Effect of pre-annealing and annealing temperature on microstructural and optical properties of multiferroic BiFeO₃ thin films prepared by chemical solution deposition (CSD)

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Abstract. BiFeO₃ thin films has been successfully grown on a quartz substrate using the chemical solution deposition (CSD) method. X-ray diffraction (XRD) used to determine the microstructure of BFO. The morphology and transmittance of BFO thin film were studied using SEM and UV-VIS. Deposition of the BiFeO₃ thin film with pre-annealing in air and variation of annealing temperature showed that the increase in annealing temperature caused crystallinity to be higher and crystallite size to increase. High annealing temperature results in a larger grain size and lower thickness. Deposition of the BiFeO₃ thin film with pre-annealing in air had a higher crystallinity compared with in O₂. The crystallite size of BiFeO₃ with pre-annealing in O₂ is greater than pre-annealing in air. BiFeO₃ with pre-annealing in air has a smaller grain size and greater thickness compared to pre-annealing in O₂. BiFeO₃ band gap with pre-annealing in air and variation of annealing temperature were obtained 1.4-3.5 eV. While the BiFeO₃ band gap with pre-annealing variation was obtained from 2.3-2.7 eV.

1. Introduction
Perovskite ferroelectric is a large group of ferroelectric material, that has a significance and wide application in electronic industry [1]. Bismuth ferrite oxide (BiFeO₃) with perovskite structure is one of the most studied multiferroic materials and a potentially important lead-free ferroelectric material because its transition temperatures are well above room temperature, which has a high Neel temperature (TN) of ~ 370°C and a Curie temperature (TC) of 830°C [2-4].

Perovskite-oxide has a structural formula of ABO₃, in which A is a large cation such as Bi³⁺, Ba²⁺, or Pb²⁺, and B is a medium-sized cation such as Fe³⁺, Ti⁴⁺, or Zr⁴⁺. These cations are located in cages formed by a network of oxygen anions[5]. Perovskite-type unit cell with a rhombohedral structure has a lattice parameter of a = b = c = 0.3965 nm and α = 89.3° at RT [6].

Some various of techniques for the synthesis of BiFeO₃ are plasma and ion-beam sputter deposition [7], electron beam or oven-induced evaporation for molecular beam epitaxy (MBE) [8], pulsed laser ablation deposition [9], (metal organic) chemical vapor deposition (CVD) [10], chemical solution
methods or chemical solution deposition (CSD) [11]. Among above methods, CSD has the advantage of easy compositional control in films with high quality and microchemical homogeneity, which is favorable for obtaining high optical transparent film [12].

A significant visible-light photovoltaic effect in BFO diode structures was recently investigated by researchers, which has further confirmed the photovoltaic application of BFO thin films [13–15]. Recently, Choi et al. and Yang et al. demonstrated photovoltaic effects in bulk and epitaxial films of the BFO and obtained low band gaps of about 2.7 eV [16]. The effect of annealing atmosphere and annealing temperature on microstructural of multiferroic BiFeO$_3$ thin films prepared by chemical solution deposition was recently investigated by researchers [17]. Only Bi$_2$Fe$_3$O$_9$ were observed as the secondary phase during deposition and the fraction of secondary phase depended upon the annealing temperature as well as the annealing atmosphere.

In this paper, we report on the effect of pre-annealing atmosphere and temperature annealing on microstructural and optical properties of multiferroic BiFeO$_3$ thin films deposited on quartz substrates prepared by chemical solution deposition (CSD) technique.

2. Experimental

BiFeO$_3$ thin films were fabricated by chemical solution deposition (CSD) on quartz substrate. Bismuth nitrate pentahydrate Bi(NO$_3$)$_3$.5H$_2$O and iron nitrate nanohydrate Fe(NO$_3$)$_3$.9H$_2$O were used as starting materials. 2-methoxyethanol and acetic acid with a ratio of 1:1 were used as solvents. 0.2 ml acetylacetone was added as stabilizing agent. The films were deposited on quartz substrate by spin coated at 3000 rpm for 30 second, dried at 150°C for 1 minute. This process was repeated several times to obtain films of desired thickness and then the films were pre-annealed at 400°C for 10 minutes in air atmosphere and heated by rapid thermal annealing at 550, 600 and 650°C for 1 hour in O$_2$ atmosphere. This process was repeated at 600°C with pre-annealing and annealing process in O$_2$ atmosphere.

X-ray diffraction (XRD) equipment (Philips PW 3710/40 kV with Cu-Kα radiation, λ = 1.5406 Å) was used for structural phase identification and the crystallite size of BFO thin films.

Crystallite size is determined using the equation:

$$D = \frac{\lambda k}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $k$ is the Schere constant, $\lambda$ is the wavelength, $\theta$ is the diffraction angle, and $\beta$ is the full width at half maximum (FWHM) and $D$ is the crystallite size.

The surface morphology and grain size of BFO films were observed by Scanning Electron Microscopy (SEM) model SU3500. The transmittance of the films was measured using an UV–VIS light spectrophotometer.

3. Result and Discussion

The characterization results using XRD equipment are shown in Figure 1. The peaks that appear are matched to the ICDD database # 200169.

XRD patterns of BiFeO$_3$ thin films with pre-annealing in air and variations of annealing temperature is shown in Figure 1(a). BiFeO$_3$ thin films have rhombohedral perovskite structures with peaks (101), (110), (111), (020), (120) and (121) that can be observed. The BiFeO$_3$ thin film was annealed at 550°C and 600°C showed a single phase BiFeO$_3$. The thin film annealed at 650°C presence of other phases, such as Bi$_2$Fe$_3$O$_9$ and Bi$_2$O$_3$. This results are match with the results observed by Xu et al. [2]. The crystallinity and crystallite size of BiFeO$_3$ with variations of annealing temperature can be seen in Table 1. Increasing the annealing temperature causes crystallinity to increase. High temperatures in annealing process produce a larger crystallite size. These results indicate that the crystallite size and crystallinity of BiFeO$_3$ thin film is very dependent on the temperature of annealing.
**Figure 1.** XRD patterns of BiFeO$_3$ thin films (a) with pre-annealing in air and variations of annealing temperature. (b) with variation pre-annealing (annealing at 600°C).

**Table 1.** Crystallite size and crystallinity of BiFeO$_3$

| Pre-annealing at 400°C | Annealing (°C) | Crystallite size (nm) | Crystallinity (%) |
|------------------------|----------------|-----------------------|-------------------|
| In air                 | 550            | 20.2                  | 9.6               |
| In air                 | 600            | 21.6                  | 10.0              |
| In air                 | 650            | 21.3                  | 9.9               |
| In O$_2$               | 600            | 23.5                  | 9.8               |

Figure 1(b) shows the XRD pattern of BiFeO$_3$ thin film with variation pre-annealing in air and O$_2$ (annealing at 600°C). XRD results indicate the presence of a single phase BiFeO$_3$ without presence of non-perovskite phases. The difference treatment in the pre-annealing process causes differences in the width of the diffraction peak. BFO with pre-annealing in O$_2$ shows a higher diffraction peak compared to pre-annealing in the air [12]. The difference treatment in pre-annealing process causes a difference crystallinity. Table 1 shows that BiFeO$_3$ with pre-annealing in air has a higher crystallinity compared to that in O$_2$. The crystallite size of BiFeO$_3$ with pre-annealing in O$_2$ is greater than pre-annealing in air. Crystallite size obtained from broad diffraction peaks, this result is in accordance with the Scherer method. These results indicate that crystallite size and crystallinity of the BiFeO$_3$ thin film is very dependent on the pre-annealing treatment [9].
Figure 2. SEM images of BiFeO$_3$ with pre-annealing in air and variation of annealing temperature

Surface morphology, grain size and thickness were studied using Scanning Electron Microscopy (SEM). Figure 2 shows the morphological surface of BiFeO$_3$ thin film on quartz substrate with variations of annealing temperature. In plain view, annealing temperature increases resulting in low homogeneity of grain. Low homogeneity causes the distance between grains to be more tenuous and the boundary between grains cannot be clearly seen. This results in a higher porosity. The grain size and thickness of BiFeO$_3$ with variations of annealing temperature can be seen in Table 2. These results indicate that high annealing temperatures produce a larger grain size [2].

Figure 3. SEM images of BiFeO$_3$ prepared with variation pre-annealing (annealing at 600°C).

Table 2. Grain size and thickness of BiFeO$_3$

| Pre-annealing at 400°C | Annealing (°C) | Grain size (nm) | Thickness (nm) |
|------------------------|----------------|----------------|----------------|
| In air                 | 550            | 66             | 325            |
| In air                 | 600            | 82             | 170            |
| In air                 | 650            | 93             | 120            |
| In O$_2$               | 600            | 103            | 162            |

Figure 3 shows the surface morphology of the BFO thin film on a quartz substrate with variation pre-annealing treatments. The difference treatment in pre-annealing process affects the morphological structure of film. The BiFeO$_3$ thin film with pre-annealing treatment in O$_2$ looks more homogeneous with a greater thickness. The homogeneity can be seen from the distance between more dense grains, the boundaries between grains are more visible, and the grain size is larger. This is caused by a good atomic vibration process. The BiFeO$_3$ thin film with pre-annealing in air has a smaller grain size compared to pre-annealing in O$_2$. This results in a low homogeneity of film and resulting in high porosity. The low homogeneity results in changes in the morphological structure of the layer.

The transmittance spectra of films are shown in Figure 4. It can be seen that the highest peak transmittance at 650°C. The optical band gap $E_g$ can be determined from absorption coefficient $\alpha$, which is calculated according to Tauc's relation using the following equation: [18]
\[(ahv)^2 = A(hv - E_g)\]  

(2)

Where \(A\) is a constant, \(\alpha\) is the absorption coefficient, \(hv\) is the photon energy and \(E_g\) is the optical band gap. \(E_g\) can be obtained by plotting \((ahv)^2\) versus \(hv\) and extrapolating the linear portion of the plot to \((ahv)^2 = 0\).

The band gaps of the BiFeO\(_3\) thin film with variation annealing at 550°C, 600°C and 650°C were 1.4 eV, 2.3 eV, and 3.5 eV, respectively. While the band gaps of the BiFeO\(_3\) thin films with variation pre-annealed in air and O\(_2\) were 2.3 - 2.7 eV. This results are match with the other research, that band gap of BFO is 2.2–2.8 eV [2,16,19].

![Figure 4](image-url)

**Figure 4.** Transmittance of BiFeO\(_3\) prepared (a) with pre-annealing in air and variation of annealing temperature (b) with variation pre-annealing (annealing at 600°C).

4. Conclusions

BiFeO\(_3\) thin films has been successfully grown on a quartz substrate using the chemical solution deposition (CSD) method. Deposition of the BiFeO\(_3\) thin film with pre-annealing in air and variation of annealing temperature showed that the increase in annealing temperature caused crystallinity to be higher and crystallite size to increase. High annealing temperature results in a larger grain size and lower thickness. Deposition of the BiFeO\(_3\) thin film with pre-annealing variation showed that BiFeO\(_3\) with pre-annealing in air had a higher crystallinity compared with in O\(_2\). The crystallite size of BiFeO\(_3\) with pre-annealing in O\(_2\) is greater than pre-annealing in air. BiFeO\(_3\) with pre-annealing in air has a smaller grain size and greater thickness compared to pre-annealing in O\(_2\). BiFeO\(_3\) band gap with pre-annealing in air and variation of annealing temperature were obtained 1.4 - 3.5 eV. While the BiFeO\(_3\) band gap with pre-annealing variation was obtained from 2.3 - 2.7 eV.

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