Structure and optical properties study of annealed CuO films for development of perovskite-based solar cells

Y Cahyono¹, S Ramadhanti¹, S Fatimah¹, Rasmianti¹, Y N K Dewi¹ and M Z Asrori¹

¹Department of Physics, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

E-mail: yoyok@physics.its.ac.id

Abstract. Synthesis and growth of CuO films have been carried out to be used as constituent materials for perovskite-based solar cells. The film was made using a spin-coating and heat treatment sol-gel method with variations in temperatures of 400 °C, 500 °C, and 600 °C, each for one hour. CuO films were then characterized using UV-Vis, XRD, and FTIR. The analysis was carried out to determine the effect of annealing temperature on the absorbance, thickness, gap energy, crystal size, crystallinity, and functional group bonds of compounds found in CuO films. In general, there is a decrease in thickness, and energy bandgap, as the annealing temperature is increased. Conversely, the absorbance, the mean grain size, and crystallinity increased as the annealing temperature was increased. The increase in grain size is one of the causes of decreasing energy bandgap when the annealing temperature is increased. Annealing treatment increases absorbance in the visible and the near-infrared spectrum (photons with lower energy levels). This is very advantageous as solar cell material. CuO film is planned to be used as a tandem for Barium Titanate (BaTiO₃) to form a solar cell system.

1. Introduction

Sunlight is a promising renewable energy source. The sun is capable of producing 100,000 TW of energy on earth. This energy has a large enough value to meet human energy needs. The amount is equivalent to 10,000 times the energy needs needed on earth. By utilizing solar cells with an efficiency of 10% and as much as 0.1% of the earth's surface, it is sufficient to meet the energy needs on earth [1]. Solar cell technology can convert sunlight into electrical energy, which is a renewable energy technology that is environmentally friendly. With these advantages, solar cell technology research will always be developed in order to increase efficiency and reduce production costs in order to be cheaper [2].

The use of sunlight as a renewable energy source has increased the use of solar cell technology. Until now, the development of solar cells has reached the third-generation. The first-generation is silicon-based solar cells, the second-generation is solar cells based on thin layer materials, and the third-generation is organic solar cells. The first and second-generation solar cells use photovoltaic technology, where the process of producing electrical energy rests on the semiconductor material used. Meanwhile, the third-generation solar cells use the photo electrochemical effect. The difference is the use of electrolytes in third-generation solar cells. Dye-Sensitized Solar Cell (DSSC) is the origin of the
third generation solar cell, which was discovered by M. Gratzel. However, DSSC has a lower efficiency value than the previous generation.

CuO is a copper oxide that is used as a material for solar cells. CuO was chosen because it has high optical absorption in visible light, non-toxic, and easy to manufacture. CuO has a monoclinic crystal structure consisting of four CuO molecules, with an energy gap of 1.2 – 1.9 eV, black color, high absorption, low-temperature emissivity [3]. The lattice parameters of the CuO crystal structure are a= 0.47 nm, b= 0.34 nm, c= 0.51 nm, and angle β= 99.54° [4]. CuO material is a p-type semiconductor.

This paper will discuss the effect of heat treatment on CuO films, especially on their optical properties, structure, and thickness. This study is important in order to obtain complete information in the use of solar cell applications, which is planned as a tandem for Barium Titanate (BaTiO₃).

2. Method

2.1. Synthesis of CuO Solutions
CuO synthesis was carried out by dissolving 0.5 grams of CuO in 10 ml of ethanol (C₂H₅OH). Then the mixture is stirred for 1 hour to form a homogeneous solution. After that, 5 ml of ethylene glycol (C₂H₆O₂) was added to the solution that had been formed and stirred, until mixed and obtained the desired CuO solution.

2.2. Deposition
The CuO film deposition process was carried out using sol-gel and spin coating methods. The substrate used as Indium Tin Oxide (ITO) which was cut to a size of 1.5 cm x 1.5 cm. Then cleaned using alcohol and ultrasonic cleaner for 30 minutes. The substrate is then placed on a spin-coater, and the conductive part is dropped with CuO solution. The spin-coating process is carried out at a rotating speed of 1000 rpm for 60 seconds.

2.3. Annealing
The annealing process was carried out in order to determine the effect of heat treatment on CuO film. This is done by heating the substrate that has been coated with CuO film in the furnace for 1 hour with temperature variations of 400 °C, 500 °C, and 600 °C.

2.4. Characterization
The analysis was performed using 3 characterizations, namely UV-Vis, XRD, and FTIR characterizations. UV-Vis characterization was used to determine the absorptivity, film thickness, and energy bandgap of the film. Information about the crystallinity or grain size of the film was obtained from the XRD characterization results. Crystallinity and grain size were used to analyze the effect of heat treatment or annealing on the film structure for different temperatures. FTIR is used to confirm that the film on the substrate is a CuO compound, and also to find out whether there are other compounds formed as a result of the synthesis.

3. Result and Discussion
Figure 1 shows the absorbance of CuO films without annealing, and annealed at temperatures of 400 °C, 500 °C, and 600 °C for one hour, the results of characterization using UV-Vis Spectrophotometer. The absorbance increase with the increasing temperature. There are many factors that affect the absorbance of the films. It is estimated that there are changes in the film due to the increasing in annealing temperatures, such as thickness, energy bandgap, defects, grain size, and the quantum size of the film. The effect of the increasing temperature caused the film to become thinner, as shown in Table 1, and it decreased the absorbance. Given that the thickness is still in the micro order, it is possible that the effect of quantum size can be neglected [5]. Figure 1 also shows a shift in absorbance that decreases in ultraviolet waves (λ < 400 nm), and increases at visible wavelengths (400 < λ < 700 nm). The annealing treatment increases the absorbance in the large wavelength spectrum (visible and
near infrared). This result is very good for solar cell material, because of the large intensity of solar radiation in the visible light region.

![Figure 1. Absorbance of CuO films.](image)

Thickness analysis of CuO films was carried out in order to determine whether CuO films made had desired thickness in order to have good level of absorption as solar cell material. Film thickness was calculated based on UV-Vis characterization results and using the Swanepoel method. Table 2 shows a thickness of CuO films for annealing temperatures of 0 °C, 400 °C, 500 °C, and 600 °C. In general, there is a decrease in the thickness of CuO film, which is thought to be due to decreasing grain size.

| Film      | Thick (µm) |
|-----------|------------|
| RT        | 6.26       |
| T = 400°C | 0.75       |
| T = 500°C | 0.32       |
| T = 600°C | 0.50       |

Decreasing in thickness can occur due to annealing treatment of film which causes grain size to be smaller. Increasing of annealing temperature will result in higher crystal order [6]. The decreased absorbance could also occur due to other factors in the form of an energy band gap which increases and increases due to increased heat treatment. Energy band gap of CuO films was calculated using the Tauc Plot method using absorbance characteristics obtained previously, namely by plotting (αhν)^n with hv. Energy bandgaps are generated using indirect transitions [7]. This shows that electron transition between valence band to conduction band does not occur directly but occurs by absorbing and radiating phonon energy. Results of determination of energy bandgap of CuO film can describe electron transition that moves from valence band to conduction band. This energy bandgap is also not affected by the thickness of the film [8]. The thickness of film only affects the absorbance of CuO film.

Table 2 shows the energy band gap of CuO film that has been annealed with temperature variations. Heat treatment of annealing on CuO film resulted in changes in energy bandgap which tended to decrease when annealing temperature increased. This indicates that there is an increase in the regularity quality of the atomic arrangement or an increase in its crystallinity. The larger energy bandgap causes energy absorption to be smaller. The energy band gap tends to decrease with the
increasing annealing temperature. Therefore, the increasing in absorbance on CuO film is caused by the changing of the energy band gap factor.

**Table 2. Energy bandgap (Eg) of CuO films.**

| Film  | Eg (eV) |
|-------|---------|
| RT    | 1.61    |
| T = 400°C | 1.57 |
| T = 500°C | 1.59 |
| T = 600°C | 1.44 |

Figure 2 shows a diffraction pattern of CuO films that have been annealed at 400 °C, 500 °C, and 600 °C. The peaks of diffraction pattern occur at angles of about 30°, 35°, 50°, and 60°. This is because the crystal plane experiences diffraction superposition with the same phase resulting in an increasing orientation of CuO fields. The diffraction intensity increases with increasing the annealing temperature. Increasing the annealing temperature causes most of the peaks formed to be higher [9]. During the annealing process film deforms into a more equilibrium structure at elevated temperatures, and is usually preceded by rearranging the position of both crystals and particles. The next process is recrystallization, which is the formation of a new lattice. The new crystal orientation is different from the orientation of the replaced crystal. Recrystallization rate depends on the amount of previous deformation, annealing temperature, and purity of the material. The final process is the growth of particles characterized by particle size that approaches crystal size (grain size).

![Figure 2. Diffraction pattern of CuO film.](image)

Table 3 shows the changes in grain size and crystallinity of CuO films for annealing temperatures of 400°C, 500°C and 600°C. As the annealing temperature increases, it is seen that grain size and crystallinity increase. The orderliness of atomic arrangement increased from three CuO films with increasing annealing temperature. Crystallinity is also proportional to the increase in grain size. This indicates that the higher annealing temperature of CuO film, crystallinity will increase. Grain size increases as annealing temperature increases, proving that the increase in grain size is one of the factors that affects the decrease in energy bandgap when the annealing temperature is increased [10].
Table 3. Grain size and crystallinity of CuO films.

| Sample  | Grain Size (nm) | Crystallinity (%) |
|---------|-----------------|-------------------|
| T = 400 °C | 35.17           | 15.50             |
| T = 500 °C | 36.69           | 15.56             |
| T = 600 °C | 59.92           | 21.35             |

Figure 3 shows the results of FTIR characterization on CuO films carried out in the wavenumber range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The peaks at wave numbers 541.94 cm\(^{-1}\) and 431.68 cm\(^{-1}\) are the vibration-stretching characteristics of the Cu-O bond [11,12], which indicates CuO film has been formed. The peak at wave number 885.13 cm\(^{-1}\) indicates another compound formed from the synthesis and deposition of CuO films, namely Cu\(_2\)O compounds. This is in accordance with the results of the xrd characterization in Figure 2.

4. Conclusion

Synthesis and deposition of CuO films using the sol-gel spin-coating method have been carried out. The films were then annealed at temperatures of 400 °C, 600 °C, and 500 °C for 1 hour. In general, the increasing temperature decrease the thickness of CuO film (0.75, 0.32, and 0.50 μm), which is thought to be due to decreasing grain size (35.17, 36.69, and 59.92 nm). The energy band gap tends to decrease with the increasing annealing temperature (1.57, 1.59, and 1.44). The higher annealing temperature of CuO film, crystallinity will increase (15.50, 15.56, and 21.35 %). The results of FTIR characterization on CuO films show that CuO films have been formed (the peaks at wave numbers 541.94 cm\(^{-1}\) and 431.68 cm\(^{-1}\)). This is all very advantageous as a solar cell material.

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