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Tuning of Optical Properties via Annealing of Bismuth Ferrite ($BiFeO_3$) Thin Films

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Abstract

In this study we are reporting annealing induced optical properties of bismuth ferrite ($BiFeO_3$) thin films deposited on glass substrate via spin coating at 5000 rpm. The structural, optical and surface morphology of $BiFeO_3$ (BFO) thin films have been studied via X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Optical absorption (UV-Vis) and Photoluminescence (PL) spectroscopy. XRD spectra confirm annealing induced phase formation of $BiFeO_3$ possessing a rhombohedral R3c structure. The films are dense and without cracks, although the presence of porosity in BFO/glass was observed. Moreover, optical absorption spectra indicate annealing induced effect on the energy band structure in comparison to pristine $BiFeO_3$. It is observed that annealing effect shows an intense shift in the UV-Vis spectra as diffuse absorption together with the variation in the optical band gap. The evaluated optical band gap values are approximately equal to the bulk band gap value of $BiFeO_3$.

Keywords

Optical Properties, Annealing, Ferroelectrics, Photo Luminescence, BFO Thin Films

1. Introduction

Multiferroic materials exhibit more than one of the ferroic properties like; ferromagnetism, ferro-elasticity and ferroelectricity in the same phase [1] [2]. The current definition of multiferroic also includes the antiferroelectric effect [3]. Multiferroic materials are used to fabricate multifunctional device with a combination of ferroelectric and ferromagnetic effect. The materials, which combine both ferroelectric and magnetic properties are extremely rare and vital for solving a wide variety of problems and are implemented in many applications.

Due to BFO's multifunctionality, the material has been subject of extensive research during the last few years. $BiFeO_3$ is the only single-phase multiferroic that exhibits both highly ferroelectric and ferromagnetic effects simultaneously at room temperature, making it one of the rare multiferroic materials [4], which leads to being considered a good choice for the application in information storage technology [5]-[8]. Bismuth ferrite has not only large remnant polarization (~100 $\mu C/cm^2$) but also narrow band gap within the visible light range which provides good opportunity for increased power conversion efficiency (PCE). Curie temperature (T_c ~ 1103 K) and Neel temperature (T_N ~ 643 K) both are above the room temperature, which is beneficial for applying in multiferroic memory devices and magnetic switch devices in harsh conditions [9] [10].

Annealing is an important technique to thin film fabrication, which can help to enhance the properties of thin films by changing the microstructure and phases. The main purpose of annealing of thin film is to improve its surface quality. Re-crystallization takes place during the annealing process of the thin films which enhances their crystallinity. Thus, residual stress could be modulated and thin film quality could be enhanced with decreased surface roughness and film flaws by annealing the films under optimal conditions [11]-[13]. $BiFeO_3$ thin films have been synthesized by various methods such as: sputtering [14], Pulsed Laser Deposition [15], Molecular Beam Epitaxy [16], Metal-Organic Chemical Vapour Deposition [17], Spin Coating, Sol-Gel (CVD) [18], Spray Pyrolysis [19] methods. The crystallization pathway to form thin films of BFO is quite different. BFO thin films have been grown via numerous methods including physical vacuum-based and chemical-based techniques but each deposition technique has drawbacks. In the present study spin coating has been used for thin films' fabrication. High deposition rate low vacuum facilities are required and thus, relatively simple setup and fast recycling are possible. It is possible to deposit multicomponent alloys and compounds with controlled amount of impurity. The fabricated thin films have been modified with the impact of annealing temperature for the optical and structural characteristics.

2. Experimental

Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ and ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ were taken as raw materials, to synthesize bismuth ferrite nanoparticles via sol-gel method. The precursor solution of bismuth ferrite was prepared by using 2-methoxyethanol and ethanol glycol as solvent and further it was mixed by ultra sonicator for 30 min. The precursor solution was coated using drop by drop on simple glass substrate, with spin coater at 5000 rpm for 25 seconds. After that, the films were dried at 150˚C for 30 minutes in vacuum oven to evaporate the solvent. To get the thin film up to working thickness, the coating and drying process was repeated for several times. The impact of annealing on multilayer films at 200˚C and 500˚C for one hour was executed in a muffle furnace. Figure 1 illustrates the schematic illustration of synthesis and modification of $BiFeO_3$ thin films.

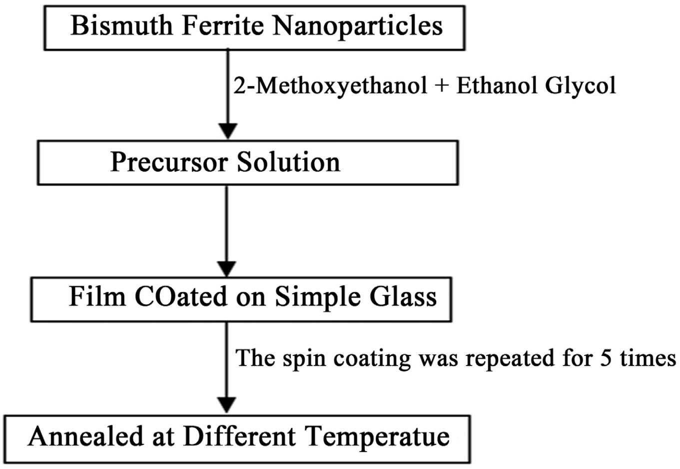

Figure 1. The schematic illustration of synthesis and modification of $BiFeO_3$ thin films.

3. Results & Discussion

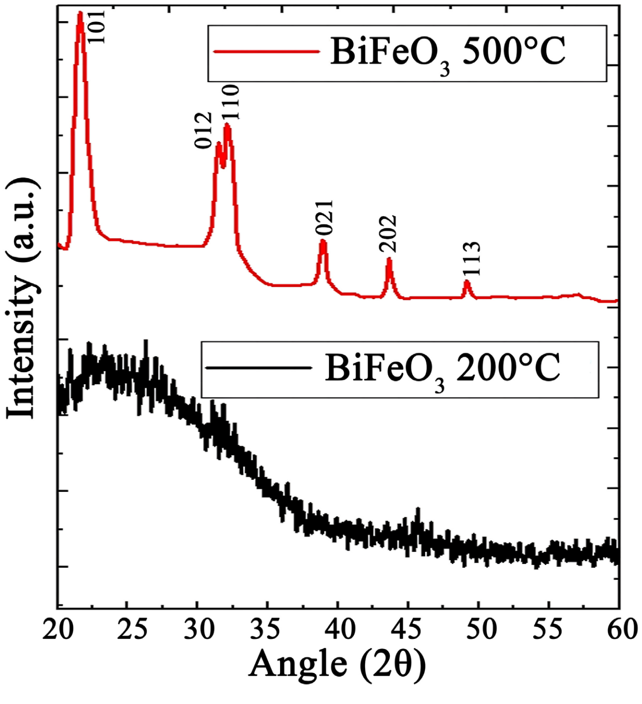

Figure 2. XRD spectra of $BiFeO_3$ thin films annealed at 200˚C and 500˚C temperature.

X-ray diffraction: Figure 2 shows X-ray diffraction pattern of $BiFeO_3$ thin films annealed at temperature of 200˚C and 500˚C. The diffraction peaks in the XRD patterns sharpens and intensifies with increasing annealing temperature, indicating improved crystallinity of the thin films and the disappearance of impurity peaks. When the sample was annealed at 500˚C, the XRD pattern revealed clearly defined diffraction peaks, and the associated d values demonstrated that the films crystallised in the $BiFeO_3$ perovskite structure. The films annealed at 200˚C were amorphous whereas, after annealing at 500˚C a hexagonal crystallized structure was found. The polycrystalline hexagonal structure of annealed $BiFeO_3$ is oriented with preference along the (101) plane. Observations show that when the annealing temperature is increased, the value of (101) peak position at 2θ increases from 21˚ to 22.50˚, approaching the standard value of the bulk BFO sample, 22˚. This indicates that the (101) interplanar spacing of films, d_{101}, gets smaller and approaches the bulk BFO sample's d_{101}. Furthermore, a sharp peak separation between the (012) and (110) peak is found with an increase in the annealing temperature and overlap at lower temperature.

FT-IR spectroscopy: Figure 3 show Fourier-transform infrared (FT-IR) spectra of annealed $BifeO_3$ thin films. It has been noted that the Bi-O and Fe-O groups overlap results in the bands at 633 cm^{-1} and 845 cm^{-1} respectively. The bending vibration of the Fe-O bond within the octahedral unit of the FeO_6 and BiO_6 groups is responsible for these bands [20]. The bending of the Fe-O of the FeO_6 group and the stretching of the O-Fe-O bond were linked to the distinctive peak at 525 cm^{-1}. The FT-IR plots show the reduced depth of vibrations due to annealing might be due to strong bonding between compounds after annealing. The bonds of compounds have been found to be increased due to increased annealing temperature.

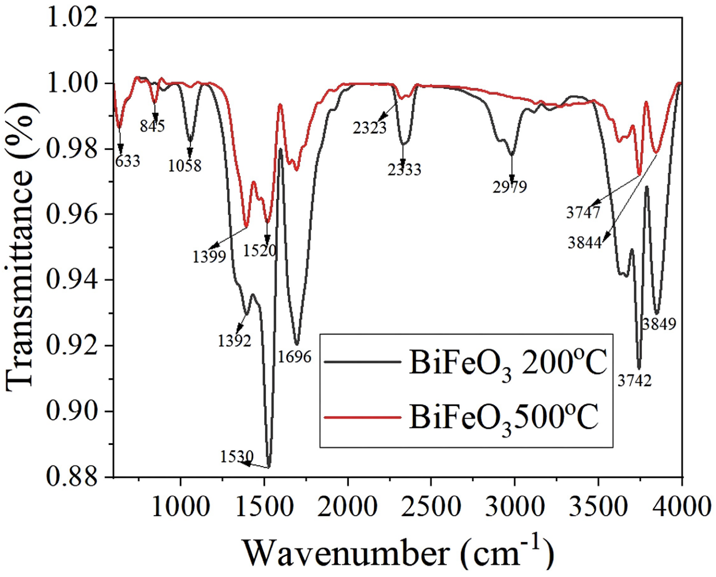

Figure 3. FT-IR spectra of $BiFeO_3$ thin films annealed at 200˚C and 500˚C.

UV-Vis spectroscopy: Annealing treatment can improve the structure and quality of the films, it should also affect the transmittance of the films and therefore change its optical band gap [21] [22]. Figure 4(A) & Figure 4(B) shows the optical absorption spectra with wavelength and Figure 4(C) & Figure 4(D) shows Tauc plots for band gap of annealed $BiFeO_3$ thin films. Band gap reduction is a typical phenomenon observed upon annealing in thin films, and is commonly attributed to either increased crystallisation or the creation of defect states in the forbidden energy band. The optical band gap E_g calculated by tauc's relation.

$$(\alpha h\nu)^2 = h\nu - E_g$$

where, α is absorption coefficient and hν is the incident photon energy. Figure 4 illustrates the plots of $(\alpha h\nu)^2$ with hν for $BiFeO_3$ thin films that were annealed. Band gap value is found to decrease from 2.73 eV to 2.61 eV as the annealing temperature increases from 200˚C to 500˚C. The enhancement in the crystallisation followed by annealing, as shown in the XRD pattern, may be responsible for the decreases in the band gap value after crystallisation.

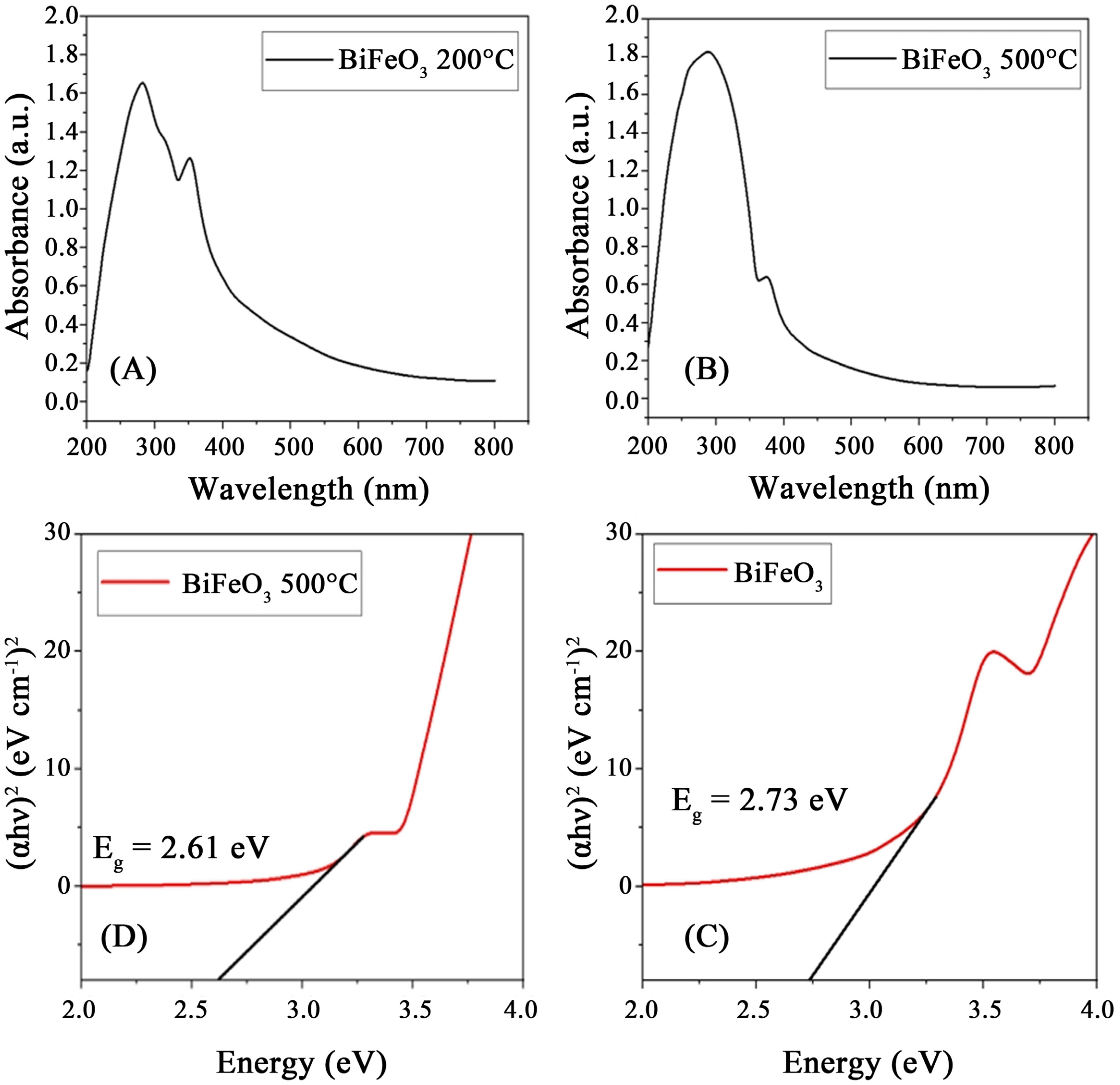

Figure 4. UV-visible spectroscopy (A) absorbance at 200˚C, (B) absorbance at 500˚C annealed $BiFeO_3$ thin films and (C) band gap at 200˚C, (D) band gap at 500˚C annealed $BiFeO_3$thin films.

Photoluminescence: Figure 5 show optical luminescence spectra of $BiFeO_3$ thin films annealed at 200˚C and 500˚C. The luminescence spectra of the nanocrystalline $BiFeO_3$ thin film is characterised by two maxima located approximately at 467 and 491. Annealed $BiFeO_3$ thin films gives emission corresponds to blue and green wavelength in visible region which is important for optical device applications. After annealing electron-hole recombination rate decreases *i.e.* the resistivity is also reduced. Conductivity is opposing to the resistivity therefore; conductivity increases when annealing temperature increased. When electron-hole recombination rate decreases the band gap also reduced.

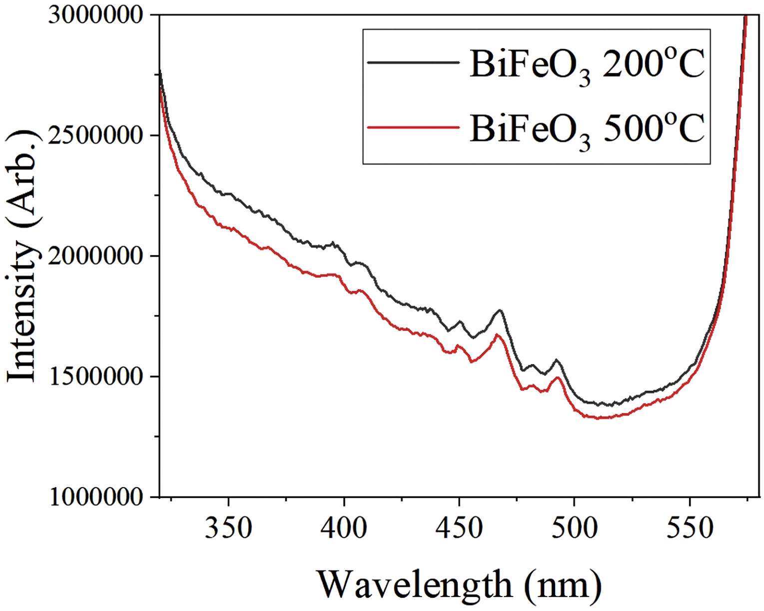

Figure 5. Photoluminescence spectra of annealed $BiFeO_3$ thin films.

4. Conclusion

In summary, investigation on spin coated $BiFeO_3$ thin films has been carried out @ 200˚C and 500˚C. The microstructure and phases changes have been confirmed from XRD results. It is found that on increasing temperature from 200˚C to 500˚C the band gap values reduced from 2.73 eV to 2.61 eV attribute the recombination rate of electron & holes is altered. The photon of wavelength ~580 nm can stimulate the electrode-hole pairs in BFO thin film, as shown in **Figure 5**. These photo-generated carriers drift towards higher wavelength under applied annealing via domain boundaries. It is concluded that, annealing is a better technique to improve the crystallinity and reduce the impurity of $BiFeO_3$ thin films.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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