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The Effect of Electrolyte Temperature on the Electrodeposition of Cuprous Oxide Films

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Cuprous oxide (Cu_2O) thin films were deposited on indium tin oxide (ITO) coated glass by electrochemical deposition at different electrolyte temperature. The electrodeposition process was found to be a reductive irreversible process with a major phase, Cu_2O, and appreciable amount of CuO. With the increasing temperature, the microstructure varied from fine grains, amorphous-like, to coarse pyramids, well-crystallized, which were identified as the texture development transforming from (200) to (111). Not only was the increasing temperature of electrodepostion found to induce the optical red-shift of band gap from 2.19 to 2.68 eV but it inhabited electrical transmittance with resistivity from 11.28 to 0.24 Ω-cm.

Keywords: electrodeposition, irreversible, phase transformation, band gap, and resistivity

1. INTRODUCTION

Transparent conductive oxides (TCOs) used as electrodes has received intense attention due to their chemical/ physical/optoelectronic properties; however, TCOs with expense scale of billions of dollars per year are still poorly understood. The optimum generation of TCO must be fast response and of wide band gap. For the former, fast response, it can be achieved by increasing its carrier mobility which has to perform without detrimental effect on optical properties. The latter, of wide band gap, could be accomplished by Moss-Burstein shift to promote its high emitting frequency.

To couple with n-type TCOs, p-type (TCOs) has been applied extensively, e.g. dye sensitive solar cell, organic light emission diode (OLED) and transparent light transistor to enhance its emission efficiency. Cuprous oxide, a p-type of metal oxide with standard energy gap of 2.1 eV, was found to possess fast electrical mobility and short diffusion length for its minority electrical carriers. In addition,

Cu_2O is abundant, un-expensive and a kind of low-toxic materials to satisfy the requirements of developing green energy. It also receives much attention in the field of solar cell as a light absorbing layer. Up to date, many techniques were developed to deposit Cu_2O layer, e.g. heat evaporation[1], magnet sputtering[2], sol-gel[3], spin coating[4], chemical vapor deposition[5], and chemical deposition[6]. Mahalingam and his co-workers deposited Cu_2O film on copper/tin oxide substrate by electrical deposition with different applied voltage [7]. Though the transparent film was prepared without preferred orientation, its energy band gap, 2.13 eV, is not high enough. Han and Tao successfully deposited homogenous p-n junction of cuprous solar cell with electrochemistry by operating conditions, e.g. pH value, electrical voltage and deposition temperature [8]. The deposited Cu_2O layer couldn't own a stable resistance ranging from 3.2×10^5 to $2.0\times10^8 \Omega$cm. Balamurugan etc. applied reactive evaporation to prepare cuprous oxide film by way of different conditions, flow rate of oxygen and substrate temperature [9]. They obtained nano-scaled thickness ranging from 4.9 to 9.0 nm but lacked for conductivity measurement in their research. Li and his co-workers declared that operation parameters with low oxygen flow rate and low sputtering power could produce almost pure Cu_2O films at temperature condition less than 100℃ to prevent from heat history [10]. They concluded that the cuprous oxide film was suitable for p-n junction of solar cell and p-type logical transistor with energy gap from 2.0 to 2.6 eV, however, the resistivity ranging from 10^2 to 10^4 Ω-cm was not low enough.

This paper applied electrochemical method to deposit the Cu_2O films. The voltammogram was employed to research the electrochemical mechanism for Cu_2O films. With the increasing temperature of the deposition solution, the variation of morphology and the microstructure were explored to elucidate the texture development and its phase transformation. The optical and electrical properties were also studied to relate with the microstructure variation.

2. EXPERIMENTAL

2.1. Preparation of the cuprous oxide film

Coated indium-tin oxide was prepared as the substrates which experienced cleaning with acetone and de-ionic water in turn ultrasonically. A stock solution including sulfuric acid 0.4 M (BASF Co.), latic acid 3 M (BASF Co.) and sodium hydroxide 5M (BASF Co.) was prepared to serve as deposition solution with pH value 9. An electro-deposition system with three electrodes, ITO glass as working, platinum as counter and saturated camel electrode as reference, was applied in the deposition solution. A potentiostat (SP-150, Biologic Co.) was employed in this research. After cyclic voltammographic searching, the applied voltage was set from -0.5V to -1.8V. The deposition temperature ranged from room temperature, 25 ^oC, to 65 ^oC. The pH value of the electrolyte was kept at 9±0.1.

2.2. Characterization of the deposited films

Scanning electron microscope (Hitach Co., S-300 SEM) equipped with energy dispersive spectrum (Horiba Co.) and Atomic force microscope (Digital Co., AFM) were applied to double-check the morphology of the deposited films. X-ray diffractometer (Rigaku Co. XRD) was applied to identify the phase of the deposited films. Ultra-visible spectroscope (Bruker Co. UV-Vis) was applied to measure its emission spectrum. Four point probe (4PP, KLA-Tencor/Prometrix Co.) was employed to measure their resistivity

3. RESULTS AND DISCUSSION

3.1. Electrochemistry

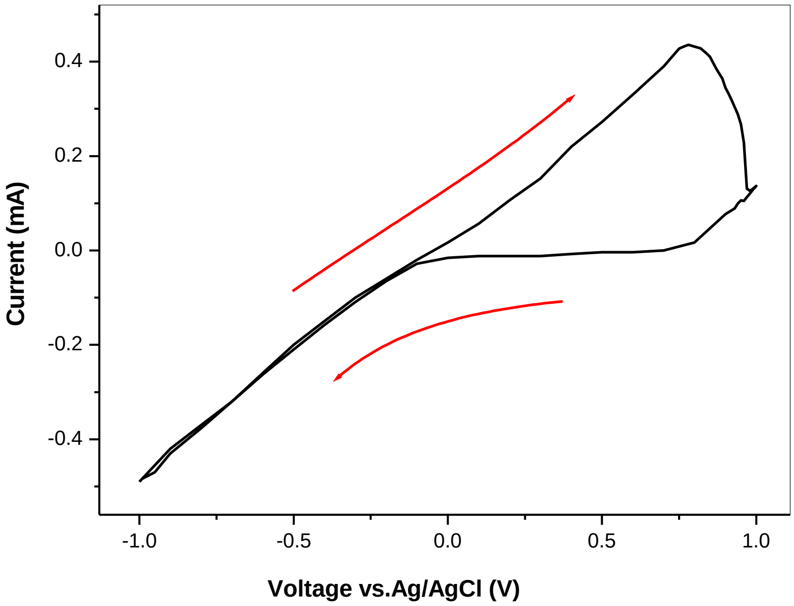

Figure 1. Directional cyclic voltammogram for the Cu_2O deposition scan with a rate 10 mV/min at 45°C.

The formation of the Cu_2O resulted from an irreversible reductive process. Figure 1 showed the cyclic voltammogram in which only a broadened wave appeared with positive current. This suggests only reduction process performing on the working electrode as expressed in the following

$$2Cu^{+2} + 2e^{-} + H_2O \rightarrow Cu_2O + 2H^{+} \qquad (1a)$$

$$Cu^{+2} + 2e^{-} + H_2O \rightarrow CuO + H_2 \qquad (1b)$$

According to Le Chatelier's principle, the hydrogen ion in Eq.(1a) was prone to neutralizing with the hydrogen oxide ion (OH^-) in the solution; therefor, the chemical potential to proceed forward reaction was stronger than Eq.(1b). In addition, because of the high activation energy for Cu_2O to further oxidize as CuO, Cu_2O hardly oxidized into CuO [11]. Cuprous oxide thus remained the matrix phase thermodynamically. Note that no negative current appeared in Fig.1, which concluded no reversal reaction occurring on the working electrode to couple with the reductive current, i.e. irreversible process.

3.2. Microstructure Investigation

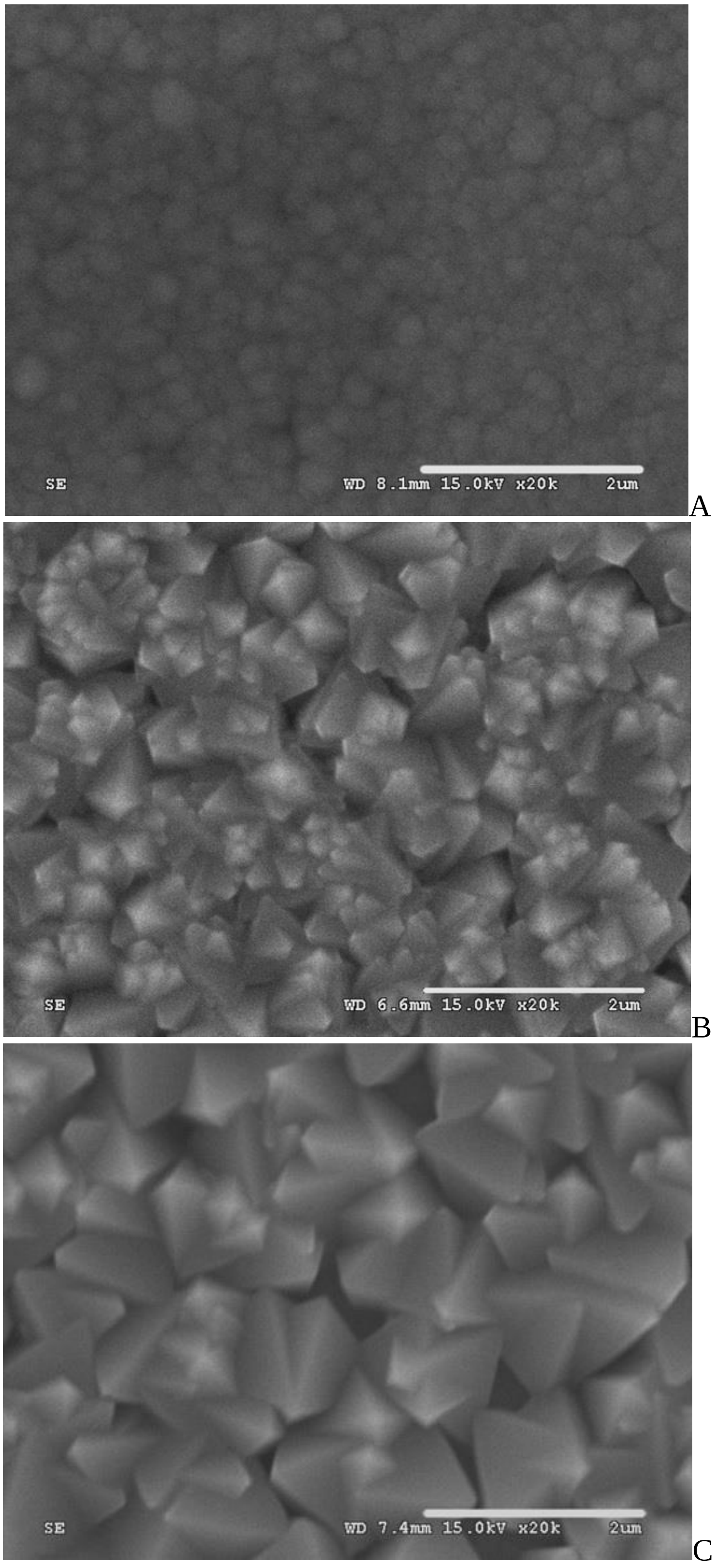

Figure 2. Morphology of the deposited Cu_2O films as a function of temperatures: (a) RT, (b) 45 ^oC and (c) 65 ^oC.

With increase of temperature, the feature revealed variation of Cu_2O microstructure as shown in Figs. 2. In Fig.2(a), the surface was composed of nano-scaled poly-crystals to indicate a multi-textural, i.e. amorphous-like, atomic arrangement. With increase of temperature, the grain coarsened and became rough as shown in Fig.2 (b). Furthermore, in Fig.2 (c), pyramids substituted for all the polyhedral feature to emerge a specific texture. This suggests a growth mechanism in which the lattice of the microstructure was not so well-defined as to nucleate with multi-orientations of texture with smooth feature exposed at low temperature, 25°C. With the increased temperature, a specific preferred orientation developed to present a texture with large grains and morphology of the stable phase, pyramids, at high temperature, 65°C [12]. The specific preferred orientation was confirmed by Askimoto and his co-workers that showed the the importance of crystallographic orientation in getting high performance in electrical rectification and photosensitivity.[13]

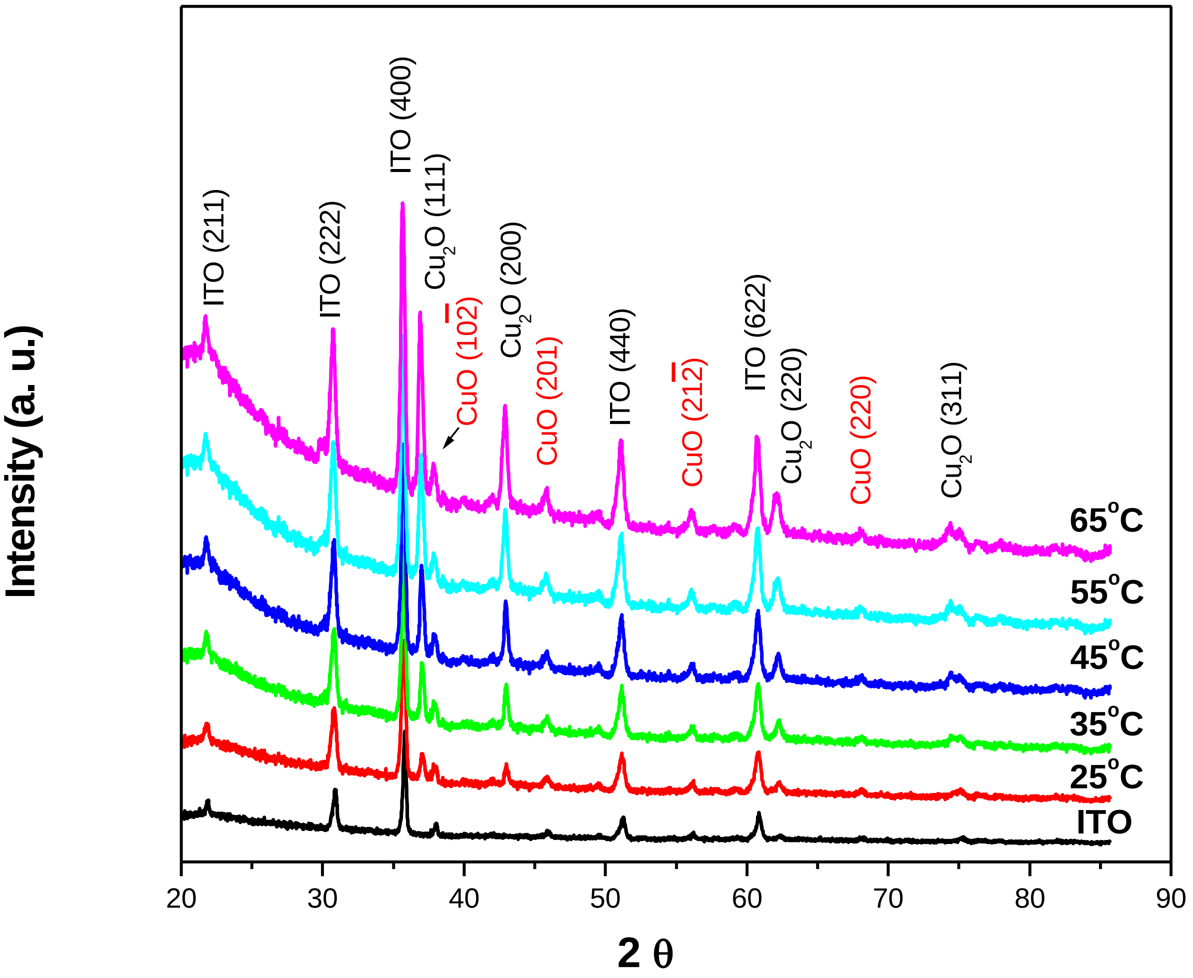

Figure 3. (a) The XRD patterns of Cu_2O/ITO deposited at different temperature under the conditions of pH=9, and working potential = -1.1V.

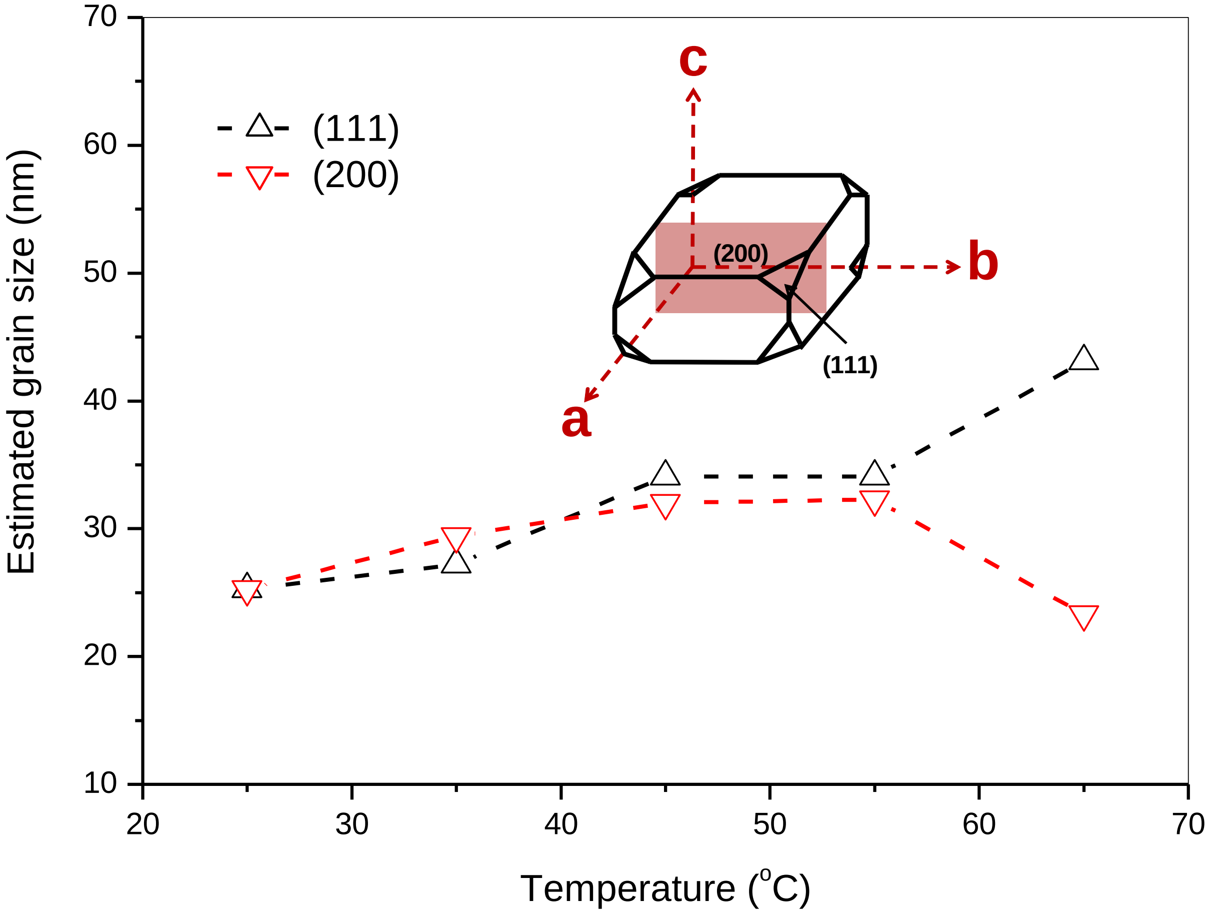

Figure 3. (b) The estimated grain size for different texture, (200) and (111), as a function of solution temperature.

Diffraction patterns showed the developing of phase transformation. Figure 3(a) represented the differential patterns with variation of temperature in which peaks of Cu_2O almost occupied the phase with appreciable amount of CuO. At low temperature, 25°C, the peaks showed small and broadened bumps; in contrast, the peaks grew high and sharp to show phases of well-crystallized at high temperatures, e.g. at 45, 55 and 65 °C. This indicates a phase change in which the film composed of fine grains or amorphous-like phase at low temperature transformed into a well-crystallized phase at high temperature as matched with the variation of morphology from Fig.2(a) to 2(c). This amorphous-like phase could be confirmed by Matsunami's report in which Cu_2O crystal orientated in (111) with a disordering atomic arrangement [14]. Particularly, in Fig.3(a) the two peaks, (111) and (200), stuck out to show a distinct growth speed of crystal orientations and their crystal sizes were estimated by Scherrer equation to show in Fig.3(b). In Fig.3(b), both the grain sizes grew appreciably at the temperature under 55°C, but they branched, i.e. one went up and the other went down, at temperature 65°C. This suggests that (200) plane shrunk but (111) plane grew. The crystal of (200) plane presented slab crystals but (111) plane presented with pyramids which matched with the previous morphology investigation in Figs.2.

3.3. Optoelectronic

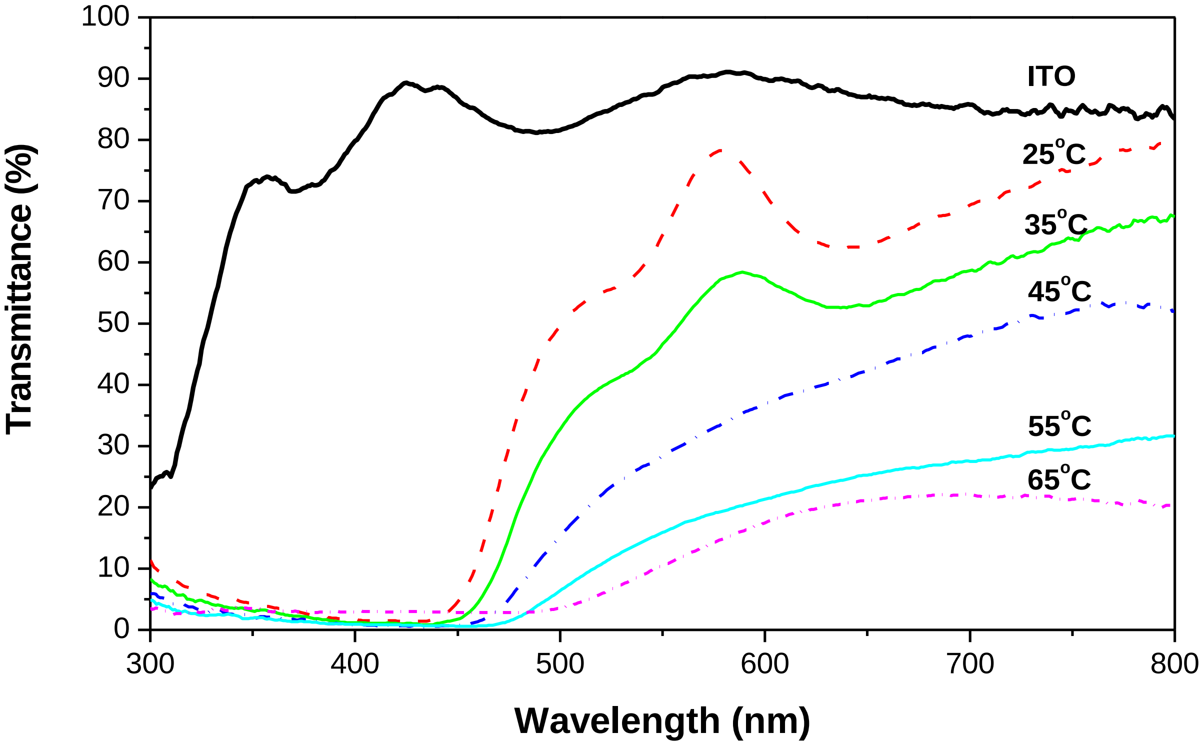

Figure 4. The transmittance of the Cu_2O deposited films as a function of the solution temperature.

The higher the deposition temperature would the more extent the red-shift, and the more devitrification the Cu_2O layer. Figure 4 showed the transmittance of those deposited films with varying temperature. The transmittance decreased with the increasing temperature in the wavelength of visual light, 450- 760 nm. This confirms the microstructure transformation from a transparent feature, i.e. amorphous-like phase, at low temperature, to devitrification, i.e. well-crystallization, at high temperature. Recall the previous deduction that low temperature benefited the formation of metastable phase with fine grains but high temperature facilitated well-crystallization with coarse pyramids. Balamurugan and his co-worker synthesized nano-crystalline Cu_2O and found that the size of the nano-crystallized Cu_2O was related to its shift of absorption edge [9]. In contrast with the transmission spectra, the transmittance edge, 444 nm, at low temperature 25 °C shifted to , 503 nm, at high temperature, 65 °C. This concludes a red-shift when the deposition temperature was increased.

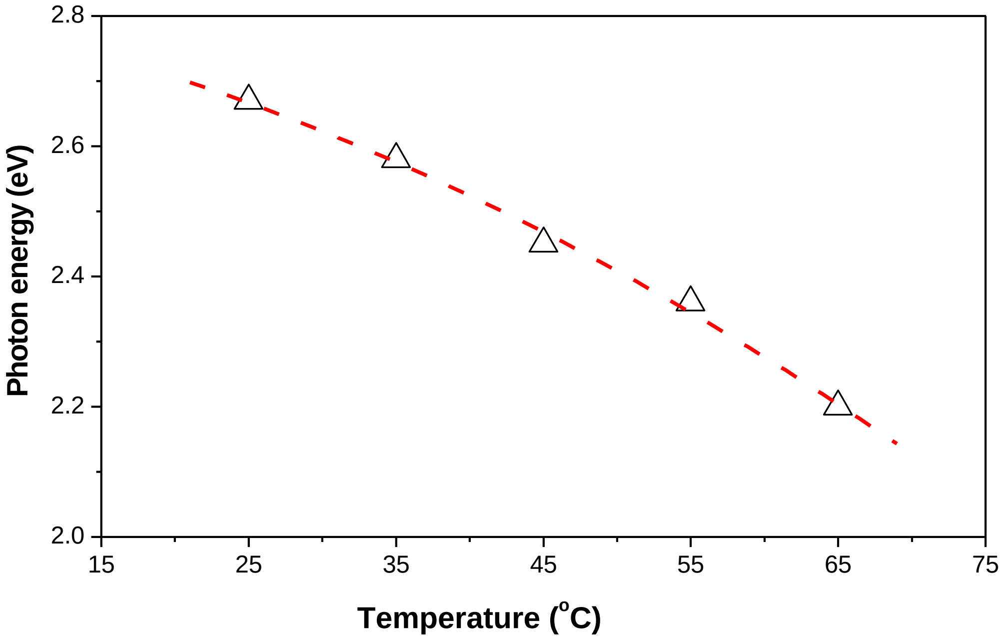

Figure 5. The optical band gap of the Cu_2O deposited films as a function of the solution temperature

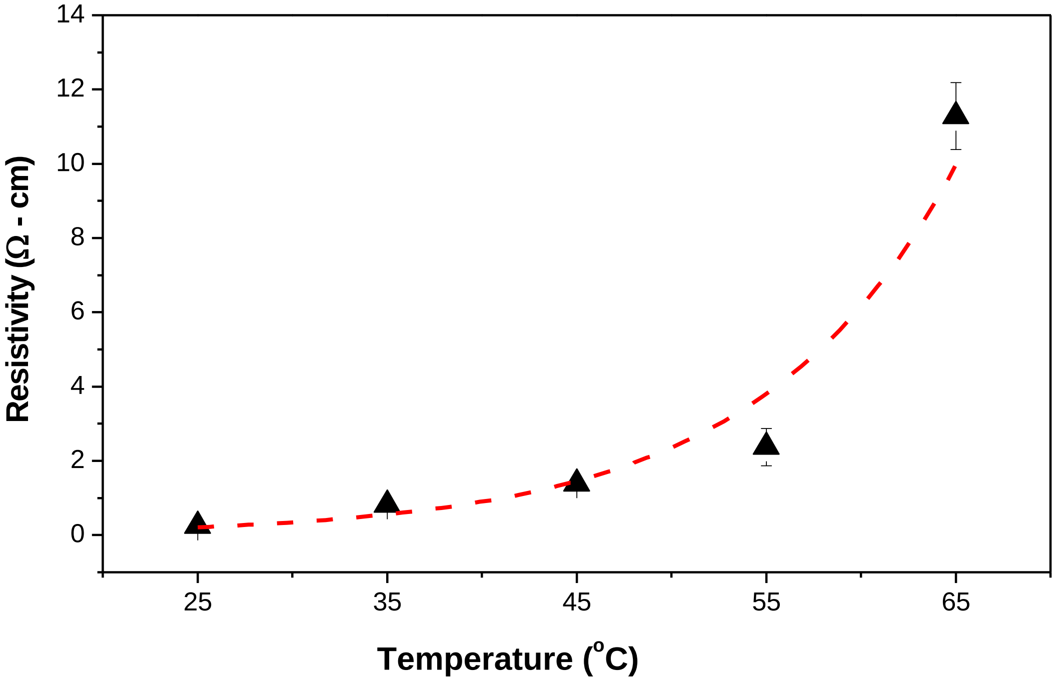

Figure 6. The resistivity of the Cu_2O deposited films as a function of the solution temperature.

The energy gap also showed a red-shift with increasing temperature. Figure 5 plotted relation of photon energy vs. temperature which was obtained from the abscissa intercepts of Tau plot. The value of the photon energy ranged from 2.2 to 2.7 eV of which the average value approximated the reported value, 2.38 eV [15]. To further verify the photon energy, the cut-off wavelengths, λ, were calculated by the formula λ(nm)=1240/photon energy (in eV) to be 464.4, 480.6, 506.1, 525.4 and 563.6 nm which approached the cut-off wavelengths of exciton in Fig.4, 451.2, 458.6, 464.8, 474.3 and 502.7 nm.

Not only did the temperature increase coarsen the grains but it squeeze the path of electron transmit. Figure 6 showed the resistivity variation at different temperature, which demonstrated vicissitudes of the pathway for electrical carriers. It is due to the morphology with fine grains which possessed high density of grain boundary to provide electron scattering path length of the electrons in the Cu film, thereby decreasing film resistivity [16]. Not only did the increase of deposition temperature induce grain growth but it reduced the density of grain boundary to inhabit electrical transmittance; therefore, the resistivity was enhanced.

4. CONCLUSION

The Cu_2O films could be electroposited in an irreversible reduction process. Cuprous oxide predominated the matrix phase regardless of the increasing temperature. With increase of the solution temperature, the morphology changed from transparent poly-crystals, amorphous-like, to devitrificated pyramids, well-crystallization. The phases were identified by x-ray diffraction to show texture development from (200) to (111) as the temperature increased. We thus concluded that the pyramidal crystal resulted from the (111) texture. The transmittance obtained from UV-Vis decreased with the increasing temperature in the wavelength of visual light, 450- 760 nm. This proved the microstructure transformation from a transparent feature, i.e. amorphous-like phase at low temperature, to devitrification, i.e. well-crystallization at high temperature. Both the transmittance edge and Tau plot's abscissa intercepts at different temperature were employed to obtain the variation of photon energy; it was found a red-shift when the deposition temperature was increased. In addition, the microstructure variation due to changing deposition temperature also affected the density of grain boundary, short-circuits for electrical carriers, and thus the speed of the electrical transmission, i.e. the resistivity.

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