CuO free p-Cu_2O nano-surfaces prepared by oxidizing copper sheets with a slow heating rate exhibiting the highest photocurrent and the H_2 evaluation rate

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Introduction

Among the various metal oxide materials for solar energy applications, p-type cuprous oxide (p-Cu_2O) is a promising non-toxic and low cost semiconductor with attracted attention for many decades (Mittiga *et al., 2006)*. It was reported that p-Cu_2O can be prepared by various fabrication processes such as thermal oxidation, electrochemical oxidation, chemical bath deposition and chemical vapor deposition. Low energy conversion efficiency of p-Cu_2O based solar energy conversion devices is due to the prevention of the photo-generated charge carrier separation in the micron–sized Cu_2O grains on the surface enhancing the recombination process. If the grains radius is reduced from micron to nano-size, the opportunities for recombination can be dramatically reduced enhancing the light absorption properties of the films. Therefore, the preparation of nano-crystalline Cu_2O thin films is a key factor to improve the performance of solar application devices without destroying the crystalline properties of the Cu_2O films. Hence, the present work is aim to fabricate CuO free nano-crystalline p-Cu_2O by thermal oxidation of copper sheets under maintaining slow heating rate for the first time. Structural and photoelectrochemical properties are also aimed to study.

Methodology

The outer layers of commercially available (99.99% purity) copper sheets 2cm×4cm were removed by sand papers and polished with Brasso Metal Polisher until obtaining a mirror like surface. Thereafter, polished copper sheets were washed with a surface detergent and distilled water several times. Well cleaned copper sheets were inserted into a Quartz Tube in a Cabolite-301 Tube Furnace opening both ends by filling normal air during the oxidation process. Initially a heating rate 10 °C/min was provided inside the furnace with copper sheets starting from the room temperature. After reaching 300 °C, 400 °C, 450 °C and 700 °C the temperature kept constant for 30min and then cooled down to room temperature. Experimentally that it was found that the 10 °C/min heating rate was the most suitable to fabricate mechanically stable p-Cu_2O on copper sheets. Samples prepared above 450 °C temperature profiles did not produce mechanically stable Cu_2O films on copper sheets. Furnace temperature below 300 °C was not sufficient to oxidize copper sheets to form quality Cu_2O surfaces.Fig.2 shows the appearance of the Cu_2O films

prepared. Four different surface colors exhibited at each temperature profile expecting four different surface morphologies.

Result and Discussion

Fig.01 shows the diffuse reflectance spectra for the samples prepared from 300ºC, 400ºC, 450ºC and 700ºC temperature profiles. For the samples prepared from 300ºC, 400ºC and 450ºC temperature profiles show absorption edges 630nm, 620 nm and 600nm, to the band gaps 1.98eV, 2.0eV and 2.1 eV due to band to band transitions of Cu_2O. Band gap 1.4eV for an absorption edge ≈850nm can be observed for CuO crystals prepared from 700ºC temperature profile. It should be mentioned that the absorption edges for Cu_2O corresponding to the 300ºC, 400 ºC and 450ºC temperature profiles cannot be observed clearly for the samples prepared at 700ºC temperature profile as shown. So that, it can be concluded the most light is absorbed by CuO regions than the Cu_2O regions for the samples prepared from 700ºC temperature profile.

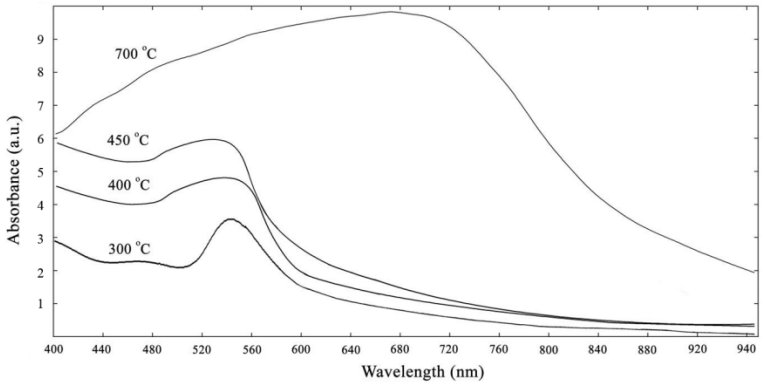

Figure01- Diffuse reflectance spectra of the p-Cu_2O thin films fabricated from 300ºC, 400ºC, 450ºC temperature profiles and p-CuO fabricated from 700ºC temperature profile

Table 01- Crystallite sizes estimated from XRD and AFM images prepared from 300ºC, 400ºC, 450ºC and 700ºC temperature profiles

	XRD (nm)	AFM (nm)
300 ºC	312.2	**308.9**
400 ºC	486.1	**488.3**
450 ºC	393.4	**395.1**
700 ºC	**320.7**	**322.3**

Table 01 shows the crystallite sizes estimated from XRD and AFM images obtained from samples prepared from 300ºC, 400ºC, 450ºC and 700ºC temperature profiles. It shows that the crystallite sizes obtained from both XRD and AFM are in good agreement of nano meter range.

According to figure 02 that the flat band potential for three samples are almost same (≈+.53 vs Ag/AgCl). Here it is assumed that the flat band potentials are nearly equal to the valance band (VB) position of the samples prepared from each temperature profile. The H^+/H_2 (-0.61V vs Ag/AgCl at pH=7) and O_2/H_2O (+.62V vs Ag/AgCl at pH=7) were obtained from the literature (Nian *et. Al., 2008)*. It should be mentioned that the conduction band (CB) position of the samples prepared from 300ºC, 400ºC and 450ºC profiles is more negative than the H^+/H_2 redox level showing a favorable CB band position to reduce water. Highest H_2 evolution rate was observed for the Cu_2O thin films prepared from 450ºC temperature profiles in the presence of 1M Na_2SO_4 at -0.4V vs Ag/AgCl biased potential may be due to the more negative CB position as shown in Figure 02. Highest photocurrent (≈ 10 mAcm $^{-2}$) was observed for sample prepared from 450ºC temperature profile under above experimental conditions is a remarkable finding.

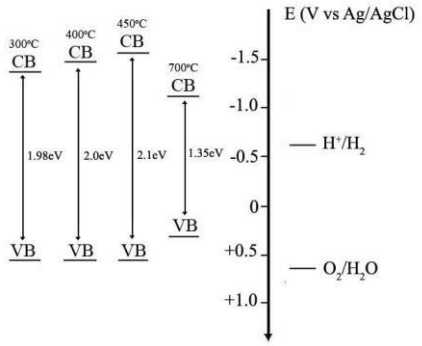

Figure 02- estimated band positions of nano-surfaces, H^+/H_2 and O_2/H_2O redox levels prepared from 300ºC, 400ºC, 450ºC and 700ºC temperature profiles

Conclusions

p-Cu_2O films prepared from 300ºC, 400ºC and 450ºC temperature profiles with 10ºC/min slow heating rate produced single phase Cu_2O nano-crystals and the films fabricated from 700ºC temperature profile coexist Cu_2O and CuO two phases. A blue shift of the band gap of Cu_2O was observed for the Cu_2O fabricated from the 450ºC temperature profile with compared to the Cu_2O films fabricated from 300ºC and 400ºC temperature profiles may due to the quantum confinement effect of the crystal sizes as exhibited from AFM micrographs. The highest H_2 evolution (≈ 6.2 Moles l^{-1} min^{-1}) and photo-current enhancement (≈ 10 mAcm $^{-2}$) from p-Cu_2O nano-surfaces fabricated from 450ºC temperature profile was observed with compared to the recent studies presented by Gratzel and co-workers (Paracchino *et al.*,2011) and the similar systems reported in the literature.

References

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