Annealing Effects on the Formation of Copper Oxide Thin Films

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Abstract. This study approached the simple method of developing CuO thin films by thermal oxidation on pure Cu sheets. The effects of annealing temperature on the formation of CuO layers have been investigated. The oxide layers have been fabricated by annealing of Cu sheets for 5 hours at different temperatures of 980 ~ 1010 °C. The morphologies and optical properties of annealed Cu sheets were studied by using SEM and UV-Vis spectrophotometer respectively. It is revealed that the annealing temperature influence the grain growth and the grain size increases as the temperature increase. The highest grain size was observed on sample annealed at 1000 °C; with average area per grain size of 0.023 mm². Theoretically, larger grain size provides less barriers for electron mobility and increase the efficiency of solar devices. The optical absorption spectra of the oxide films was also measured. Interference pattern was noted at wavelength about 900 nm corresponding to the formation of CuO film. The interference noise observed could be due to the coarse surface and the presence of powdery oxide deposits that causes the scattering loses from the surface. CuO film obtained by this method may be further studied and exploited as low cost photovoltaic device.

1. Introduction
Thin film solar cells comprising of nontoxic, stable and abundant materials are widely studied in recent decades for renewable photovoltaic applications. The implementation of of new solar energy conversion device requires the use of less expensive materials that can make solar energy more competitive. Cuprous oxides (Cu₂O) are of interest because of their potential to reach 20% power conversion efficiency [1, 2]. It is said that this type of semiconductor could be utilized for fabrication of low cost solar cells. However, doping this material is proved to be challenging as Cu₂O has stability condition under limited range of temperature and pressure. Below 400˚C, CuO is more stable than Cu₂O [3]. After a sufficient expose time to oxidation, CuO is formed [4]. This will result in poor mobility of minority carrier and limited light absorption. However, this could be improved by tuning the microstructure of Cu₂O/CuO layer through heat treatment.

Recently, the preparation of Cu₂O/CuO film by including annealing method in the process has been reported [4-6]. For example, Musa et. al. [4] studied the thermal oxidation conditions on the properties of plasma evaporation prefabricated cuprous oxide film. The mobility of minority carrier is reported improved for annealed samples. Johan et. al. [5] studied the annealing effects on the...
properties of copper oxide thin film pre-prepared by chemical deposition. The proportion of the two forms of copper oxides was reported varies with oxidation temperature. They also reported that photoluminescent intensity is greatly improved with the temperature increment. Sentra et al. [6] studied the band gap energy of copper oxide film grown by plasma evaporation method. Band gap energy of Cu$_2$O is higher than CuO and both were indicated as p-type semiconductor.

This study approached the simple method of developing CuO thin films by thermal oxidation on pure Cu sheets. This is carried by annealing the samples in varied temperatures and the effect of the soaking temperature on the oxide layer is studied. The morphologies and optical properties of annealed Cu sheets were studied by using SEM and UV-Vis spectrophotometer respectively.

2. Experimental Methods

Experiment has been carried out using pure Cu as substrate (99.9%). Cu sheets (dimension 20 mm x 20 mm x 0.2 mm) were cleaned and dried. To ensure the surface is free from contaminants, the sheets were immersed in acetone for 3 minutes. Annealing process was done for 5 hours at different temperatures; starting from 980 °C, 990 °C, 1000 °C, and 1010 °C. The heat treatment consists of heating up to destined temperature, then soaking the samples in predetermined temperature for 5 hours and cooling off within the furnace with controlled atmosphere. At cooling temperature of 500˚C, the samples were taken out and were left in open air at ambient temperature. The formation of Cu$_2$O/CuO layer is then investigated.

Analysis is carried out by physical inspection, SEM micrograph and UV-Vis spectroscopy. The sample’s surface topography and morphology as well as the composition information was performed with Scanning Electron Microscope (SEM) and Energy Disperse X-ray (EDS). ImageJ application was used to analyse the average measurement of length, perimeter, and surface area of grains structure. The optical absorption spectra were measured using a UV-Vis-near-infrared spectrophotometer with reference to the bare substrate of Cu sheet. The absorption scale start from 1500 nm to 300 nm with the scan rate 300 nm/min.

3. Results and Discussions

Experimental result has been analysed by characterizing the samples’ physical appearance, morphology by Scanning Electron Microscopy (SEM), elemental properties (EDS) and light absorbance (UV-VIS)

3.1 Morphology

The initial appearance of the Cu sheets is standard pure copper colour shown in Fig. 1(a). By colour identification, it has been indicated that Cu$_2$O is formed first and at high temperature, dominant CuO is formed. Mixed oxides of Cu$_2$O and CuO are formed at temperatures below 1000 °C and at atmospheric pressure [7]. The nonstoichiometry of the oxides is formed from the reaction between the oxide crystal and O$_2$ surrounding the material [8].

Prior to annealing the samples from metallic brown changed to greyish black colour as depicted in Figure 1 (b,c,d and e). This is standard identification of the formation of CuO layer and surface coarsening occurred.
Figure 1. (a) Physical appearance of as-received Cu sheet; the annealed Cu sheets; (b) 980 °C, (c) 990 °C, (d) 1000 °C, and (e) 1010 °C.

Figure 2 (a,b,c,d) shows the microstructure of CuO layer images annealed at 980 °C, 990 °C, 1000 °C and 1010 °C by using SEM. Recrystallization and grain growth were observed on the microstructure. SEM morphology was taken before the specimens’ oxidation took place at room temperature. Based on the micrographs, a considerable grain growth were observed on all the annealed specimens. Surface area per grain was obtained by triangulation method. There are discreet gaps difference on the grain boundaries, which attributed by inconsistent grain growth. The gaps between grains are the area full of defects such as dislocations and vacant spots [6].
The growth of the CuO layer increases with the annealing temperature. Largest surface area per grain was observed on CuO layer of 1000 °C annealing temperature with average area per grain of 0.126 µm as which is evident in Figure 3. Theoretically, large grain size increase the mobility and reduce the resistivity for a carrier to move from one grain structure to the adjacent grain structure [9].
Figure 3. Magnified surface morphology of the CuO layer after annealed at temperature 1000 °C.

Figure 4 illustrates the average area of grain after annealing at different temperatures. The average area of grain for the crystal of annealed CuO sample were estimated to be 0.004 mm$^2$, 0.007 mm$^2$, 0.023 mm$^2$, and 0.005 mm$^2$ respectively to the annealed temperature. An increase in grain size tend to convert polycrystalline structure obtained after the oxidation process to single or nearly single crystal material.

Figure 5 is a magnified image of grain boundaries. Besides the noticeable grain growth, imperfections are evident along the boundaries. An ideal single orientation of crystalline structure of CuO layer could probably increase the mobility of electron inside CuO layer [10]. Because of perfect structure such as that does not exist, real crystalline structures includes several kinds of linear defects (Fig. 6) such as voids and uneven boundaries resulting from dislocations of grains [8].

Large grain size contributes to an increment in the mobility and reduce the resistivity of an electron movement from one crystal to another crystal structure. Thin boundary tends to let an electron to move smoothly with a low barrier across the grain boundaries. Several functional properties of metal oxides, particularly the photoreactivity and charge transport are related to defect disorders [8].

Figure 5. Grain boundary of surface morphology of CuO sample showing defects such as voids and uneven thickness of grain boundaries.
3.2. Elemental Properties
The CuO layer growth is in proportion with oxidation time. It was observed that the outermost layer has already developed the stable CuO oxide layer. This agrees with the EDS analysis exhibited that the highest content of oxygen was detected on sample annealed at 1010°C. Cu$_2$O is formed at lower temperature (~200°C) and followed by the formation of CuO layer as the temperature increase. The mixed oxides of Cu$_2$O and CuO could be found at temperatures below 1000 °C and at atmospheric pressure.

Figure 6 shows the images of distribution of element in annealed Cu sample at temperature of 980 °C, 990 °C, 1000 °C, and 1010 °C and Figure 7 summarizes the percentage of O$_2$ content. Cu and O$_2$ elements were detected in the CuO layer and thus, the composition of O$_2$ was focused. Based on the EDS analysis, an increment of amount of oxygen was increased along with the increase of annealing temperature. And the highest amount of O$_2$ of 18.8% after annealed at 1000 °C compared to other samples. While at temperature 980 °C and 990 °C O$_2$ was distributed uniformly and was estimated to be 15.4% and 15.7% respectively as per shown in lateral distribution of elements from Figure 6 (a) and Figure 6 (b). The percentage of O$_2$ slightly increased from low to the high annealing temperature. However, the O$_2$ concentration is slightly reduced to 14.5% at temperature 1010 °C as per shown in Figure 6 (d).

Figure 6. Percentage of element in annealed Cu sample at temperature (a) 980 °C, (b) 990 °C, (c) 1000 °C and (d) 1010 °C.
3.3 Optical Properties

Optical analysis was carried out with UV VIS spectroscopy in wavelength range of 300 to 1000 nm. A typical recording of light absorption of the oxide layer is shown in Figure 8. The curve exhibits that the surface is slightly coarse at wavelength approximately 500 nm. The CuO layer showed an optical absorption threshold at 900 nm and the interference pattern was noted at wavelength at around 500 nm. The interferences may be due to the coarse surface and the presence of powdery oxide deposit that causes the scattering loses from the surface. This probably would continuously reduce the light transmittance of the material [5].

\[ \alpha = \frac{(\ln T^{-1})}{t} \]  
\[ (1) \]

where \( t \) is the film thickness and \( T \) is the transmittance [9]. The equation is simplified by linear equation :

\[ a hv = A (h v - E g)^{n/2} \]  
\[ (2) \]

In theory, the conversion of \( \text{Cu}_2\text{O} \) into CuO can be testified by the determination of band gap. For this, the optical absorption coefficient, \( \alpha \) was evaluated using the following Equation (1):

\[ \alpha = (\ln T^{-1})/t \]

Figure 8. Absorption spectra for \( \text{Cu}_2\text{O}/\text{CuO} \) sheet annealed at 1000°C.
where \( \alpha \) is the absorption coefficient, \( A \) is a constant, \( n \) is the exponential integer depending upon the quantum selection rules for the particular material and \( h\nu \) is the photon energy obtained from \textbf{Equation (3)} [5]:

\[
E = h\nu = \frac{hc}{\lambda}
\]

where \( h \) is Plank’s constant, \( c \) is the speed of light and \( \lambda \) is the wavelength.

Optical properties of a materials depend on physical characteristics of the films. Oxide layer consists of dominant CuO component has lower energy band gap (1.4 eV) compared to superior Cu\(_2\)O component (2.1 eV) [5]. The lower energy band gap may be contributed by defects on the microstructure namely dislocations, vacancies, pits and pores.

4. Conclusion
In summary, all annealed samples were grown with CuO thin film. This was identified by its typical greyish black in colour. Though CuO has lower band gap energy than Cu\(_2\)O, the mobility was expected to improve with the recrystallization and grain growth after annealing. The result of CuO thin film formed as deduced from SEM, EDS and UV-VIS spectroscopy showed different growth behaviour with different annealing temperature. Grain growth has been evaluated in CuO thin film by measurement of its grain size at different temperatures. Highest grain growth was observed on samples annealed at 1000 \( ^\circ \)C. In general, CuO layer grown with increasing temperature. This was determined by the \( O_2 \) concentration by EDS analysis. The highest concentration of CuO layer was identified on the same samples with largest average area per grain. Poor mobility of an electron inside the oxide layer can be further improved by preparing a single orientation of CuO thin film. Larger grain size provides less barriers for electron mobility. The presence of defects on the boundaries also may contribute to the properties of the oxide thin film and could be potentially tailored for specific applications [8]. Hence, CuO film obtained by this method may be further studied and exploited as low cost photovoltaic device.

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