The effects of annealing temperature and angular velocity variation on microstructure and optical properties of barium titanate (BaTiO$_3$) using chemical solution deposition method

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Abstract. This study is aimed to find out the energy gap value of BaTiO$_3$ thin film since this study has a purpose to reduce the energy gap so that it can be used for photovoltaic applications. The making of Barium Titanate (BaTiO$_3$) thin film was carried out on the quartz substrate using the Chemical Solution Deposition (CSD) method with the technique of depositing spin coating. The making of BaTiO$_3$ thin film was carried out using variation of angular velocity at 4000 rpm and 5000 rpm and variation of annealing temperature at 750$^\circ$C, 800$^\circ$C, 850$^\circ$C. The samples in this study were annealed at 750$^\circ$C, 800$^\circ$C, 850$^\circ$C with a holding time of 1 hour and an increase in temperature of 3$^\circ$C/minute. The microstructure characterization of the samples was carried out using X-Ray Diffraction (XRD) equipment, and the thickness of the thin film characterization and grain size of samples using Scanning Electron Microscopy (SEM) equipment. The annealing temperature increase, the intensity becomes higher. As the annealing temperature increase, then the crystallinity, crystallite size and grain size of BaTiO$_3$ thin film will get bigger. The annealing temperature increase is resulted the thickness and energy gap are smaller. The intensity value of the XRD remains decrease along with the angular velocity increase. The higher angular velocity causes the crystallinity and crystallite size of BaTiO$_3$ thin film becomes higher. However, the angular velocity increase then the grain size will become smaller. The angular velocity higher, then the BaTiO$_3$ thin film gets thinner. The angular velocity gets higher, then the smaller energy gap produced. The energy gap value was produced between 3.00 – 3.50 eV.

1. Introduction

This very rapid technological development can occur due to the existence of certain material. The forms of development in the material are advanced materials, one of which is ferroelectric material. Ferroelectric is a material that has good potential as a solar cell, lighting where the optical sensor is affected by anomalous photovoltaic effects [1]. The photovoltaic effect is the result of the conversion of light energy into electrical energy that occurs directly [2]. Ferroelectric has a higher photovoltaic voltage of two to four times ($10^3$-$10^5$ V/cm) than a bandgap (Eg), and the photovoltaic characteristics can be regulated and controlled by an electric field [3].
Several types of ferroelectric materials which are often used including Barium Titanate [4], Barium Strontium Titanate (BST) [5], Barium Zirconium Titanate (BZT) [6], Lead Zirconat Titanate (PZT) [7], and Strontium Titanate (SrTiO3) [8]. These ferroelectric materials can be made with various methods such as Pulsed Laser Deposition (PLD) [9], Chemical Vapour Deposition (CVD) [10], Chemical Solution Deposition (CSD) [11] and Co precipitation [12].

The well-known ferroelectric materials have ABO3 perovskite structures are Barium Titanate (BT), Barium Strontium Titanate (BST), and Barium Zirconium Titanate (BZT). ABO3 perovskite structure is a structure characterized by the diameter of atom A which is bigger than atom B. Atom A is located at the end of the rib cube, whereas B atom is located in the diagonal space, and O atom is located in the diagonal plane [13]. Barium Titanate (BT) has a perovskite structure of ABO3, which has five types of crystal structures, they are: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral, each of which depends on the temperature of the phase [14]. Barium titanate has no response to the sun since it has a wide bandgap (Eg > 3 eV) [1]. In order that barium titanate can be used as one of the ferroelectric solar cells, it must be doped to reduce the semiconductor bandgap. The doping material given can affect the crystal structure, microstructure, and optical structure of the barium titanate. Barium titanate can be doped by adding La3+, Pb2+, Na+, Ga3+, Nd3+, Th Cr4+, for replacing the position of A or Ba2+, meanwhile, Zr4+, Fe3+, Al3+, In3+, Cr3+, Nb5+, Ta5+, Sb5+, W6+ are used for replacing the position of B or Ti4+ [13].

In this study, BaTiO3 was made using the Chemical Solution Deposition (CSD) method using the spin coating process. The samples annealing process was carried out with a temperature of 750°C-850°C, which was held for 1 hour with a heating rate of 3°C/minute. Before conducting the annealing process on the samples, the solutions were deposited on a quartz substrate with an angular velocity of 4000 and 5000 rpm. The variations carried out in this study were annealing temperature and angular velocity variation. The characterization of the BaTiO3 thin film was carried out using XRD equipment characterization to determine the crystal structure of the BaTiO3 thin film. Meanwhile, the characterization of BaTiO3 thickness and grain size was carried out using SEM equipment.

2. Experiment

The thin film of BaTiO3 was grown using Chemical Solution Deposition (CSD) method. The raw materials were used in this study were Barium Acetate [Ba(CH3COO)2] 99.00%, Acetic Acid [(CH3COOH)] 100%, Titanium Isopropoxide [Ti(OC3H7)4] 97%, Ethylene Glycol [(HOCH2CH2OH)] 100%. The solution of BaTiO3 was made with several stages. The solutions were deposited on the quartz substrate with a spin coating technique at 4000 rpm and 5000 rpm for 30 seconds. This process was repeated with the specified angular velocity to obtain the desired number of films. Then, the substrate that has been deposited was annealed with varying temperatures of 750°C, 800°C, 850°C with a holding time of 1 hour and a heating rate of 3°C/minute. The samples were characterized using XRD equipment to identify the structural phase and crystallite size of the BaTiO3 thin film. The samples testing was carried out using SEM equipment to determine the surface morphology and grain size. The samples were characterized using a UV-VIS spectrophotometer to determine the amount of absorbance and transmittance of the thin film.

3. Result and Discussion

The thin film of BaTiO3 that has been created then was characterized using XRD equipment to find out the crystal structure with Cu 1.5406Å. The data of XRD test results were obtained by displaying a graph of the relationship between 2θ with intensity. The diffraction peaks were compared to the database ICDD #8318880, and by using this procedure, it can be indicated that the peaks are the diffraction peaks of the samples. Based on the results of XRD characterization of samples with variations of annealing temperature and variations of angular velocity produce seven diffraction peaks as can be seen in Figure 1. All the angle 2θ from the graphic of XRD has a different value of intensity.
Based on the results of the characterization carried out using the XRD equipment, it can be seen that as the annealing temperature increase, the intensity value will get higher. Annealing temperature does not affect the angle of diffraction, but it affects the peak intensity. It can be seen in Figure 1 (a) and (b) that when the angular velocity gets higher, then the intensity will reduce. The result of this study is consistent with the results observed by Naat et al., when the angular velocity increase then the intensity of crystal orientation area will reduce [15].

Table 1. Crystallinity and crystallite size of BaTiO$_3$ using annealing temperature and angular velocity variations

| Sample              | Crystallinity (%) | Crystallite Size (nm) |
|---------------------|-------------------|-----------------------|
| 4000rpm, 750°C      | 9.8               | 35                    |
| 4000rpm, 800°C      | 9.9               | 49                    |
| 4000rpm, 850°C      | 10.3              | 56                    |
| 5000rpm, 750°C      | 9.8               | 44                    |
| 5000rpm, 800°C      | 10.4              | 52                    |
| 5000rpm, 850°C      | 10.5              | 58                    |

The crystallinity was calculated from the intensity of the peak diffraction formed. The crystallinity formation of samples with annealing temperature variations is an overview of the regularity crystals formed in each film. The calculation of crystallinity formation from the samples can be seen in Table 1. As the annealing temperature increase, the crystallinity of the films will get higher. This condition influenced by the annealing temperature increase then there is a vibration of atomic, so the atomic become more organized, which cause the crystallinity gets higher. At an angular velocity of 5000 rpm, the crystallinity of samples gets higher too. This result is the same as the result observed by Darmasetiawan et al., when the angular velocity increase, then the crystallinity film increase [16]. The crystallinity was produced between 9.8% - 10.5%.
The crystallite size was obtained by measuring the half-width of the highest peak or Full-Width Half Maximum (FWHM). The crystallite size of the BaTiO$_3$ thin film can be calculated using the equation of Scherrer as follow:

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

Where, the value of $\beta$ is the value of FWHM, $\theta$ which is the diffraction angle, $k$ is the Scherrer constant where 0.9, and $\lambda$ is the wavelength of the X-ray [1]. The measurement of the sample items can be seen in Table 1.

Based on the variations of annealing temperature when made the samples, it can be seen that when the annealing temperature increase, the crystallite size of the BaTiO$_3$ thin film will get bigger. In accordance with the increase of annealing temperature, when the angular velocity increase, the crystallite size will get bigger. The crystallite size was produced between 35 - 58 nm.

![SEM image of BaTiO$_3$ thin film](image)

**Figure 2.** SEM image of BaTiO$_3$ (a) 750°C, 4000 rpm, (b) 750°C, 5000 rpm, (c) 800°C, 4000 rpm, (d) 800°C, 5000 rpm, (e) 850°C, 4000 rpm, (f) 850°C, 5000 rpm

The morphology of the BaTiO$_3$ thin film it can be seen in Figure 2. The thin film of BaTiO$_3$ with annealing temperature variation higher then the porosity of thin film decrease however, the grain boundaries are visible but not clear. This is happened because between the grain in the thin film has experienced diffusion. As the angular velocity increase, then the resulting thin film is thinner so the porosity decrease. However, when the angular velocity gets higher, the grain boundaries are visible and clear.

Based on the result of the characterization of SEM, obtained the grain size and the thickness of the samples of BaTiO$_3$ as can be seen in the following Table 2.
Table 2. Grain Size and thickness with annealing temperature and angular velocity variations

| Sample            | Grain Size (nm) | Thickness (nm) |
|-------------------|-----------------|----------------|
| 4000rpm, 750°C    | 123             | 595            |
| 4000rpm, 800°C    | 198             | 478            |
| 4000rpm, 850°C    | 227             | 417            |
| 5000rpm, 750°C    | 104             | 443            |
| 5000rpm, 800°C    | 126             | 426            |
| 5000rpm, 850°C    | 197             | 395            |

The annealing temperature increase, then the grain size increase. The angular velocity increase, the grain size will be smaller and more homogeneous. This result is matched with the research by Naat et al., [15].

The results of cross-section measurements on samples with variations of annealing temperature and angular velocity obtained thickness, as seen in Table 2. The thickness of the BaTiO3 thin film gets thinner when the annealing temperature gets higher. This condition occurs since the higher annealing temperature causes more water to be evaporated. Thus, at an annealing temperature of 850°C the thickness of the resulting film is smaller. The higher of angular velocity, the thickness of the film becomes thinner. The result is matched with the result observed by Naat et al., when the angular velocity increase, then the thickness of thin film decrease [15].

The calculation of band gap values using the method of tauch-plot by using the equation:

\[(\alpha h\nu)^2 = A(h\nu - E_g)\]  \(\text{(2)}\)

Where \(h\nu\) is the photon energy, \(A\) is constant, \(\alpha\) is the absorption coefficient dan \(E_g\) is the optical band-gap [1].

The transmittance spectrum of the quartz substrate was grown with BaTiO3 is shown in Figure 3. In this figure, it can be seen that the annealing temperature and the angular velocity higher, the transmittance value get higher. Based on Figure 3, it can be seen that at an annealing temperature of 850°C, the transmittance value was highest. This result is matched with the research Bao et al., when the annealing temperature increase, the absorbance value is lower, and the peak of absorbance has shifted towards the right (towards the visible area) [17]. The transmittance value increases at a wavelength of 400 – 800 nm, where the wavelength is a visible area. Besides thickness, the absorption coefficient value also affects the amount of the energy gap value. The energy gap value was produced between 3.00 – 3.50 eV.
Figure 3. Transmittance of BaTiO$_3$ (a) 750$^\circ$C, (b) 800$^\circ$C and (c) 850$^\circ$C

Table 3. Energy Gap with annealing temperature and angular velocity variations

| Sample               | Energy Gap (eV) |
|----------------------|-----------------|
| 4000rpm, 750$^\circ$C| 3.50            |
| 4000rpm, 800$^\circ$C| 3.25            |
| 4000rpm, 850$^\circ$C| 3.15            |
| 5000rpm, 750$^\circ$C| 3.25            |
| 5000rpm, 800$^\circ$C| 3.15            |
| 5000rpm, 850$^\circ$C| 3.00            |

As the annealing temperature increase, then the energy gap of the BaTiO$_3$ thin film will get smaller. This is because as the annealing temperature increase the crystallinity and crystallite size were increase. These results are matched with the result observed by Xu & Shen, where the energy gap is affected by the microstructure of the film [18]. The angular velocity gets higher than the smaller energy gap produced.
4. Conclusions

The annealing temperature increase, the intensity becomes higher. As the annealing temperature increase, then the crystallinity, crystallite size and grain size of BaTiO$_3$ thin film will get bigger. The annealing temperature increase results in the thickness and energy gap are smaller.

The intensity value of the XRD remains decrease along with the angular velocity increase. The higher angular velocity causes the crystallinity and crystallite size of BaTiO$_3$ thin film becomes higher. However, the angular velocity increase then the grain size will become smaller. The angular velocity higher, then the BaTiO$_3$ thin film gets thinner. The angular velocity gets higher, then the smaller energy gap produced. The energy gap value was produced between 3.00 – 3.50 eV.

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6. References

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