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Influence of Thickness on Surface Texture and Optical Parameters of Spin Coated Bismuth Titanate ($Bi_4Ti_3O_{12}$) Thin Films

A.Amali Roselin[1], N. Anandhan[1*], I. Joseph Paneerdoss[2]

[1*]*Advanced Materials and Thin Film Laboratory, Department of Physics, Alagappa University, Karaikudi-630 003, India.*
2Department of Physics, T.B.M.L College, Porayar, Nagai District, Tamil Nadu-609 307, India

Abstract - *In this work, we presented the influence of thickness on morphological and optical properties of Bismuth titanate ($Bi_4Ti_3O_{12}$) thin films prepared on glass substrates by sol-gel spin coating method. Their microstructural, morphological, luminescent and optical properties were investigated by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and UV-Visible spectroscopy (UV-Vis). X-ray diffraction analysis revealed that the prepared films are polycrystalline nature with increasing crystallinity with respect to coating cycle. The preferential growth of the prepared films having orthorhombic structure along (117) plane increased with annealing temperature. Surface morphology of the coated films was noticed by means of Scanning Electron Microscopic (SEM) technique. The PL spectra peak at 520 nm is ascribed to the electron-hole recombination of localized exciton. All the films are highly transparent in the visible region of the electromagnetic spectrum. All the films are highly transparent in the visible region. The band gap of the prepared films decreases with increasing the coating cycles.*

Keywords: *Optical properties, sol-gel, spin coating method, BTO thin films.*

I. INTRODUCTION

Ferroelectric materials have attracted considerable interest due to their tremendous importance in applications for non-volatile memories and multi-functional devices used in microelectronics and opto-electronics**[1-2].** In recent decades, more research work have been carried out on several types of ferroelectric materials including, Barium Titanates($BaTiO_3$), Strontium Titanates($SrTiO_3$), Calcium Titanates($CaTiO_3$), Bismuth Titanates($Bi_4Ti_3O_{12}$) etc**[3-6]**. Among these, Bismuth titanate have been considered as promising candidate material for non-volatile ferroelectric random access memories(NvFRAM) due to their low coercive field, large remnant polarization, high curie temperature of 675° C and fatigue free property**[7-8].** Bismuth-layered perovskite structure family with a general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where m represents an integer value, A is a relatively large mono, divalent or trivalent cation(A=La,Nd, Sm and Y), and B is a small, highly charged cation with valence 4,5 or 6 such as Ti^{+4}, Nb^{+5}, or Ta^{+5}. It has been recently reported that some A-site or B-site substitution in Bismuth titanate($Bi_4Ti_3O_{12,}$ BTO) thin films could improve their ferroelectric and fatigue properties**[9-11].** A-site substitution can be attributed to the enhanced stability of the oxygen in the Ti-O octahedron layer. The B-site substitute with high valent cations assist the elimination of defects like oxygen vacancy **[12-14].**

A number of methods have been successfully developed to prepare BTO thin films including r.f sputtering**[15]**, pulsed laser deposition**[16]**, chemical solution deposition**[17]**, metal organic solution deposition**[18]**, electron beam evaporation**[19]**and sol-gel process**[20]**. Aforementioned methods, sol-gel process is widely acknowledged to be advantageous over other techniques; due to their simple equipment assembly, ability for exact stoichiometry control, large area homogeneity, low temperature processing conditions, and low cost. In this work, we report the preparation of $Bi_4Ti_3O_{12}$(BTO) thin films using sol-gel spin coating technique and the effect of thickness on structural, optical, luminescent and surface morphology of the prepared BTO thin films are interpreted for the development of optoelectronic devices.

II. EXPERIMENTAL DETAILS

Bismuth acetate($Bi(C_5H_{11}COO)_3$), Titanium di-isopropoxide ($C_{16}H_{28}O_6Ti$), Manganese acetate ($(CH_3COO)_2Mn.4H_2O$) were used as the starting materials. Acetic acid(CH_3COOH) and Acetylacetone ($C_5H_8O_2$) were used as the solvent for the starting materials respectively. 5% of excess ($Bi(C_5H_{11}COO)_3$) was added to compensate evaporation of bismuth during annealing. First, an appropriate amount of Bismuth acetate, Manganese acetate dissolved in acetic acid and acetylacetone under constant stirring for 2h until to get appropriate a clear solution. Then certain amount of titanium diisopropoxide was added to the above solution, thereafter the solution was further stirred for 2 h to promote homogeneity. The obtained solution appeared as a golden color sol. Finally, the obtained solutions were spin coated on glass substrates at a spin rate of 2500 rpm for 20s. To obtain desired thickness, the coating process was repeated for 2,4 and 6 times. After each coating steps, the films were pyrolyzed at 300°C for 10 mins on a hot plate before annealing. After multi-coating, the prepared films were subjected to annealing at 650°C for 1 hr.

The crystalline structure of the thin film was analyzed by X-ray diffraction (XRD: X'pert PRO,PAN Analytic) with Cu-K_{α} radiation and operating an accelerating voltage and an emission current of 40Kv and 30mA respectively. The morphology of the thin film was observed on a scanning electron microscope(SEM:ZEISS). Thickness of the films was estimated using Surface Profilometer (MITUTOYO). The transmittance and absorbance properties of the films were measured by UV-vis spectrophotometer (Ocean Optics HR 2000). The luminescent properties of the films were analyzed by Photoluminescence (PL) spectroscopy (Varian Cary Eclipse Spectrometer).

III. RESULTS AND DISCUSSION

A. Stylus Profilmometry

Stylus Profilometry have been utilized to find the thickness of the prepared films with different coating cycles such as 2,4 and 6. Fig 1 shows the variation of film thickness with different coating cycles. It is noted that, film thickness increases linearly with respect to the increasing coating cycles. The thickness of the films resulting from the 2 to 6 repetitions of spin coating and annealed at 600ºC were found to be 26.7 nm, 69.9 nm, 102.7 nm.

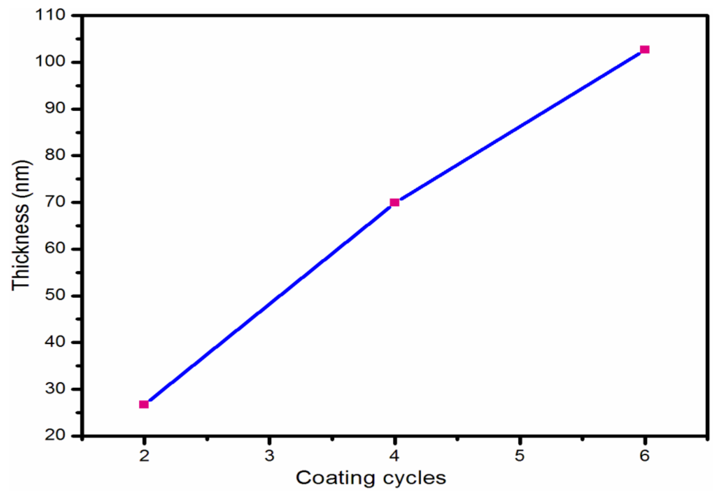

Figure 1. Dependence of thickness for BTO thin films as a function of different coating cycles

B. Structural Analysis

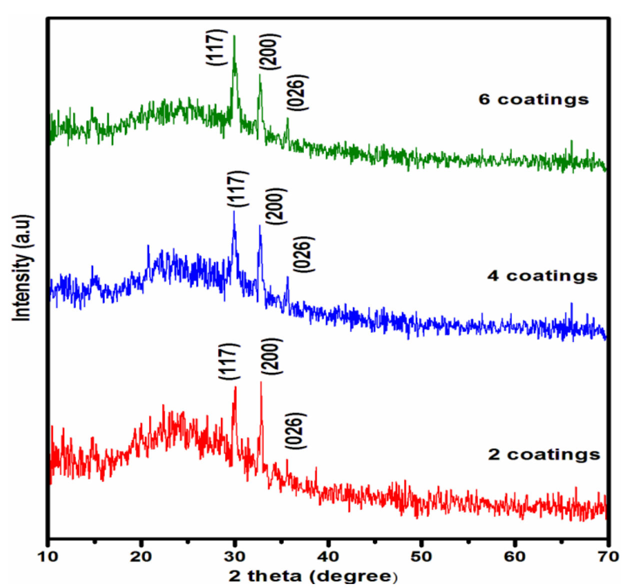

Figure 2. XRD patterns for BTO thin films as a function of different coating cycles

The XRD patterns of $Bi_4Ti_3O_{12}$(BTO) thin films at a different coating cycles such as 2,4 and 6 times and annealed at 600ºC are shown in Figure 2. X-ray diffraction studies revealed that all the films were polycrystalline in nature. The stronger diffraction peak observed at 30.3º corresponds to (117) plane of orthorhombic phase of BTO thin film [JCPDS card No.(35-0795)]. It also evidenced by various diffraction satellite peaks at an angles 33.37º, 35.74º which corresponds to lattice planes (200) and (026) respectively. These planes infer that the crystallites of the prepared films are strongly orientated along c-axis (117) plane with orthorhombic structure. The intensity of particular preferential orientation increased with increasing coating cycles but its orientation did not alter, which may be due to the quality of the thickness of the film gets improved. Our data are well coincided with earlier reports[21-23].

The average particle size, dislocation density and strain were calculated for as prepared samples with increasing spinning speed shown in **Table 1**. The full width at half maximum (FWHM) of the intense diffraction peaks was used to calculate the crystalline size of the prepared film using the Debye-Scherrer formula

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad [1]$$

Where,

λ = 1.5407 Å

β = Full width Half maximum

θ =Diffracting angle

The dislocation densities and strain of the prepared films are calculated by the below equation (2) and (3)

$$\delta = \frac{1}{D^2} \text{ (lines/m}^2\text{)} \quad [2]$$

$$\varepsilon = \frac{\beta}{4\, tan\theta} \text{ (lines/ m}^2\text{)} \quad [3]$$

The intensity of the plane get increases as the spinning rate increased from 2 to 6 coating cycles, might be to the increase of the particle size, decrease in dislocation density and decrease in strain. This is clearly observed from **Table 1.** The intensity of the plane get increases as the coating cycles increased from 2 to 6, might be to the increase of the particle size, decrease in dislocation density and decrease in strain. This is clearly observed from **Table 1.**

Table 1: Structural parameters of the prepared BTO thin films with different coating cycles

Sample Name	**Particle size D (nm)**	**Dislocation density ($\times 10^{14}$) (lines/m^2)**	**Strain ($\times 10^{-3}$) (lines.m^{-4})**
2 coatings	45.26	0.4050	2.97
4 coatings	47.75	0.3812	2.83
6 coatings	48.12	0.3312	2.64

C. Surface morphological analysis

The surface morphology of the prepared films was studied by using scanning electron microscope (SEM). Fig 3.3 surface morphology of the BTO thin film with coating cycle 2, were observed as the non uniform distribution agglometrated grain like structure without any pinholes and cracks. When the coating cycles is increased from 2 to 6, we observed that uniform distribution of morphology like spherically shaped grains over the surface of the substrate due to nucleation over growth and the film surface is smooth observed to be more compact structure.

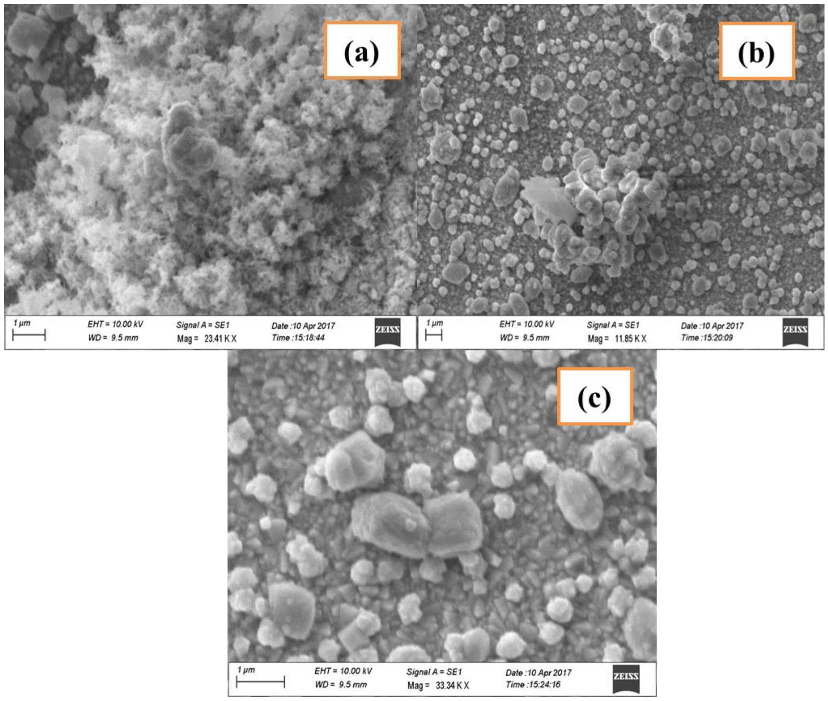

Figure 3 Surface textures for BTO thin films as a function of different coating cycles

3.4. Optical Analysis

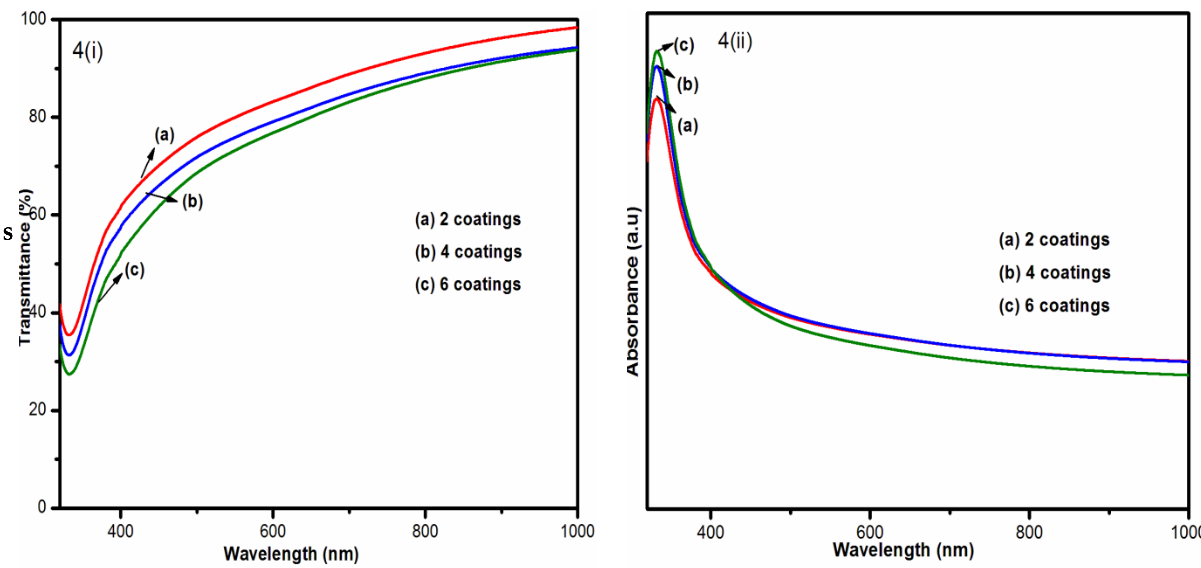

Figure 4(i) & (ii) Transmittance and absorbance spectra for BTO thin films as a function of different coating cycles

Figure 4(i) shows the UV-Visible transmittance spectra of BTO thin films for different number of coating cycles in the wavelength range 300-1000 nm. All the films are highly transparent in the visible region. Transmittance values for the BTO thin films were found to be 80%, 76%, and 65%, for the 2 coatings, 4 coatings and 6 coatings respectively. According to the transmittance spectra, the prepared thin films of transmittance decreased from 80 to 65% with increasing thickness and a sharp absorption edge of the BTO thin films was observed in the UV-region which might be due to the direct transitions of electrons from valence band to conduction band[24]. Figure 4(ii) shows the absorption spectra of BTO thin films with increasing coating cycles, it is found that, in the visible region; the films have explored good absorbance. In the IR region the absorbance decreases and the films became transparent. Further it is observed from the Figure 4(ii), that there is an increase in optical absorption value with increasing coating cycles. In addition, it is clear from the absorbance spectra, that the absorption edges shift towards the higher wavelength, indicating a systematic reduction in the optical band gap with increasing coating number it can be seen from Figure 5. Since the highest thickness and adhesion of more number of particles at the substrate surface may the reason for diminishing transmittance and elevated absorption edge[25].

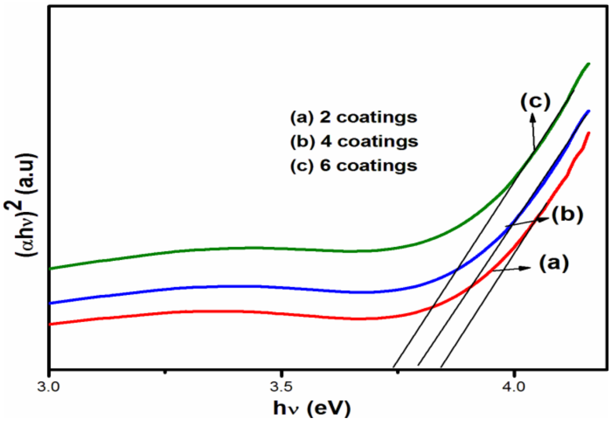

Figure 5. Band gap for BTO thin films as a function of different coating cycles

The optical band gap for the prepared films have been calculated from the relation between absorption coefficient (α) and the incident phonon energy (hν) can be written as

$$(\alpha h\nu)=A(h\nu-E_g)^n \qquad (5)$$

The plot of $(\alpha h\nu)^2$ versus hν, is shown in Figure 6. Extrapolating the linear portion of $(\alpha h\nu)^2$ to x-axis gives the allowed direct band gap value for the as deposited films**[26].** The band gap energy of the prepared films is found to decrease from 3.84 eV to 3.74 eV as the increasing number of coating cycles . In general, the value of optical energy gap decreases as film thickness increases, since the increase in the thickness leads to filling structural gap and hence increasing localized states within the gap, which also might be the result of the change in film density and increase in the crystalline size**[27-28].**

3.5 Photoluminescence studies(PL)

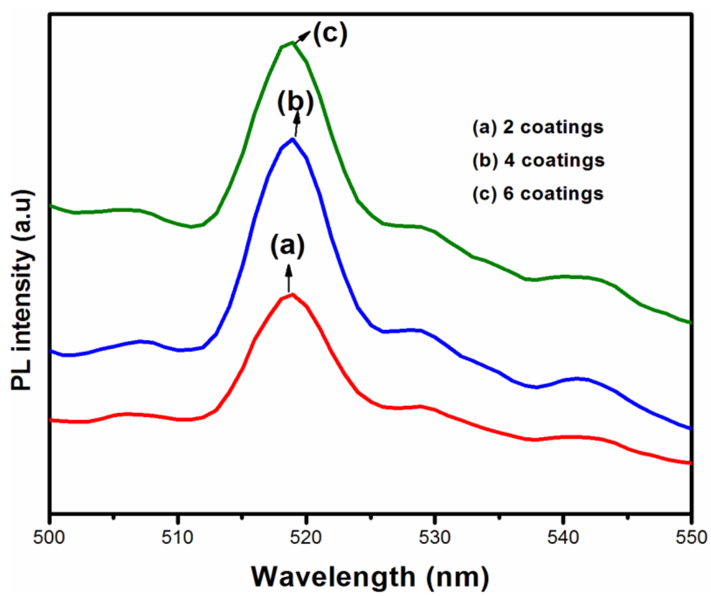

Figure 6. Photoluminescence spectra of BTO thin films as a function of different coating cycles

Photoluminescence spectroscopy is a non-destructive and high sensitivity tool, which is widely used to study photochemistry and photophysics and semiconductor materials in the photocatalysis field. In addition, PL can supply information such as lattice defects, grain boundary and surface oxygen vacancies as well as the separation and recombination of photo induced charge carriers. Figure 6 showed that PL spectra with range 400-700nm of the thin films prepared at different coating cycles were carried out at an excitation wavelength of 405nm at room temperature. PL spectra showed a strong emission peak at 520 nm is ascribed to the electron hole recombination of localized excitons which associated with oxygen vacancies can be a possible reason for this emission. The emission intensities for the BTO films increase with increasing thickness indicates a higher recombination rate of photo-generated electrons and holes in the former case under UV radiation**[29-30].**

IV. CONCLUSIONS

BTO thin films have been successfully deposited on a glass substrate using sol-gel spin coating method with different coating cycles. The optical analysis revealed that, the transmittance and the optical band gap decreased. From the X-ray diffraction analysis the as prepared thin films are found to be a orthorhombic structure it is also observed that the crystalline size increases but dislocation density, micro strain and the number of crystallites decreased with increasing coating cycles due to increase in film thickness. Photoluminescence spectra of BTO thin films revealed that strong emission observed at 520 nm. UV visible spectra exhibited that the transmittance decreased from 80% to 65% and optical band gap of BTO thin films was also varied from 3.84 eV to 3.74 eV due to the increasing coating cycles. Surface morphology of the coated films shown that the morphology evolved from non uniform distribution to uniform distribution and ultimately to spherical shape by increasing the coating cycle.

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