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STRUCTURAL, MICROSTRUCTURAL AND OPTICAL CHARACTERIZATION OF DEPOSITED CUPROUS OXIDE (Cu_2O) THIN FILM

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Abstract

Cuprous Oxide (Cu_2O) thin film has been grown onto indium tin oxide (ITO) coated glass substrate by spin coating technique using different additives, namely, polyethylene glycol and ethylene glycol. It was found that the organic additives added had a significant influence on the formation of Cu_2O films and lead to different microstructures and optical properties. The films were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Ultraviolet-Visible Spectroscopy (UV-Vis). The Cu_2O thin films were used as electron collection layer in the application of solar cells.

***Keywords*:** Cuprous Oxide, Thin Film, ITO, Spin Coating

Introduction

Copper oxide thin films are semiconductor which is used as an active layer in various types of solar cells and a passive layer in solar selective surfaces. Copper forms two well-known oxides; Cu_2O and CuO. Cuprous oxide is very attractive as a photovoltaic material because of its high absorption coefficient in visible regions, non-toxicity and low cost to produce. Cuprous oxide (Cu_2O) is an interesting p-type semiconductor with direct energy band gap of 1.5 eV - 2.2 eV. Cu_2O forms a cubic crystal structure with a lattice parameter of 4.27 Ǻ and this material is a promising material in solar energy applications.

Cu_2O thin films can be prepared by various methods like electrodeposition, vacuum evaporation, plasma evaporation, chemical vapor deposition, thermal oxidation, anodic oxidation, spray pyrolysis, r.f. magnetron sputtering, reactive evaporation, sol-gel method, chemical deposition methods and spin coating process. Among these, spin coating is

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the simplest, low cost production and convenient technique to investigate the behavior of Cu_2O thin film under different additives.

Spin coating is one of the most common techniques for applying thin films to substrates. The use of spin coating in organic electronics and nanotechnology is widespread and has built upon many of the techniques used in other semiconductor industries. It also has some differences due to the relatively thin films and high uniformity required for effective device preparation, as well as the need for self-assembly and organization to occur during the casting process. Cu_2O thin film was deposited onto indium tin oxide (ITO) coated glass using spin coating technique with two different polymer additives such as polyethylene glycol and ethylene glycol because of it is a soft bottom-up approach to achieve a good control over film composition and microstructure.

Investigations had shown that additive polyethylene glycol; effectively improve the Cu_2O properties under relatively low temperature. To prepare Cu_2O thin film onto indium tin oxide (ITO) coated glass substrate for solar cell application by means of spin coating technique ad to investigate the behavior of Cu_2O thin films under different additives. The as-prepared films were annealed at 250˚ C in order to get single phase Cu_2O films.

The annealing temperature of 300˚ C is the optimum annealing temperature to prepare the single phase Cu_2O films. If annealing temperature is increased to 350˚ C, other phases exist such as Cu or CuO comes into existence. However, spin coating method became a favorite technique due to simple equipment involved and cheaper compared to other techniques.

Using the spin coating technique to form Cu_2O films on ITO substrates and conduct a detailed microstructures and optical investigation of Cu_2O films.

Materials and Method

Cu_2O thin films are characterized to investigate their microstructures and optical properties. The crystallinity and the phase composition of as-prepared films on indium tin oxide (ITO) substrates were examined with X-Ray diffractometer (XRD). The size of the particles and morphology of

Cu_2O films were studied by Scanning Electron Microscopy (SEM). Optical transmission and absorption spectra were measured for Cu_2O films grown on glass substrates using Shimadzu UV-Vis spectrophotometer (UV-1800).

Preparation of substrates

Indium tin oxide (ITO) coated glass was used as substrates. To prepare Cu_2O thin films by using spin coating technique on ITO glass slides with dimension (1cm x 1cm x 0.1cm) were used as the substrates. To get a high quality of thin film, the ITO glass substrates were soaked in acetone for a few minutes and rinsed in deionized water. The glass was taken out and dried in air at room temperature and baked the glasses about 15 minutes at 200°C to ensure good adhesion at the surface. Baking creates an ultra-thin layer of Cu_2O on the substrate surface, which proved to be an excellent solution to the problem of poor adherence for some of the materials.

Preparation of copper oxide solution

In this process, the starting materials used were copper (II) acetate, isopropyl alcohol and diethanolamine (DEA, $C_4H_{11}NO_2$) solution and mixed polyethylene glycol and ethylene glycol. 0.5 molar concentration of solution was formed by dissolving 0.5 gram copper acetate powder in 9 ml isopropyl alcohol and 0.5 ml diethanolamine which act as precursor, solvent and complexing agent respectively. There were three set of samples; (a) sample 1 (sample without any additive), (b) sample 2 (sample with polyethylene glycol), (c) sample 3 (sample with ethylene glycol). Small amount of polyethylene glycol and ethylene were added into the solution and the copper oxide solutions were continuously stirred for 24 hours using magnetic bar. The solutions were filtered using 10~15μm filter prior to spin coating process.

Preparation of copper oxide thin films deposition by spin coating method

Films were prepared by depositing the solution at room temperature by spin coating technique onto the substrates. The compound solutions were spread onto the substrates with spinning speed at 3000 rpm for 40 seconds. Immediately after coating process, the samples were dried for 5 minutes at

200°C for each layer to evaporate the solvent. The process was repeated to produce three layers of coating. After the drying of the last layer, samples were annealed for 1 hour at 300 °C. The flow diagram of sample preparation of Cu_2O thin films is shown in Figure 1. Figure 2 shows the photograph of sample preparation sequence for Cu_2O thin films using spin coating technique.

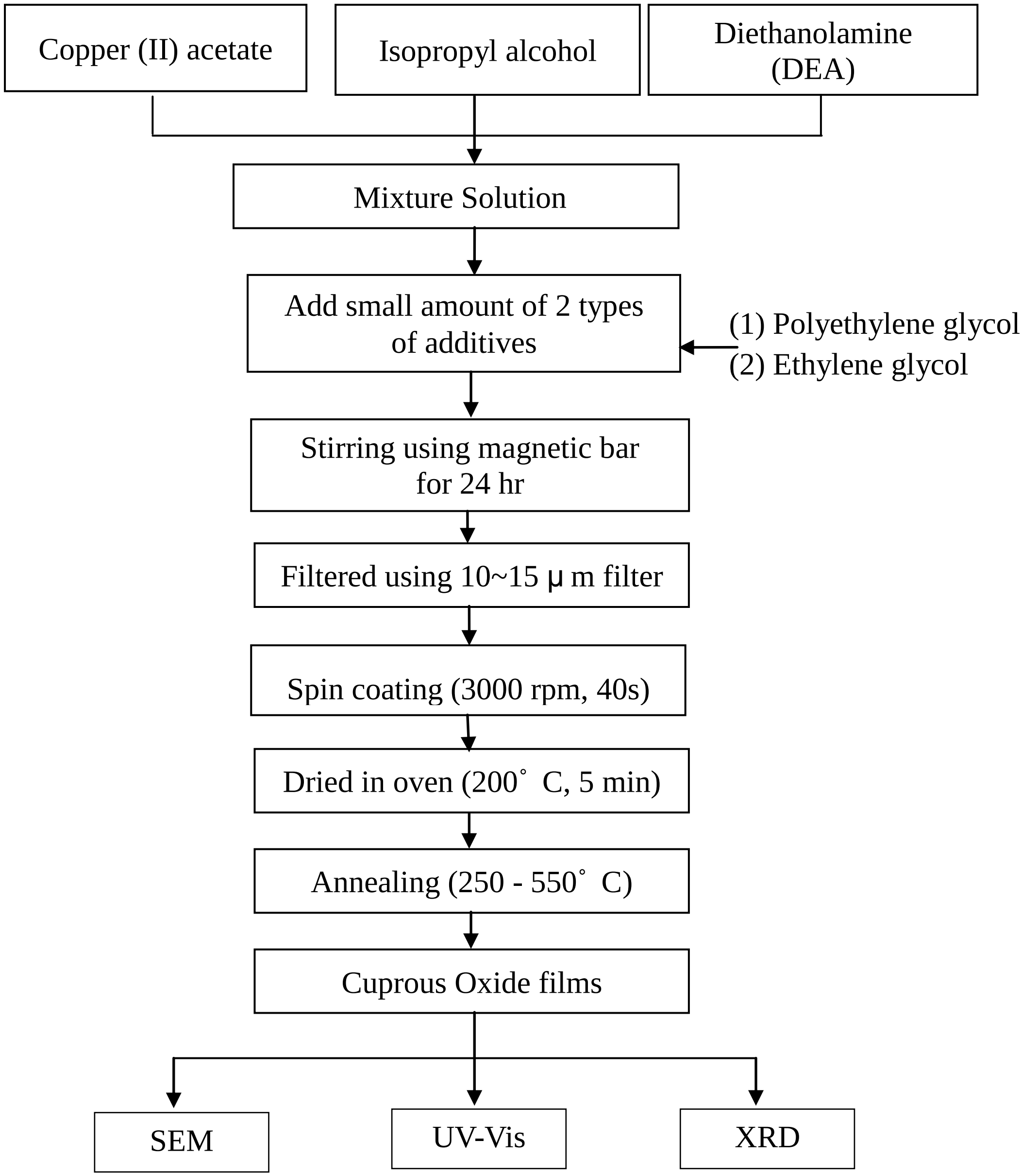
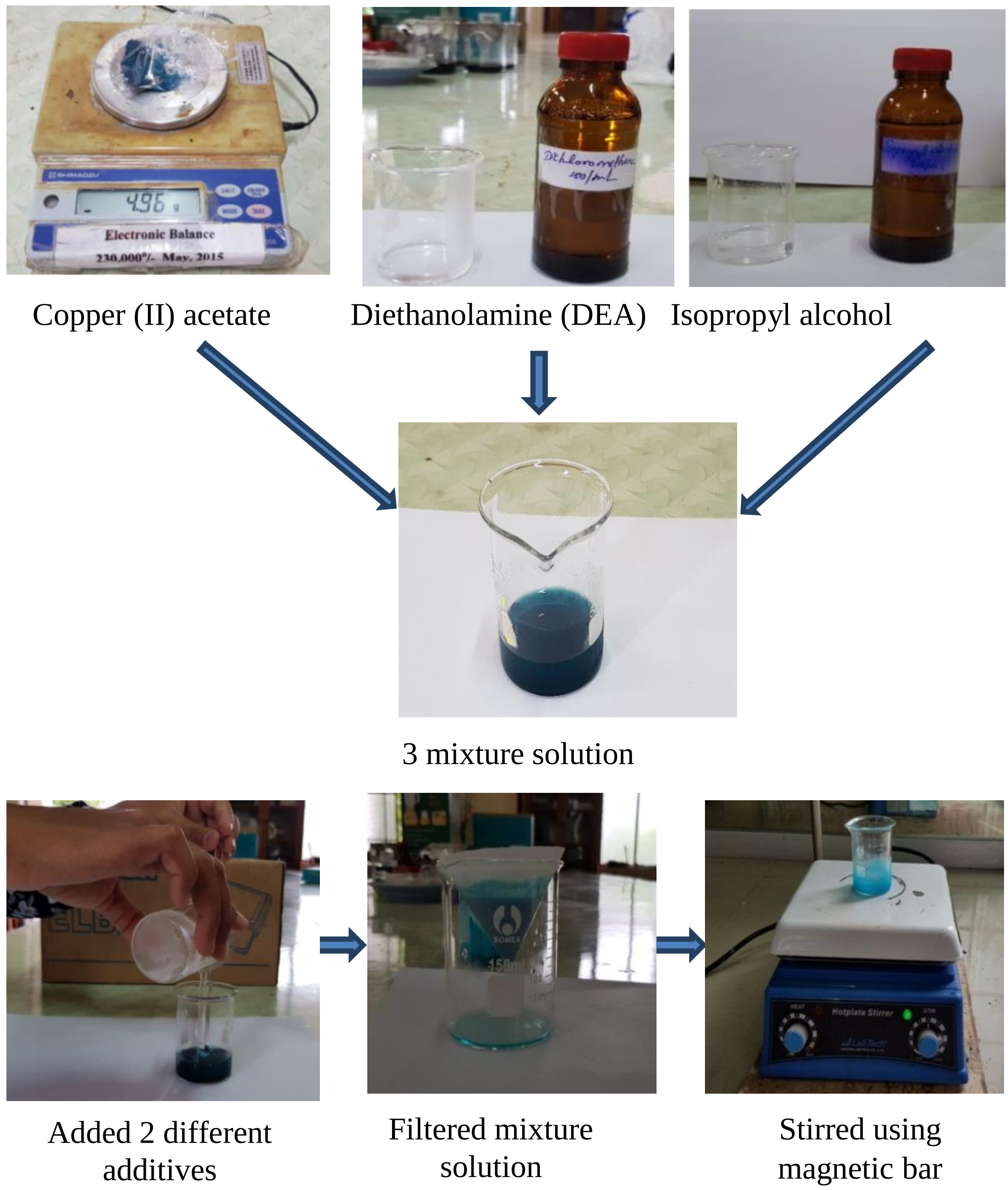
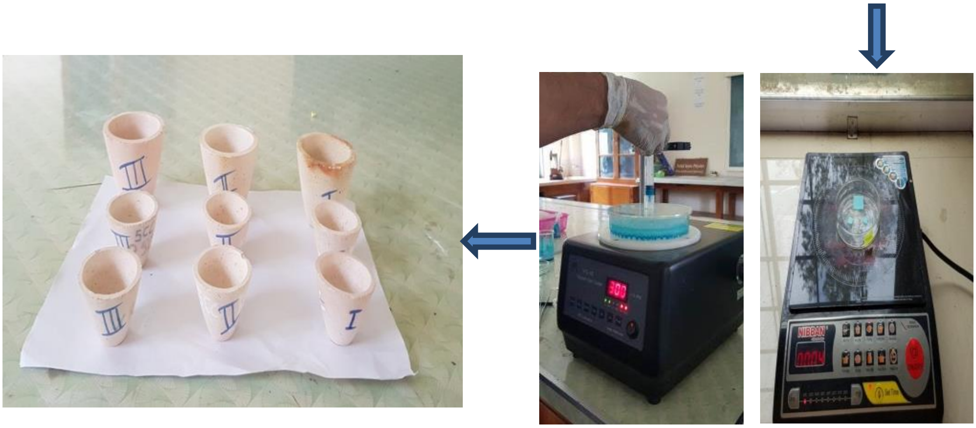


Figure 1: Flow diagram of sample preparation


Electronic Balance
Copper (II) acetate
Diethanolamine (DEA)
Isopropyl alcohol
3 mixture solution
Added 2 different additives
Filtered mixture solution
Stirred using magnetic bar



Annealed the samples Spin coating and heat treated

Figure 2: The photograph of sample preparation sequence for Cu_2O thin films using spin coating technique

Result and Discussion

XRD Analysis

The XRD patterns of obtained samples with different additives are shown in Figure 3 (a), (b) and (c). All diffraction peaks can be indexed to the cubic phase of Cu_2O crystals a match well with standard data. No other phases such as CuO or Cu are found in XRD patters confirming that all the samples exist as main Cu_2O phase. The single phase of Cu_2O films can be prepared at temperature of 300 $^{\circ}$C and time of annealing of 1 hour. When the temperature is lower or the time is shorter, it is hard to reduce cupric acetate to cuprous oxide completely, whereas if the temperature is too high or the reaction time is too long, it is easy to get copper rather than cuprous oxide.

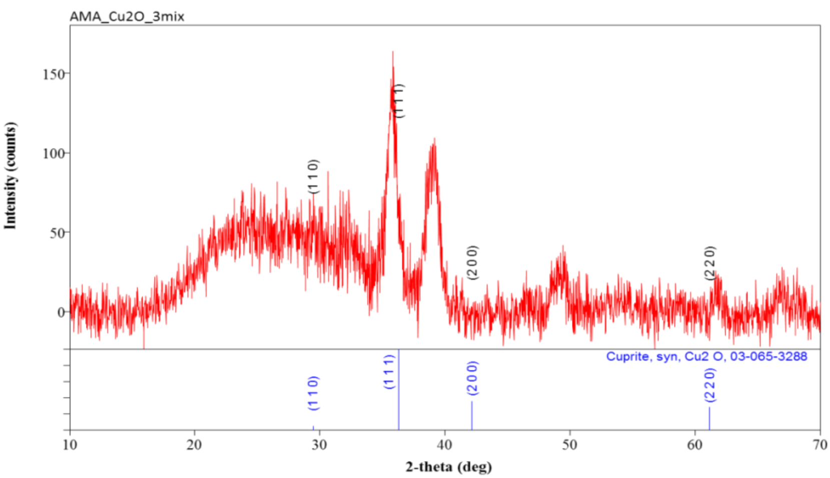
The film deposited onto ITO glass, two diffraction peaks are observed and identified as Cu_2O (111) and (200) directions. The strongest peaks in the XRD spectrum represent the crystal direction of Cu_2O (111). The lattice parameter for the films is the same and it is in agreement with the standard value of a 4.27Å. An average value of the crystallite size at the (111) plane can be obtained by applying the Debye-Scherer's equation

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

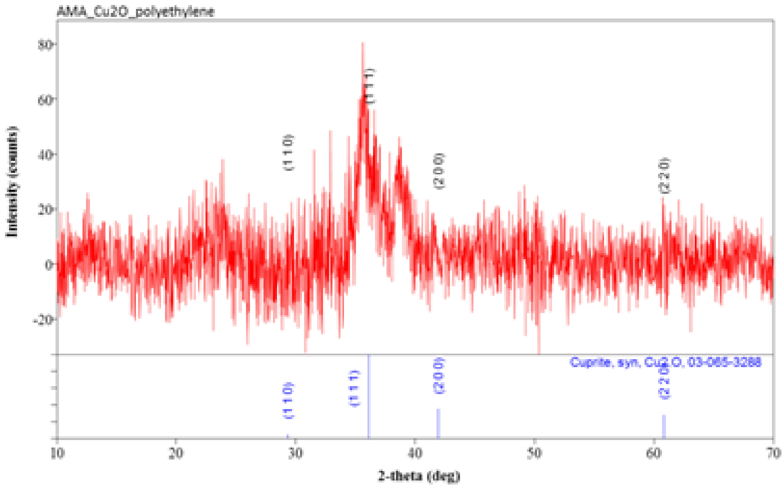
Where D is the crystallite size, λ is 1.5406Å for $CuK_{\alpha 2}$, β is the full width at half maximum (FWHM) of the peak in radian and θ is the Bragg angle indicated the calculated grain size of the Cu_2O diffraction peak. ITO glass used is a polycrystalline isotropic material with no preferred orientation. The Cu_2O film deposited on this substrate shows (111) preferential orientation, which may suggest that the fastest growth direction of Cu_2O is along the (111) direction. Table 1 summarized XRD analysis results of Cu_2O samples on ITO glass substrates at (111) plane.

Table 1: The energy gap, grain size and crystallite size of Cu_2O thin films

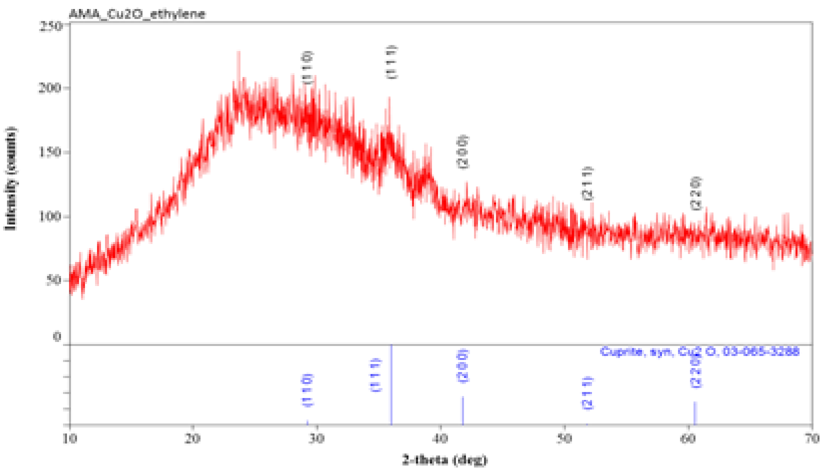
Samples	**Energy Gap (eV)**	**Grain Size (μm)**	**2θ (deg.)**	**Crystallite size (nm)**	**FWHM peak (deg.)**	**Plane (*hkl*)**
1	2.06	122	35.51	32.69	0.24	(111)
2	2.17	97	35.39	20.02	0.39	(111)
3	1.49	106	35.40	45.68	0.19	(111)



(a) sample 1



(b) sample 2

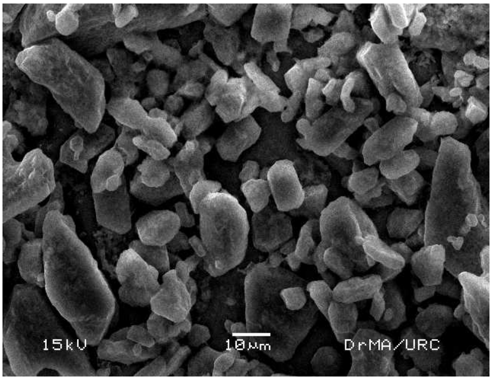


(c) sample 3

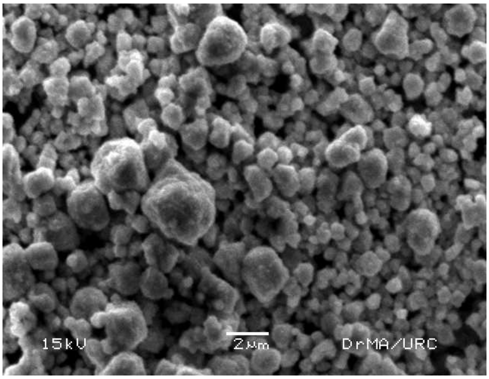
Figure 3: XRD patterns of Cu_2O thin film annealed at 300 °C for 1 hour (a) sample 1 (b) sample 2 and (c) sample 3

Film Morphology

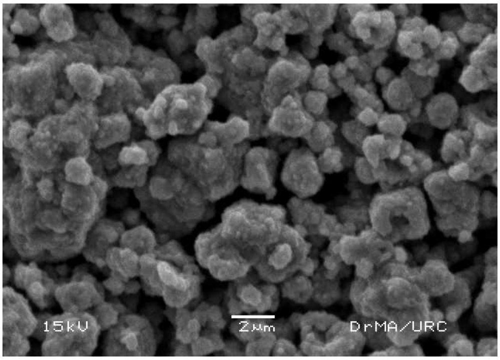
Figure 4 shows the surface morphology of three set of samples. It is showed that the surface morphology depends on the addition of additive and the films grown on ITO substrates are uniform. The average grain sizes of the Cu_2O films for the samples are shown in Table 1. After adding polyethylene glycol, the grain size reduces from 122 µm to 97 µm. It shows that the addition of polyethylene glycol increases the viscosity of the solution due to chain length effects. The addition of ethylene glycol has been widely used in the polyol synthesis of metal and metal oxide due to its strong reducing ability and relatively high boiling point (~197˚ C). The Cu_2O samples grains were irregular shape.



(a) sample 1



(b) sample 2



(c) sample 3

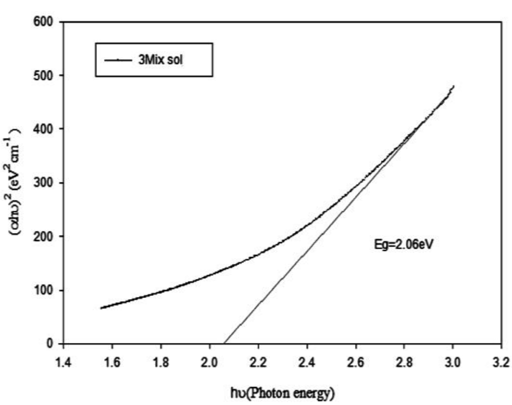
Figure 4: SEM images of Cu_2O Thin film at 250°C with different additives (a) sample 1 (b) sample 2 and (c) sample 3

Optical properties

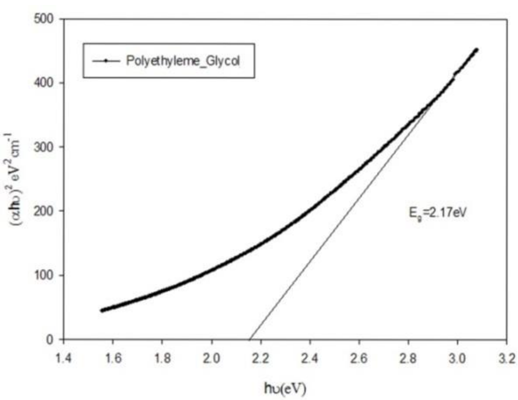
The UV-Vis spectra of different Cu_2O samples are shown in Figure 5 (a), (b) and (c). The absorbance of sample may be influenced by grain size, shape and coverage of sample. There is a possibility of increasing of absorbance contribute by scattering at grain size. The highest absorbance obtained for sample 2 (with polyethylene glycol addition) is due to it had the thickest film and smaller grain size. The film of sample 2 is more compact compared to other samples. The addition of polyethylene glycol will produce cracking free films with high optical absorbance. The polyethylene glycol additive can avoid the particle aggregation occurring in the solution, the sample 2 with polyethylene glycol has finer crystalline grain (97 µm) and thus decreases scattering at crystalline boundary. The absorption coefficient α , of the Cu2O film is related to the photon energy hυ .

$$(\alpha h\upsilon)^2 = (h\upsilon - E_g)^{1/2}$$

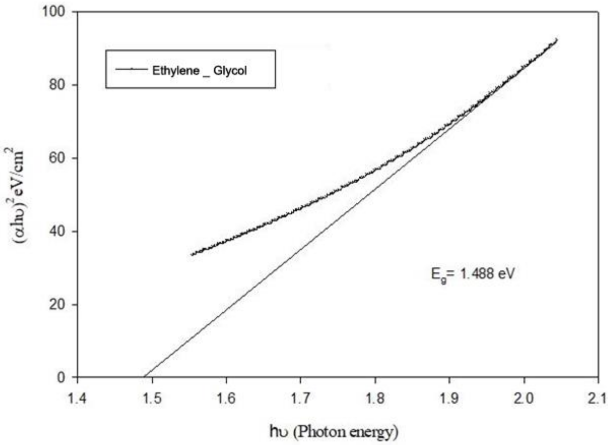
Where hγ is the photon energy and E_g is the optical energy gap. These energy gaps are calculate from the intercept of straight line on the photon energy (hυ) of the $(\alpha h\upsilon)^2$ vs (hυ) plot and the value listed in Table 1. The energy gap for these films was found to be in the range of 1.49 -2.17 eV and was found to be influence by film thickness and also the optical absorbance. The addition of polyethylene glycol produced the thickest film with higher energy gap and high optical absorbance.



(a) sample 1



(b) sample 2



(c) sample 3

Figure 5: Plots of $(\alpha h\upsilon)^2$ vs $(h\upsilon)$ to determine the energy of the optical absorption coefficient for Cu_2O films deposited onto ITO samples with different additives(a) sample 1 (b) sample 2 and (c) sample 3

Conclusion

Cu_2O thin film has been successfully grown on ITO substrates by spin coating with different additives and annealed at 300°C. Various properties of Cu_2O thin films have been characterized. The addition of polyethylene glycol to the parent solution can be enhance various properties of the films, such as decreasing grain size but increasing optical absorbance and energy gap of films. Based on the grain size of film prepared by polyethylene glycol has smallest grain of about 97μm with irregular shape. The highest optical absorbance film was obtained by the addition of polyethylene glycol. The energy band gap for these films was found to be in the range of 1.5 – 2.2 eV which is in a good agreement with the value of optical band gap for Cu_2O. The results indicate that the Cu_2O thin film prepared by spin coating technique can be used for solar cell. Then, the samples were characterized by means of XRD, SEM and UV-Vis measurement.

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