PREPARATION OF SINGLE PHASE $BiFeO_3$ FILM USING SPIN COATER AND THEIR CHARACTERIZATION

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Abstract : The present paper describes a simple low-temperature synthesis method of preparing single phase bismuth ferrite thin films by sol-gel route, using bismuth nitrates and iron nitrates and ethylene glycol. The film was layer by layer deposited on substrate (quartz) using spin-coater. The thickness of the layers was controlled by viscosity of the solutions and withdrawing speed parameters. After specific annealing, in air, the samples were characterized by X-ray diffractrometer (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), optical properties measured by ultraviolet visible spectrophotometer (UV-Vis). Thickness of the film was calculated by interference method proposed by swanepol [1]. The influence of the processing parameters on microstructure and optical properties, especially band gap, were studied.

Keywords - single phase $BiFeO_3$, Sol-gel, Thin Film, XRD, SEM,FTIR, UV-Vis.

I. INTRODUCTION

Multiferroic materials, which exhibit coexistence of ferroelectricity, ferromagnetism, and/or ferroelasticity in a certain range of temperatures, have attracted much attention. Among these materials, $BiFeO_3$ is the only single phase multiferroic material which possesses a high Curie temperature (TC ~1103 K), and a high Néel temperature (TN ~ 643 K) at room temperature. The BFO has a relatively low crystallization temperature, and a rhombohedral distorted perovskite structure with space group R3c [2]. Its excellent optical and electrical properties show its potential and demonstrated applications such as infrared detector and integrated ferroelectric devices. Recent researches indicate that a substantial visible-light photovoltaic effect was observed in $BiFeO_3$ diode structures [3], which has demonstrated a new application of $BiFeO_3$ films. It is therefore desirable to study the optical properties of $BiFeO_3$. Bismuth ferrite thin films have been prepared by various methods such as pulsed laser deposition, sputtering, molecular beam epitaxy, liquid phase deposition and sol-gel process.

Among these methods, sol-gel processing has an edge over other deposition techniques in terms of good homogeneity, chemical composition control, high purity, low processing temperature and applicable to large areas, using simple and inexpensive equipment. In this present work, $BiFeO_3$ thin film was prepared on quartz substrate and focusing on its optical properties.

II. EXPERIMENTAL DETAIL

Bismuth nitrate [$Bi(NO_3)_3.5H_2O$] and iron nitrate [$Fe(NO_3)_3.9H_2O$] were used to prepare 0.3 M concentration precursor solution by dissolving it in ethylene glycol using sol-gel method. The solution was heated to 80ºC /1h and allowed for ageing at 60ºC/12h. Viscosity of the sol was 20cP. Thin film was prepared on the quartz substrate, cleaned with acetone, isopropyl alcohol and de ionized water, by spin coating the sol at 4000rpm for 20s. Coated film was dried at 150ºC/10min using hot plate and then pyrolized at 450ºC/5min using tubular furnace. Spin coating, drying and pyrolysis actions were repeated to get film of required thickness and finally annealed at 600ºC/1h.

Structural characterization of the film was investigated by Xpert Pro PANalytical X-Ray diffractometer operating at 40KV, 30mA with Bragg Brentano geometry using Kα radition. Hitachi S-4500 Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX) was used to assess the shape and percentage of the synthesized silver nanoparticles respectively. A Scanning Electron Microscope, Fourier transform infrared (FT-IR) spectra were recorded in the range of 400- 4000cm^{-1}. The UV transmittance spectra of thin film were measured at RT on a Tech comp 2301 UV-Vis double-beam spectrophotometer.

III. RESULTS AND DISCUSSION

3.1 Structural and morphological analysis

Fig.1 shows the XRD pattern of the $BiFeO_3$ film annealed at 600ºC/1h obtained by sol-gel method. It shows that the $BiFeO_3$ film is polycrystalline with (0 1 2), (1 0 4), (1 1 0), (2 0 2), (0 2 4), (1 1 6), (2 1 4) and (2 0 2) peaks were observed. Absence of any unwanted peaks suggests that the sample is in single phase. The peak position 2θ, Relative intensity, measured and standard value of d-spacing and (h k l) planes are listed in table 1. The standard values are taken from the (PDF# 71-2494)

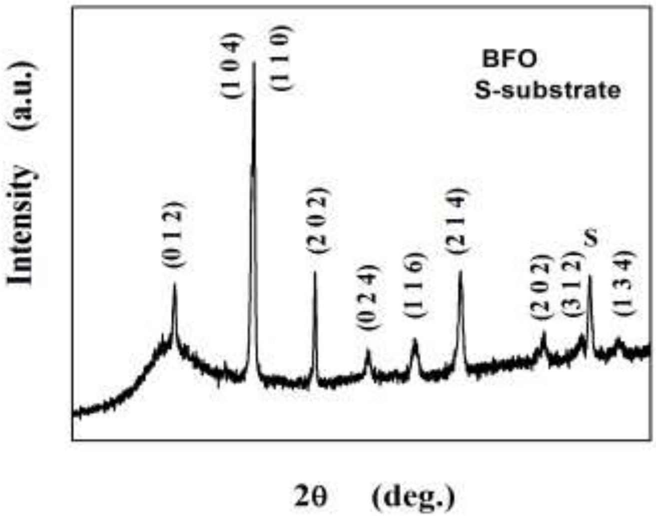

Fig. 1 XRD pattern of pure BFO thin film

Table 1 XRD values of pure BFO thin film

S.No	2θ (deg.)	Relative Intensity (%)	d (Å) measured	d (Å) standard	*(h k l)*
1.	22.3564	15	3.97674	3.9681	*0 1 2*
2.	31.6298	100	2.82881	2.8181	*1 0 4*
3.	31.9674	29	2.79970	2.7938	*1 1 0*
4.	39.3855	14	2.28781	2.2844	*2 0 2*
5.	45.8317	27	1.97991	1.9840	*0 2 4*
6.	51.4548	10	1.77599	1.7808	*1 1 6*
7.	56.9059	28	1.61813	1.6176	*2 1 4*
8.	67.0924	14	1.39509	1.3969	*2 0 2*

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Crystalline size was measured using debye Scherrer's equation for $BiFeO_3$ thin film is 31 nm. The lattice parameters are calculated by UNIT CELL software respectively. The calculated lattice parameters are listed in table 2. The observed feature shows that the $BiFeO_3$ film is polycrystalline in nature and it exhibits rhombohedral crystal system. Fig. 2 shows the surface micrograph of the $BiFeO_3$ film, was clear dense and homogeneous surface.

Table 2 Calculated lattice parameters of $BiFeO_3$ unit cell.

Cell Parameters	Hexagonal Measured	Hexagonal Standard ICDD 71-2494	Rhombohedral Cell values using eqn. (3.1 ,3.2 & 3.3)
a (Å)	5.5777	5.5870	a' = 5.6394 Å α' = 59.28^0 V = 374.19/3= 124.73 $(Å)^3$
c (Å)	13.887	13.867	
V $(Å)^3$	374.20	374.94	

3.2 FTIR study

Fig.3 shows the FTIR spectra of $BiFeO_3$ film recorded at room temperature. Fundamental absorption is observed in the wavelength region 450 to 600 cm^{-1}. This bands is attributed to the bending vibration of the Fe-O band in the FeO_6 octahedral unit and also due to the bending vibration of the Bi-O band in the BiO_6 octahedral unit.

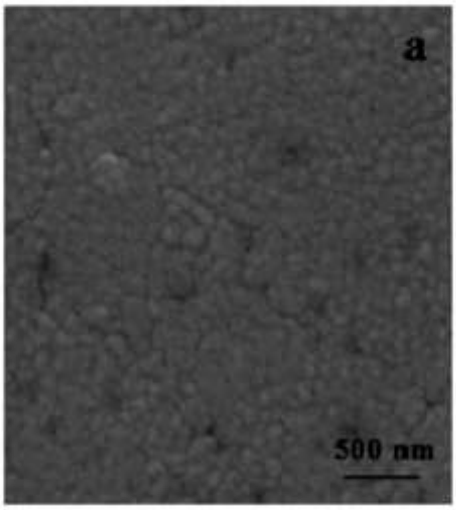

Fig. 2 SEM image of pure $BiFeO_3$ thin film

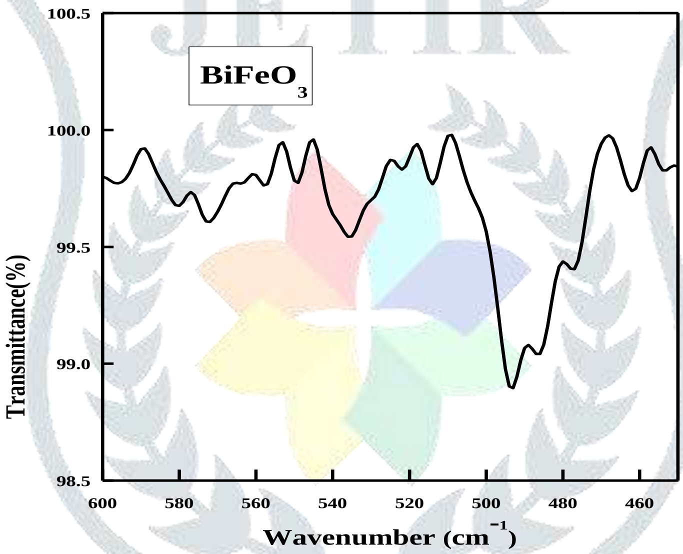

Fig.3 FTIR spectrum of $BiFeO_3$ thin film

3.3 UV-Vis absorption study

Fig.4 shows the transmittance spectra of $BiFeO_3$ thin film in the range from 300-1100nm. The pronounced oscillation in the transmittance spectra illuminates that the $BiFeO_3$ film had flat surface, which can be proved from the surface of morphologies of $BiFeO_3$ film in fig.3. Obviously, the transmittance for all the films decreases to zero at the wavelength of 440nm. It is clearly seen that the $BiFeO_3$ film is highly transparent with transmittances in the visible and near-infrared wavelength region. Furthermore, the spectra indicate that the absorption edge is around 600 nm for the $BiFeO_3$ film.

Thickness (t) of thin films was estimated as ~ 175nm using the interference method reported by Swanepoel [1]. Absorption coefficient (α) was calculated using the formula $\alpha = \ln(1/T)/t$ where T is the transmittance and t is the thickness of the thin film. Optical band gap was calculated from Tauc's relationship, **$(\alpha h\nu) \propto (h\nu - E_g)^n$** [4]. Here, n=2 for the indirect allowed transition.

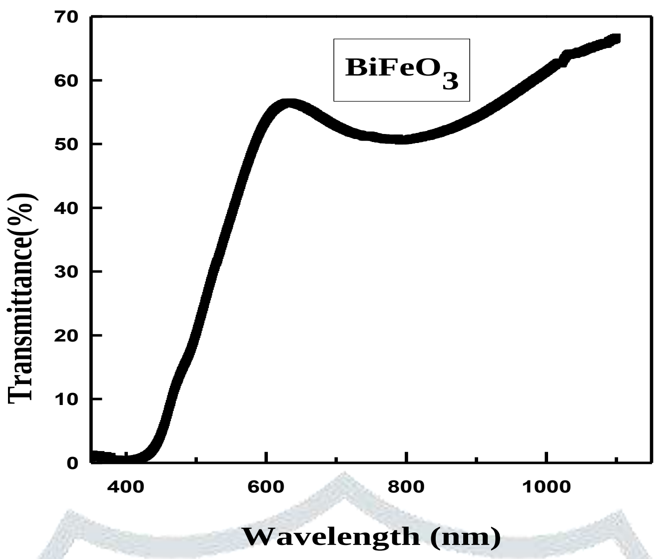

Fig.4 The transmittance spectra of $BiFeO_3$ thin film

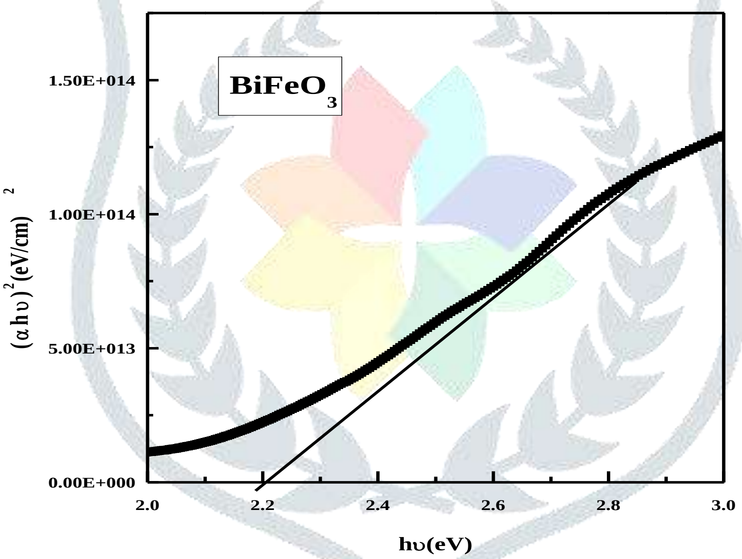

Fig.5 The Tauc's plot of $BiFeO_3$ thin film

A plot between $(\alpha h\nu)^2$ and hν is shown in Fig.5 Linear extra-polation of $(\alpha h\nu)^2$ to 0 eV^2/cm^2 gives the Optical band gap value of 2.22 eV that shows it is an indirect band gap and the optical transition supports the d-d transition. This Optical band gap value for BFO thin film obtained from present work matches well with that of previously reported for Robertson et al estimated the band gap of ~ 2.8 eV. Interestingly the experiments showed that band gap of $BiFeO_3$ is in the visible range found to be direct and ~ 2.7 eV by some authors and indirect band gap of ~ 2.4 eV by others[5].Thus the simple and cost effective sol–gel spin coating method provides an opportunity to the researchers to carry out the tunable band gap studies by substituting different chemical elements at A-site or B-site or both sites of $BiFeO_3$ and hence to exploit the potential of these tunable band gap data in improving the photovoltaic efficiency.

IV. CONCLUSION

In summary, phase pure poly-crystalline BFO/quartz thin films were prepared using low cost spin coating method. Polycrystalline films have been obtained. Thickness of the film is 175nm. The film has a band gap of 2.22 eV. It is found that $BiFeO_3$ thin film has lower band gap and higher absorption coefficient and it is suitable for photovoltaic applications .

V. Acknowledgment

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