Effect of annealing hold time on thickness and optical properties of barium titanate solar cell material

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Abstract. The development of perovskite-based solar cells has recently attracted the attention of many researchers because the efficiency value increases rapidly in a short span of time. Third generation solar cells have the potential to achieve Shockley-Queisser Limit of 31% for single energy bandgap solar cells. Besides that, this solar cell technology is economically very promising because the manufacturing costs are cheaper. The main drawback of this solar cell is its low stability (lifetime), which is caused by degradation over its lifetime. In addition, most of the high efficiency perovskite-based solar cells still use lead (Pb), so they are not environmentally friendly. Another alternative perovskite material is required. One promising material is Barium Titanate (BaTiO₃). As a material for solar cells, not much research has been done. BaTiO₃ film has been successfully made, which is then given annealing treatment at temperature of 500 °C, with annealing time of 30 minutes, 60 minutes, 90 minutes, and 120 minutes. In general, increasing the annealing time increases absorbance, decreases film thickness, decreases energy bandgap, and tends to reduce grain size of film. Energy bandgap tends to decrease with the increasing grain size. The grain size of film decreases with the decreasing thickness. More in-depth characterization and analysis are needed, especially those related to microstructure analysis.

1. Introduction
The development of perovskite-based solar cells has recently attracted attention of many researchers because efficiency value increases rapidly in a short time span. Perovskite structure materials have high energy absorption coefficient and very promising economically due to cheaper manufacturing costs. The main drawback of perovskite-based solar cells is their low stability (lifetime), which is caused by degradation over their lifetime [1]. Most of the high efficiency perovskite-based solar cells use lead (Pb) which is toxic, so it is not environmentally friendly. Several solutions to reduce this weakness are being pursued, but the results are still not optimal. Therefore, this research must be continued and developed.

One promising perovskite structure material is Barium Titanate (BaTiO₃). BaTiO₃ has interesting properties because it has very stable chemically and mechanically, exhibits ferroelectric properties above room temperature, has Curie temperature at 120 °C, has high dielectric constant ≥1500 at room temperature, has low dielectric loss, and has very large energy bandgap [2-4]. A solar cell based on perovskite material will be developed, where the BaTiO₃ film will be matched with the CuO film to form the structure of the BaTiO₃/CuO solar cell. The structure of this solar cell has not been widely researched and developed by other researchers. However, there are still many things that must be done.
and known before the fabrication is carried out, especially those related to optical properties, structure and electrical properties. This paper will discuss the effect of annealing hold time on thickness and optical properties of BaTiO$_3$ film.

2. Method
The manufacture of BaTiO$_3$ film begins with synthesis process of Titanium Dioxide (TiO$_2$) solution. TiO$_2$ solution was prepared by mixing 1 ml of Titanium (III) Chloride (TiCl$_3$) solution, 20 ml of 2-Propanol, and 5 ml of Toluene. The three solutions were put in a measuring cup and stirred over hotplate stirrer for 30 minutes at a temperature of 80 °C. The resulting TiO$_2$ solution dissolves completely and is clear in color. Furthermore, 2.5 grams of Ba(OH)$_2$.8H$_2$O (Barium Hydroxide) powder was mixed with 5 ml of 1 M HCl, and 5 ml of distilled water. Then the three ingredients are mixed in a measuring cup and stirred like the TiO$_2$ solution-making process above. After that the solution formed is mixed with TiO$_2$ solution and stirred on hotplate stirrer for 1 hour, and clear BaTiO$_3$ solution will be formed. BaTiO$_3$ films were made using spin-coater tool. BaTiO$_3$ solution was dropped on ITO substrate and rotated at 1000 rpm for 30 seconds, then accelerated to 2000 rpm for 10 seconds. Furthermore, BaTiO$_3$ film formed is fed into furnace for the annealing process. Treatments of annealing hold time were 30 minutes, 60 minutes, 90 minutes, and 120 minutes with annealing temperature of 500 °C respectively. Furthermore, characterization of grain size and optical properties was carried out using X-Ray Diffractometer (XRD), and UV-Vis Spectrophotometer.

3. Result and Discussion
Figure 1 shows samples of BaTiO$_3$ film produced using sol-gel and spin coating methods. Sample (a) was without annealing treatment, while samples (b), (c), (d) and (e) were treated with annealing hold time of 30, 60, 90, and 120 minutes respectively with annealing temperature of 500°C.

![Figure 1. Film of BaTiO$_3$ (a) without annealing, and (b) 30, (c) 60, (d) 90, (e) 120 minutes.](image)

Figure 2 shows absorbance of BaTiO$_3$ film as function of wavelength of optical properties testing results using UV-Vis spectrophotometer. Respectively, for film without annealing and films with annealing time of 30 minutes, 60 minutes, 90 minutes, and 120 minutes at annealing temperature of 500 °C. The absorbance increase with the increasing annealing time of BaTiO$_3$ film. When BaTiO$_3$ film is not annealed, which is at room temperature, the absorbance is around (0.114 - 0.200) a.u. The absorbance value increases to (0.125 - 0.256), (0.10 - 0.24), (0.184 - 0.177), and (0.328 - 0.337) a.u at temperature annealing 500 °C for 30, 60, 90, and 120 minutes, respectively.

The absorbance is also affected by the bandgap energy width. The increasing photon absorption is due to the decreasing bandgap energy. Figure 2 shows the occurrence of red shifted phenomenon where absorption edge shifts to the right towards larger wavelength. The absorption edge for films with annealing time \( t = 0, 30, 60, 90, \) and 120 minutes were 371.5, 371.5, 374, 382.5, and 384.5 nm, respectively. This absorption edge shift indicates that the increased absorbance shifts towards the lower energy photon. This is in accordance with the results of the calculation of the energy bandgap for each film. An example of calculating the bandgap energy is shown in Figure 3.
of thickness and energy bandgap calculations are shown in Figure 4. It can be seen that thickness and bandgap energy of film decreases for increasing the annealing time. The increase in absorbance above the absorption edge indicates film defect that acts as an electron trapper that absorbs some of photon energy by electrons to move to the conduction band.

![Figure 2](image-url)

**Figure 2.** Absorbance as wave function with variations in annealing time of BaTiO3 film.

Energy bandgap of BaTiO3 film was calculated using Tauc Plot method for various variations of annealing time. Tauc Plot equation used is shown by equation (1)

\[(\alpha h\nu)^2 = B(h\nu - E_g)\]  

(1)

where equation (2) shows film absorption coefficient.

\[\alpha(\nu) = \frac{A}{d}\]  

(2)

and B is constant, \(A\) is absorbance, \(d\) is thickness of film, \(h\) is Planck constant, \(\nu\) is frequency of photons, \(h\nu\) is photons energy, and \(E_g\) is film energy bandgap.

![Figure 3](image-url)

**Figure 3.** Energy bandgap for films with temperatur annealing of 500°C, with annealing time of (a) 30 minutes, and (b) 90 minutes.
Figure 4. Film thickness and energy band gap with variation annealing time and grain size.

Film thickness \( d \) is calculated using optical equation approach, namely

\[
d = \frac{1}{2n_1(\frac{1}{\lambda_1} - \frac{1}{\lambda_2})}
\]

(3)

Where \( \lambda_1 \) and \( \lambda_2 \) are wavelengths at the peaks of first and second spectrum, \( n_1 \) is refractive index of film which can be obtained from equation (4)

\[
n_1 = \frac{(1 + n_0) + \sqrt{(1 + n_0)^2 - 4n_0 - T_0}}{2\sqrt{T_0}}
\]

(4)

\( n_0 \) is refractive index of glass, and \( T_0 \) is minimum transmittance (%).

Figure 5 shows the results of calculating grain size of film energy bandgap with various variations of annealing time using XRD characterization. Grain size is calculated using Scherrer formula in equation (5)
Where $D$ is crystal size, $\lambda$ is wavelength of X-rays used, $\theta_B$ is Bragg angle, $B$ is the FWHM of the Miller indices $hkl$ of peak [5]. Energy bandgap tends to decrease with increasing grain size. This indicates that height of barrier decreases as grain size of film increases [6]. Film grain size decreases, as thickness decreases [7], which corresponds to the results described in Figure 4. In general, energy bandgap dependence on thickness can occur due to changes in barrier height caused by changing film grain size. Effect of quantum size is negligible because film thickness and grain size are relatively large [7].

4. Conclusion
BaTiO$_3$ film has been successfully carried out. Treatments of annealing time were 30, 60, 90, and 120 minutes, respectively, with annealing temperature of 500 °C. In general, increasing the annealing time increase absorbance, decrease film thickness, decrease energy bandgap, and tends to reduce grain size of film. Energy bandgap tends to decrease with the increasing grain size. The grain size of film decreases with the decreasing thickness.

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