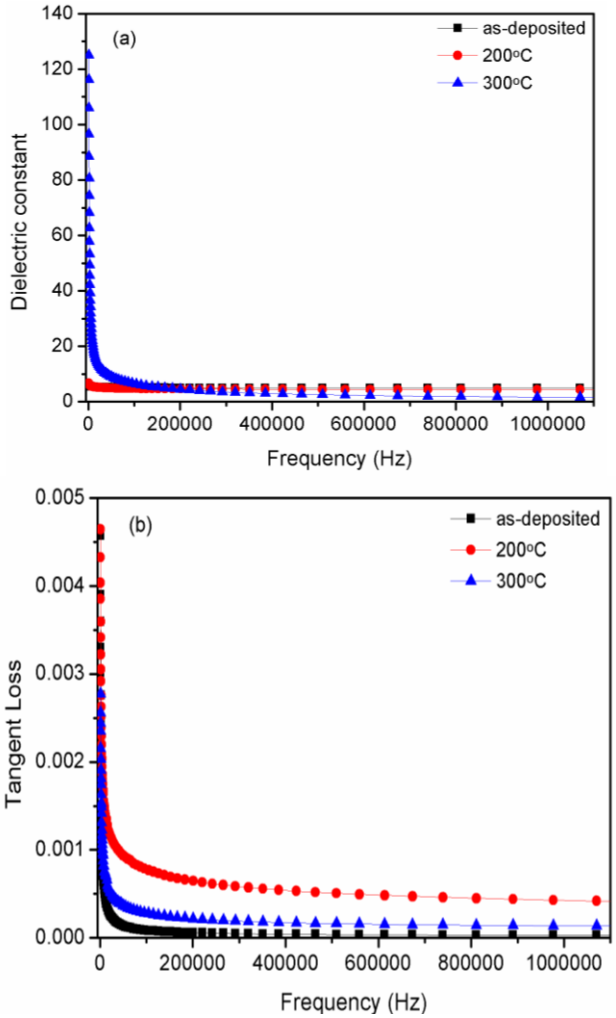

Fig. 2 (a) Dielectric constant (b) tangent loss as a function of frequency

4. CONCLUSIONS

Bismuth iron oxide thin films were prepared using sol-gel method. Structural and dielectric properties of bismuth iron oxide thin films were studied under as-deposited and annealed (200˚C and 300˚C) conditions. Under as deposited conditions, presence of bismuth rich phase along with $BiFeO_3$ was observed. Whereas, bismuth rich phase vanished as the films were annealed at 300˚C. The films showed dielectric constant of 125 with tangent loss of 0.0027 at annealing temperature of 300˚C. Comparatively, low value of dielectric constant and high tangent loss were observed for films under deposited and 200˚C anneal conditions.

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