Effect of Rotational Speed on Microstructure and Optical Properties of Bismuth Ferrite Oxide (BiFeO$_3$)

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Abstract. BiFeO$_3$ films were deposited on quartz substrate using chemical solution deposition (CSD) and spin coating techniques with variations of rotational speed (1000 rpm, 2000 rpm, and 3000 rpm) and several films (4 layers and 8 layers). It characterized microstructure of films using X-Ray Diffraction (XRD), morphology, and cross-section using SEM and optical properties using UV-Vis. The results of characterization showed that an enhancement rotational speed causes the intensity of crystal field orientation to decrease, crystallite size, and crystallinity are the same. Surface morphology is getting smoother, flatter, lower porosity and the grain to be homogeneous with thinner thickness. Addition on the number of films causes higher intensity, crystallite size and crystallinity are the same. The film gets thicker, the morphology gets rough, and the boundaries between grains become clearer. Increasing the rotational speed and number of films causes the refractive index and extinction coefficient to be smaller. The light disperses measurement shows a linear relationship between photon energy and refractive index. Energy band gap generated between 2.2-2.5 eV.

1. Introduction

Bismuth ferrite oxide (BiFeO$_3$) film is an interesting material for electrical and optical applications due to ferroelectric and ferromagnetic properties. BiFeO$_3$ is a unique material and belongs to multiferroic material with high ferroelectric transition temperatures ($T_c \sim 1043$ K) and anti-ferromagnetic transitions ($T_N \sim 647$ K) [1,2]. BFO is a lead-free material that can show good ferro electromagnetism at room temperature. Besides, BFO films show greater remnant polarization and lower band gap values than conventional ferroelectric materials such as BaTiO$_3$, Pb(Ti,Zr)O$_3$ [3]. This makes BFO a very promising candidate for photovoltaic applications, because the depolarization fields produced throughout the film region have the potential to separate electrons and excited holes [4].

Chen et al. (2015) have researched on the effect of thickness on ferroelectric and photovoltaic properties of BiFeO$_3$ films using sputtering methods. The results showed that the film can absorb visible light easily if the film is thinner. BFO synthesis on ITO substrates shows a better photovoltaic effect than Pt. Santika et al. (2019) has conducted research related to the effect of thickness on optical properties of BFO films grown on quartz substrates. The results showed the band gap obtained was 2.61 eV. These results indicate it is still too large for photovoltaic applications [6].

BiFeO$_3$ growth methods include sputtering (Chang et al. 2013), solution evaporation method [7], and the CSD or sol-gel method [8,9]. CSD method is used because it is easy to control the composition and...
homogeneity of solution, which is advantageous for obtaining a good transparent film [10]. In this study, the BiFeO$_3$ film will be made using the CSD method. This study aims to examine the effect of rotational speed on microstructure and optical properties of bismuth ferrite oxide (BiFeO$_3$) deposited on a quartz substrate.

2. Experiment

Synthesis of BiFeO$_3$ film using chemical solution deposition method with materials used are bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$.5H$_2$O (Kojundo, 99.99%)) and iron nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O) (Kojundo, 99.9%) acetic acid (CH$_3$COOH) (Sigma Aldrich, ≥99.9%) and 2-methoxyethanol (Sigma Aldrich, ≥99.8%) as solvent and acetylacetone (Sigma Aldrich, ≥99.3%) as stabilizing. BiFeO$_3$ solution deposited on quartz substrate with rotational speeds of 1000, 2000, and 3000 rpm for 30 seconds. Repeat this process with a predetermined rotation speed to get 4 and 8 layers. Annealing at 600°C for 60 min. Microstructure identification using X-Ray Diffraction (XRD). Morphology characterization and cross section using Scanning Electron Microscopy (SEM) model SU3500. To determine the optical properties used UV-Vis spectrophotometer equipment.

3. Result and Discussion

3.1. X-Ray Diffraction (XRD)

Characterization of BiFeO$_3$ film using X-Ray Diffraction (XRD) equipment is obtained the relationship between intensity (I) and diffraction angle (2θ). The diffraction patterns of XRD characterization results were matched with BiFeO$_3$'s ICDD # 861518 and for Bi$_2$O$_{2.3}$, Bi$_2$Fe$_4$O$_9$ and Fe$_{21.34}$O$_{32}$ were matched with ICDD # 762477, # 741098, and # 802186 to identify BiFeO$_3$ film.

![XRD pattern of BiFeO$_3$ variations rotation speed (a) 4 layers (b) 8 layers](image)

Figure 1 shows that intensity of crystal field orientation BiFeO$_3$ decreases with increasing rotation speed. The intensity of field orientation of 110 in BiFeO$_3$ film decreases with increasing rotation speed (rpm). The higher the rotational speed is, the greater centrifugal force is produced so that more BiFeO$_3$ solution is dispersed out the substrate as a result the thickness of film decreases [11]. The thickness of film is linearly correlated with intensity of crystal structure [6]. The reduced thickness causes the number of atoms making up BiFeO$_3$ to decrease. The low number of atoms making up the crystal causes the probability of formation BiFeO$_3$ decreases so that the resulting XRD intensity is low [12]. Increasing the number of films causes higher intensity.

Crystallite size ($D$) is calculated using the Scherrer equation [13]. The results of crystallite size calculation shown in Table 1. This is supported by thickness data BiFeO$_3$ film of the cross-section SEM image (cross-section) which shows the thickness decreases with increasing rotational speed [14]. The crystallite size obtained in variation rotational speed and the number of film is relatively the same,
ranging between 11-12 nm. This shows that generally variations of rotational speed and several films do not affect the crystallite size.

**Table 1. Analysis of the XRD BiFeO$_3$ results data**

| BiFeO$_3$ | Lattice parameter $a=b$(Å) | $c$(Å) | Lattice Strain | Crystallite size (nm) | Crystallinity (%) |
|-----------|--------------------------|--------|---------------|----------------------|-------------------|
| 4 layers/1000 rpm | 5.574 | 13.829 | 0.0027 | 18 | 90 |
| 4 layers/2000 rpm | 5.570 | 13.859 | 0.0096 | 11 | 87 |
| 4 layers/3000 rpm | 5.566 | 13.855 | 0.0086 | 12 | 86 |
| 8 layers/1000 rpm | 5.556 | 13.859 | 0.0099 | 12 | 87 |
| 8 layers/2000 rpm | 5.584 | 13.866 | 0.0093 | 12 | 86 |
| 8 layers/3000 rpm | 5.589 | 13.852 | 0.0099 | 12 | 86 |

The crystallinity of the sample is calculated from the magnitude of maximum and minimum peak intensities [15]. Material crystallinity shows the level of regularity crystals that form in film. Table 1 shows the results of calculation crystallinity BiFeO$_3$ samples. BiFeO$_3$ film variations rotational speed and several films indicate that the higher the rotational speed and several films, the relative crystallinity. Rotating speed serves to spread the solution on the surface of the substrate so that the solution is spread evenly. The higher the rotational speed, the layer will be even and homogeneous. Variation number of the film affects the thickness film. While BFO crystallization occurs in the annealing process, so that variations rotational speed and number of film do not affect the crystallinity, only affect the intensity formed in the XRD pattern.

Based on Table 1, the results of the lattice parameters hardly change with increasing rotational speed and number of film. Lattice parameters resulting from the Rietveld method approach the lattice parameters in the ICDD database namely $a = b = 5.577$ and $c = 13.861$. Lattice strain ($\varepsilon$) is calculated using equation [16].

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan \theta}$$  

Table 1 shows the results of the relatively similar lattice strain along with the increasing rotational speed and number of film.

**3.2 Scanning Electron Microscopy (SEM)**

Morphology of BiFeO$_3$ film is shown in Figure 2. Increased rotational speed causes the resulting film to be thinner and more evenly distributed. High homogeneity, the boundaries between grains appear more clearly, the grains are denser so the porosity is low. BiFeO$_3$ film with variations number of films, it appears that the number of film 8 is much more homogeneous, lower porosity, the boundary between grains is more clearly visible compared to number of film 4 and thicker films. This is caused by the thermal treatment given.
Figure 2. Morphology BiFeO$_3$ film variation of rotational speed (a, b, c) 4 layers and (d, e, f) 8 layers

The cross-section results on samples 1000, 2000, and 3000 rpm for 4 layers respectively 291 nm, 246 nm and 179 nm. The cross-section results on samples 1000, 2000, and 3000 rpm for 8 layers respectively 337 nm, 327 nm and 244 nm. The cross-section results showed that the higher the rotational speed, the thinner the resulting film. BiFeO$_3$ film thickness variation is thinner as the number of film increases. These results are same with the results observed by Naat et al. (2013) when the rotational speed increases, the thickness of the thin film decreases.

3.3 Optical Properties

Figure 3. Transmittance of BiFeO$_3$ film variations rotational speed (a) 4 layers (b) 8 layers

Transmittance spectra of BiFeO$_3$ film grown on quartz substrates are shown in Figure 3. The graph results showed that the higher the rotational speed and the number of film, the higher the peak transmittance value. Figure 3 shows the transmittance spectrum at a low wavelength is 200-400 nm which then increases at a wavelength of 400-800 nm. It shows that BFO material is able to absorb photons well in the UV region yet can not absorb photons well in the Visible region. The amount of the transmittance value is inversely proportional to the amount of the absorbance value.

The refractive index ($n$) can be explained from the transmittance spectrum using *swanepoel* method [17].

\[ n = N_1 + N_2s + 2 \]

Where $N_1 = 2sT_m + s + 2$, $s = 1T_s + 1T_s - 1$, $T_m$ is sample transmittance, $T_s$ is substrate transmittance [18]. Figures 4a and 4b shows $n$ for a vulnerable wavelength of 800-500 nm stable, then an increase in refractive index value at a wavelength of 400-200 nm. The higher rotational speed causes the lower refractive index of film. This is due to the thinner and more transparent film.
The equation used to determine the extinction coefficient \( k \) is [19]:

\[
k = \alpha \lambda 4 \pi \tag{3}
\]

Where \( \alpha = -\ln T d \), \( \lambda \) = wavelength, \( \alpha \) = absorption coefficient. Figure 4 shows a graph of the extinction coefficient of BFO material against a wavelength of 400 nm-600 nm. Figure 4 shows that increasing the number of film causes a decrease in the value of \( k \). The higher rotational speed causes \( k \) values to be lower. This shows the ability of material to weaken photons is still low. This can be seen in Figure 4. The higher the rotational speed, the smaller the values of \( n \) and \( k \). This is due to the thinner and more transparent film so that the photons absorbed are smaller and cause a large transmittance value [20]. The greater the transmittance value at a particular wavelength, the smaller the values of \( n \) and \( k \) at that wavelength.

The equation used to determine the relationship of refractive index with photon energy is [21].

\[
n^2E = 1 + E_m E_d E_{m2 - E_2} \tag{4}
\]

\( E_m \) and \( E_d \) are single oscillator energies and dispersion energies, so the plot graph is obtained relation \( 1/(n^2-1) vs. E^2 \). Figures 5a and 5b are graphs of the relationship \( 1/(n^2-1) vs. E^2 \). The graph shows a linear relationship between photon energy and refractive index. Figures 5a and 5b showed that the higher the rotational speed and a number of films, the lower the dispersion energy. The calculation of the band gap value uses the touch-plot method with the following equation [22]:

\[
(ahv)^2 = A(hv - E_g) \tag{5}
\]
Figure 5. Plot $1/(n^2-1) vs E$ of BiFeO$_3$ film variation rotation speed (a) 4 layers (b) 8 layers and band gap of BiFeO$_3$ film variations rotation speed (a) 4 layers (b) 8 layers

The calculation of band gap energy using tauc-plot method is shown in Figures 5c and 5d. The band gap energy results on samples 1000, 2000, and 3000 rpm for 4 layers respectively 2.4 eV, 2.5 eV, and 2.5 eV. The band gap energy results on samples 1000, 2000, and 3000 rpm for 8 layers respectively 2.3 eV, 2.2 eV, and 2.4 eV.

4. Conclusions

The results of the characterization show that an enhancement rotational speed causes the intensity of crystal field orientation to decrease, crystallite size and crystallinity are the same. Surface morphology is getting smoother, flatter, lower porosity and the grain to be homogeneous with thinner thickness. The addition of the number of films causes higher intensity, crystallite size and crystallinity are the same. The film gets thicker; the morphology gets rough, and the boundaries between grains become clearer. Increasing the rotation speed and number of film causes the refractive index and attenuation coefficient to be smaller. The light disperses measurement shows a linear relationship between photon energy and the refractive index. Energy band gap generated between 2.2-2.5 eV.

Acknowledgments

The authors wish to thank Penelitian Unggulan Terapan 2020 PNBP UNS No.452/UN27.21/PP/2020 for the financial support.

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