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# Sulfidation of electrodeposited microcrystalline/nanocrystalline cuprous oxide thin films for solar energy applications

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## Abstract

Grain size of polycrystalline semiconductor thin films in solar cells is optimized to enhance the efficiency of solar cells. This paper reports results on an investigation carried out on electrodeposited n-type cuprous oxide ( $\text{Cu}_2\text{O}$ ) thin films on Ti substrates with small crystallites and sulfidation of them to produce a thin-film solar cell. During electrodeposition of  $\text{Cu}_2\text{O}$  films, pH of an aqueous acetate bath was optimized to obtain films of grain size of about 100 nm, that were then used as templates to grow thicker n-type nanocrystalline  $\text{Cu}_2\text{O}$  films. XRD and SEM analysis revealed that the films were of single phase and the substrates were well covered by the films. A junction of  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  was formed by partially sulfiding the  $\text{Cu}_2\text{O}$  films using an aqueous sodium sulfide solution. It was observed that the photovoltaic properties of nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  heterojunction structures are better than micro  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  heterojunction solar cells. Resulting Ti/nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  solar cell structure produced an energy conversion efficiency of 0.54%,  $V_{\text{oc}} = 610$  mV and  $J_{\text{sc}} = 3.4$  mA cm<sup>-2</sup>, under AM 1.5 illumination. This is a significant improvement compared to the use of microcrystalline thin film  $\text{Cu}_2\text{O}$  in the solar cell structure where the efficiency of the cell was limited to 0.11%. This improvement is attributed mainly to the increased film surface area associated with nanocrystalline  $\text{Cu}_2\text{O}$  films.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Cuprous oxide ( $\text{Cu}_2\text{O}$ ) is an attractive material for photovoltaic and other applications such as gas sensing and hydrogen production. Cuprous oxide has received attention because it is a low cost, nontoxic material with a direct band gap of 2 eV. It has been well established that  $\text{Cu}_2\text{O}$  is generally a p-type semiconductor material due to the cuprous ion vacancies that exist in the crystal lattice [1–6]. However, electrodeposition

has the ability to control both conductivity type (n- or p-type) and morphology of the  $\text{Cu}_2\text{O}$  films. Moreover, the associated low fabrication cost and scalability make electrodeposition a more attractive method to deposit  $\text{Cu}_2\text{O}$  thin films [7–9].

$\text{Cu}_2\text{O}$  thin films have not been commonly used for  $P$ – $V$  conversion because of its low energy conversion efficiency (<2%) which results from the fact that light generated charge carriers in micron sized  $\text{Cu}_2\text{O}$  grains are not efficiently transferred to the surface but are lost due to the recombination. For randomly generated charge carriers, the average diffusion time from the bulk to the surface is given by  $\tau = r^2/\pi^2D$

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where  $r$  is the grain radius and  $D$  is the diffusion coefficient of carriers. If the grain radius is reduced from micro to nanoscale, the opportunities for recombination are dramatically reduced. Also nanoparticles increase the effective surface area of films by orders of magnitudes making them very beneficial for improving the efficiency of solar cell devices. However, in nanocrystalline films, the number of grain boundaries will be higher than that in microcrystalline films. As a result, the negative effects of the grain boundaries will also contribute to the efficiency of solar cells. This drawback in nanocrystalline films may be overcome if the grain boundary problem is over compensated by the improvements made due to the increase in the area of the active junction. So the preparation of nanocrystalline  $\text{Cu}_2\text{O}$  thin films is a key to improving the performance of solar cells [10–12].

It is found in general, that the resistance of electrodeposited  $\text{Cu}_2\text{O}$  films is higher than that of the  $\text{Cu}_2\text{O}$  films prepared using other techniques [8, 13]. It has been reported earlier that sulfidation of electrodeposited p-type  $\text{Cu}_2\text{O}$  films could be used to improve the output characteristics of solar cells made with electrodeposited  $\text{Cu}_2\text{O}$  films by increasing their surface conductivity [14, 15]. In particular, Briskman [15] used sulfided p-type  $\text{Cu}_2\text{O}$  films deposited on Cu substrates using a lactate bath to obtain a solar cell of efficiency of 0.06%,  $V_{oc} = 380$  mV and  $J_{sc} = 600 \mu\text{A cm}^{-2}$ . Wijesundara *et al* [16] sulfided n-type  $\text{Cu}_2\text{O}$  films deposited on ITO substrates using an acetate bath to make a heterojunction of n- $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  and obtained  $V_{oc}$  of 255 mV and  $J_{sc}$  of  $1.6 \text{ mA cm}^{-2}$ . In all of the reported work on sulfidation of electrodeposited  $\text{Cu}_2\text{O}$  films, microcrystalline films deposited on various substrates have been investigated. To our knowledge, electrodeposition of n-type nanocrystalline  $\text{Cu}_2\text{O}$  films and sulfidation of them for solar energy applications have not been reported previously. In this work, electrodeposition of  $\text{Cu}_2\text{O}$  thin films on the Ti substrate was investigated using acetate baths [17] of different pH values in order to control the grain size of the polycrystalline films. We report the electrodeposition of nanocrystalline n-type  $\text{Cu}_2\text{O}$  thin films on Ti substrates and partial sulfidation of the films to obtain  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  heterostructures.

The partial sulfidation of the cuprous oxide forms a thin degenerating nanocrystalline semiconductor layer of copper sulfide ( $\text{Cu}_x\text{S}$ ) which forms a heterojunction with  $\text{Cu}_2\text{O}$  facilitating the collection of the photogenerated carriers and thereby improving the output characteristics of the cells.

We observed that, for the first time to our knowledge, nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  a heterojunction solar cell structure produced the highest open-circuit voltage and the short-circuit current density ( $V_{oc} = 610$  mV and  $J_{sc} = 3.4 \text{ mA cm}^{-2}$ , under AM 1.5 illumination) reported for the electrodeposited  $\text{Cu}_2\text{O}$ -based thin film solar cells. Even though the band gap of  $\text{Cu}_2\text{O}$  is far away from the optimum band gap for a single junction cell, this device would be useful as a tandem top cell or for special applications where a high voltage is more important than the efficiency.

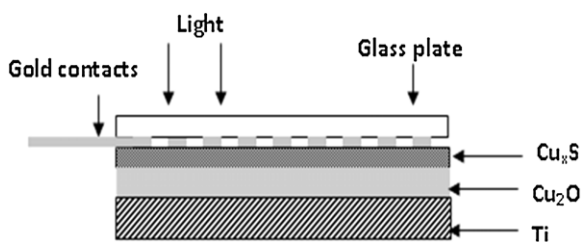
## 2. Experimental details

$\text{Cu}_2\text{O}$  thin films were deposited on Ti substrates by the electrodeposition method. Prior to the film deposition, substrates were cleaned with detergent, diluted  $\text{HNO}_3$  and finally with distilled water. Electrodeposition of  $\text{Cu}_2\text{O}$  thin films on Ti substrates was accomplished in a three-electrode electrochemical cell containing aqueous solutions of 0.1 M sodium acetate and 0.01 M cupric acetate [17]. The temperature of the electrolyte was maintained at  $60^\circ\text{C}$  and the electrolyte was continuously stirred using a magnetic stirrer. The counter electrode was a platinum plate and a saturated calomel electrode (SCE) was used as the reference electrode. Electrodeposition was carried out under a potentiostatic condition of  $-200$  mV versus SCE. pH of the electrolyte was adjusted by adding a dilute sodium hydroxide solution to the bath.

Spectral responses of all  $\text{Cu}_2\text{O}$  films were investigated in a three electrode photoelectrochemical cell containing a 0.1 M sodium acetate solution. The contact area of the film with the electrolyte was  $\sim 4 \text{ mm}^2$ . The counter electrode was a platinum plate and the reference electrode was an SCE. Spectral responses of the electrodes were measured using a phase sensitive detection method to monitor the photocurrent signal produced by a chopped monochromatic light beam. The chopping frequency was 63 Hz. A monochromator (Sciencetech-9010), a potentiostat (Hukoto Donko HAB-151), a lock-in amplifier (Stanford Research-SR 830 DSP) and a chopper (Stanford-SR 540) were used with a pc for the spectral response measurements.

X-ray diffraction measurements were obtained using a SHIMADZU (XD-D1) x-ray diffractometer. The surface morphology of the films and devices was determined by scanning electron microscopy (Philips XL40) and element composition of the films was investigated by energy dispersive x-ray spectroscopy (SHIMADZU SXS-550).

In order to grow n-type nanocrystalline  $\text{Cu}_2\text{O}$  films, first  $\text{Cu}_2\text{O}$  films were deposited on Ti substrates using an acetate bath of pH 7.5 for 30 min duration. The resulted films were p-type and therefore a brief annealing in air for 5 min duration was performed at  $200^\circ\text{C}$  to make them n-type. These films were then used as templates for depositing thicker n- $\text{Cu}_2\text{O}$  films using an acetate bath of pH 6.2 for a duration of 30 min. For comparison, n-type films were also deposited on Ti substrates using an acetate bath of pH 6.2 for 60 min duration without using the templates.  $\text{Cu}_2\text{O}$  films were sulfided by reacting at  $200^\circ\text{C}$  with a thin layer of an aqueous solution of 0.01 M  $\text{Na}_2\text{S}$  formed on the surface of the films. These thin layers of solution were formed on the films using a liquid droplet maker. After sulfidation, films were thoroughly rinsed with distilled water and then dried in air. To reduce the resistivity of sulfided samples, additional sulfidation on the already sulfided films was carried out by exposing them to ammonium sulfide gas at room temperature for about 2 s. A gold grid of thickness 100 nm was evaporated onto the sulfided  $\text{Cu}_2\text{O}$  film using a thermal evaporator to make the front ohmic contact, to fabricate the  $\text{Ti}/\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  thin film solar cell structure shown in figure 1. These structures



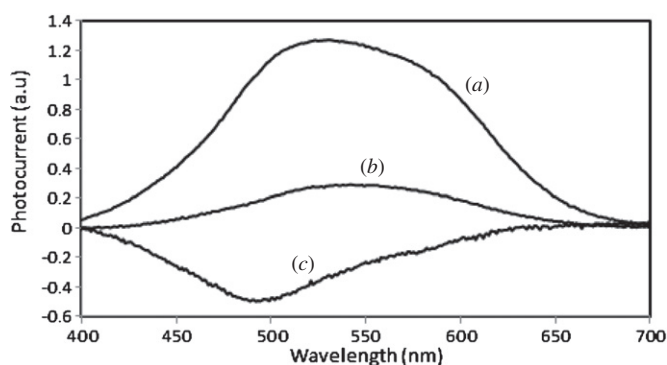
**Figure 1.** Ti/nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  solar cell structure with electrical contacts.

were characterized by current density–voltage ( $J$ – $V$ ), open-circuit voltage, short-circuit current and incident photon to current efficiency (IPCE) measurements.

### 3. Results and discussion

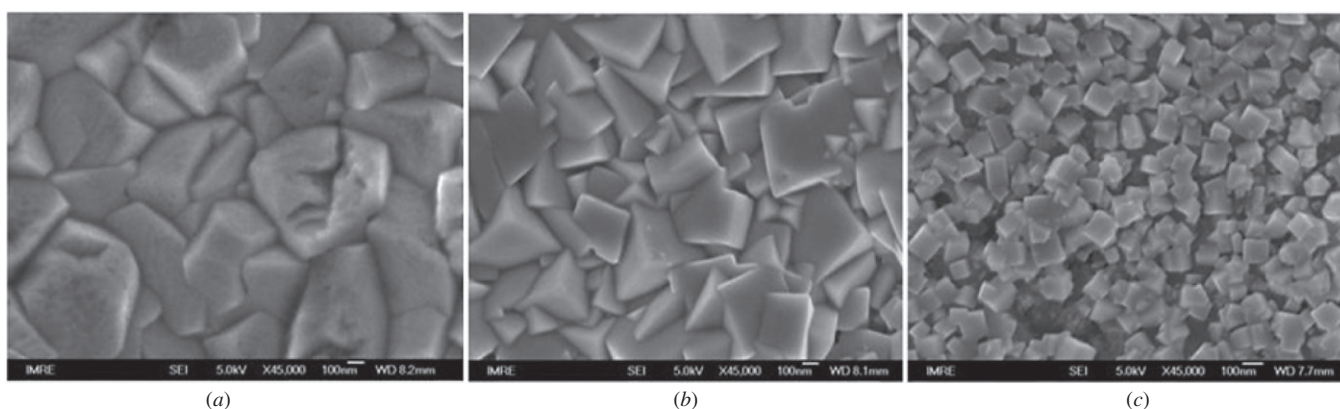
We observed that the morphology of the electrodeposited  $\text{Cu}_2\text{O}$  thin films strongly depends on the pH value of the deposition bath. For example, figure 2 shows the SEM pictures of the films deposited in acetate baths containing 0.1 M sodium acetate and 0.01 M cupric acetate at pH values (a) 6.2, (b) 6.9 and (c) 7.5, respectively. Similar results of dependence of morphology of the  $\text{Cu}_2\text{O}$  films on the pH of the deposition bath have been reported earlier [18–21]. It is important to note here that at the pH of 7.5, the size of the crystal grains is small and is about 100 nm.

However, we observed that if the deposition time in this bath was increased to obtain thicker films, the grain size of the films was increased. The photocurrent spectral responses of the films prepared at pH (a) 6.2, (b) 6.9 (c) 7.5 are shown in figure 3. The films prepared at pH value 6.2 and 6.9 produced n-type photosignal, as shown in figures 3(a) and (b), while the film prepared at pH 7.5 produced p-type signals, as shown in figure 3(c). It is well known that  $\text{Cu}_2\text{O}$  films electrodeposited using basic baths produced p-type films while films deposited in near neutral or acidic baths produced n-type films [13, 22–24]. We observed that if the film prepared at pH 7.5 producing p-type signal is heat treated in air at 200 °C for 5 min, it is transformed to n-type. We did not investigate this p-type to n-type transformation of the films in detail and it will be a subject for future investigations.

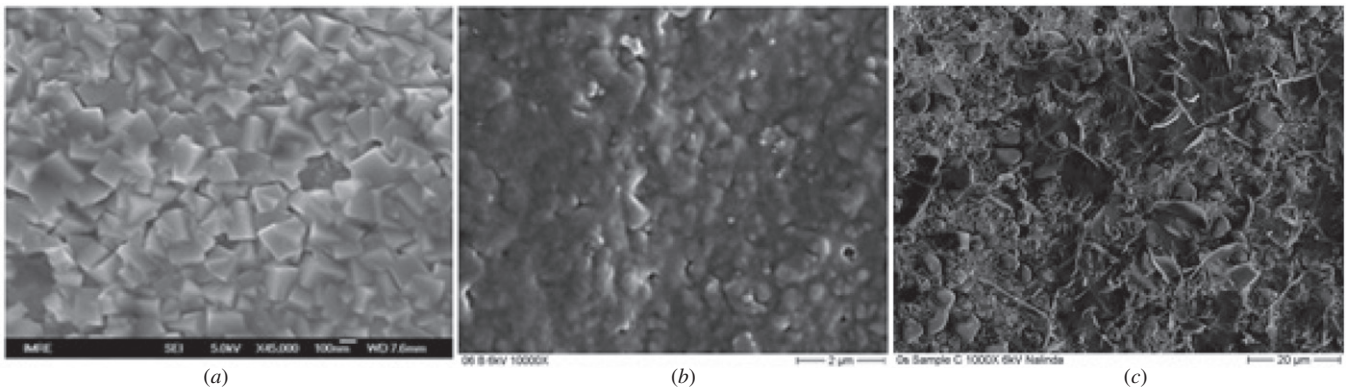


**Figure 3.** The photocurrent spectral responses of the films prepared at pH (a) 6.2, (b) 6.9 (c) 7.5.

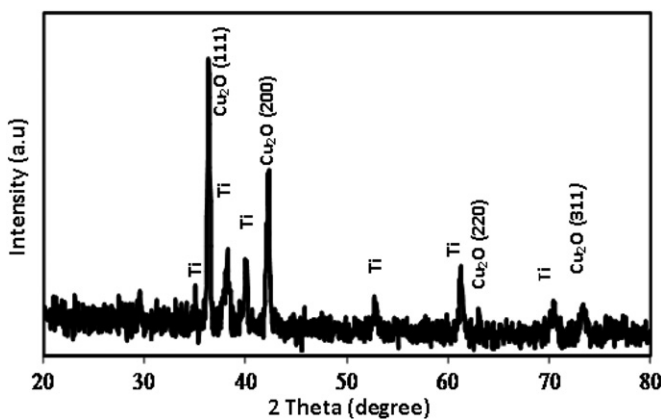
In order to obtain thicker n-type  $\text{Cu}_2\text{O}$  films of small crystal size, the films deposited using the acetate bath of pH 7.5 followed by annealing in air at 200 °C for 5 min were employed as templates. The acetate bath used to obtain thicker n-type  $\text{Cu}_2\text{O}$  films using these templates was a solution containing 0.1 M sodium acetate and 0.01 M cupric acetate at pH 6.2. Figure 4(a) shows the SEM picture of an n- $\text{Cu}_2\text{O}$  film prepared using the 100 nm  $\text{Cu}_2\text{O}$  template and it is evident in figure 4(a) that the size of the crystals in the resulting film is about 100 nm. It is important to note here that if only the Ti substrate, without the templates, was used for the deposition in the acetate bath at pH 6.2, as shown in figure 2(a), the crystal size is about 1  $\mu\text{m}$ . Thus, in order to obtain thicker n-type  $\text{Cu}_2\text{O}$  films with a nanocrystalline structure, use of the nanocrystalline template was essential. Otherwise, although the film obtained in the bath is n-type, the resulting crystal size of the film will be of the order of 1  $\mu\text{m}$ . Figure 4(b) shows the SEM picture of the film shown in figure 4(a) after the sulfidation by using  $\text{Na}_2\text{S}$ . The film in figure 4(b) was obtained by heating the  $\text{Cu}_2\text{O}$  film shown in figure 4(a) at 200 °C with a thin layer of 0.01 M aqueous solution of sodium sulfide on the surface of the film. Then this sulfided film was briefly (2 s) exposed to ammonium sulfide vapor to reduce the resistivity of the top layer. The corresponding SEM pictures are shown in figure 4(c). It is clear in figures 4(b) and (c) that the surface is covered by a film due to the sulfidation. The visibility of the  $\text{Cu}_2\text{O}$  film surface through the sulfide layer is indicative of the transparency and the thinness of the  $\text{Cu}_x\text{S}$  layer.



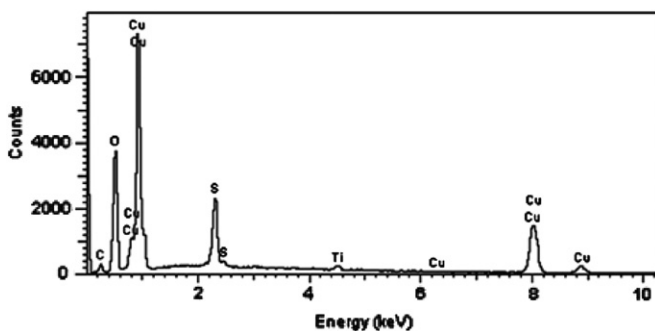
**Figure 2.** SEM pictures of electrodeposited thin films prepared in acetate baths of pH (a) 6.2, (b) 6.9 and (c) 7.5 on the Ti substrate at 60 °C.



**Figure 4.** (a) SEM picture of an n-Cu<sub>2</sub>O film prepared using the 100 nm Cu<sub>2</sub>O template (b) SEM picture of sulfided nanocrystalline Cu<sub>2</sub>O sample sulfided by Na<sub>2</sub>S (c) SEM picture of sulfided nanocrystalline Cu<sub>2</sub>O sample further sulfided by NH<sub>4</sub>S.



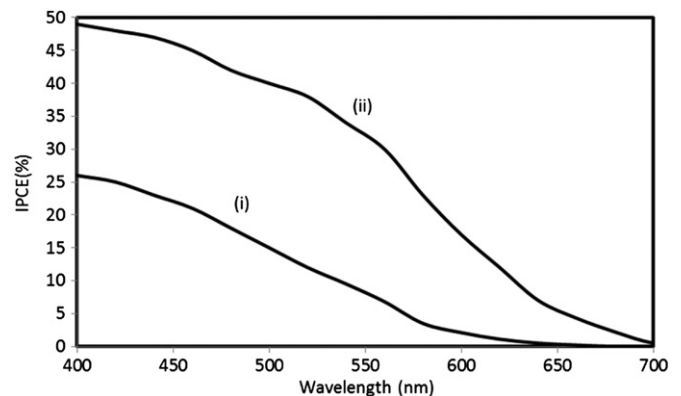
**Figure 5.** X-ray diffraction spectrums obtained for the sulfided Cu<sub>2</sub>O film.



**Figure 6.** EDX spectrums obtained for the sulfided Cu<sub>2</sub>O film.

XRD spectrum of the sulfided Cu<sub>2</sub>O film is shown in figure 5. It is evident that only Cu<sub>2</sub>O peaks are present in the XRD spectrum and peaks due to Cu<sub>x</sub>S are absent. The EDX spectrum of the sulfided film is shown in figure 6 and it confirms that due to the sulfidation of the film, sulfur is incorporated into the film. Due to the amorphous nature of the Cu<sub>x</sub>S layer formed by the partial sulfidation, Cu<sub>x</sub>S peaks are absent in the XRD spectrum shown in figure 5.

The IPCE curves of the solar cells made with sulfided (i) microstructure and (ii) nanostructured Cu<sub>2</sub>O films are shown in figure 7. By comparing the two IPCE curves (i) and (ii) shown in figure 7 it can be clearly seen that a remarkable

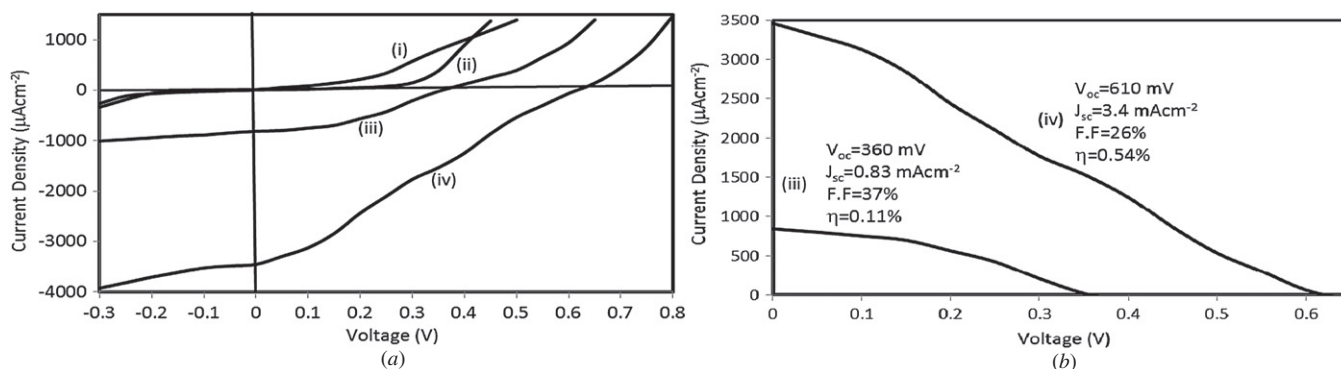


**Figure 7.** IPCE spectra of (i) micro Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au and (ii) nano Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au solar cells.

improvement of IPCE has resulted due to the presence of the nanocrystalline layer of Cu<sub>2</sub>O.

As shown in figure 7, it is clear that mainly the carrier generation is limited to the Cu<sub>2</sub>O layer, because only the contribution from the photons having energy greater than the band gap energy of Cu<sub>2</sub>O (2 eV) is dominant. However, a little improvement of long wavelength response is evident in nano Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au solar cell structure, curve (ii). In the solar cell structure that we have studied here, as shown in figure 1, the light is incident through the Cu<sub>x</sub>S layer. Therefore, short wavelengths absorbed by the Cu<sub>x</sub>S layer may not contribute to the photocurrent. If the light is incident through the Cu<sub>2</sub>O layer (as a window layer), on the other hand, further enhancement of the response of the shorter wavelengths could be expected. Indeed, we are currently investigating this possibility of improving the efficiency of the solar cell device by sulfidation of the nanocrystalline Cu<sub>2</sub>O films deposited on ITO substrates.

Figure 8(a) shows *J-V* characteristics of the solid-state photovoltaic devices (i) nano Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au, (ii) micro Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au solar cells in the dark, (iii) micro Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au and (iv) nano Cu<sub>2</sub>O/Cu<sub>x</sub>S/Au under illumination. Figure 8(b) illustrates *J-V* characteristics in the fourth quadrant of figure 8(a) redrawn in the first quadrant for the sake of clarity. From figure 8(a), it is clear that considerably strong rectification characteristics can be observed for both



**Figure 8.** (a)  $J-V$  characteristics of the solid-state photovoltaic devices (i) nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$ , (ii) micro  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  solar cells in the dark, (iii) micro  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  and (iv) nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  under illumination, (b)  $J-V$  characteristics in the fourth quadrant of (a) redrawn in the first quadrant for the sake of clarity.

junctions. The efficiencies of both solar cell devices are limited by the poor fill factors and this may be due to high resistivity of both  $\text{Cu}_2\text{O}$  and  $\text{Cu}_x\text{S}$  films.

Increase in the surface roughness of a film due to the nanostructure is being exploited here. However, in nanocrystalline films, number of grain boundaries is higher than that in microcrystalline films. As a result, even though increased surface area has enabled an improved photon collection in the device, it may have at the same time introduced increased interfacial defects lowering the fill factor further. This problem in nanocrystalline films may be overcome if the grain boundary problem is over-compensated by the improvements made due to the increase in the area of the active junction. Thus, the nanocrystalline films could be used to improve the efficiency of solar cell devices.

This effect is clearly illustrated by figures 8(a) and (b). All the conditions used to prepare the microcrystalline solar cell device were as same as for nanocrystalline cell, except that the nanocrystalline template was not used for the deposition of the microcrystalline  $\text{Cu}_2\text{O}$  film. It can be seen from figure 8(a) that the  $J-V$  characteristics in the dark for the nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell (curve (i)) deviates more from ideality compared to that in the case of micro  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell (curve (ii)). This is attributed to the relatively poor nature of nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  junction of the nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell compared to that of the micro  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell caused by the higher interfacial defects in nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  junction. However, it can be seen that under illumination, the nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell has produced a much larger photocurrent and a photovoltage (curve (iv)). While the relatively poor junction has given rise to an even lower fill factor for the nano  $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Au}$  cell, it can be clearly seen in figure 8(b) that the efficiency of the nanocrystalline solar cell has increased to 0.54% compared to that in the microcrystalline which is 0.11%. Therefore, the presence of the nanocrystalline film is responsible for the enhancement of the output characteristics of the solar cell made by sulfidation of n- $\text{Cu}_2\text{O}$  films.

In summary, the solar cell structure produced by the sulfidation of nanocrystalline  $\text{Cu}_2\text{O}$  film results in an energy conversion efficiency = 0.54%,  $V_{oc} = 610$  mV and  $J_{sc} = 3.4$  mA cm $^{-2}$ , at AM 1.5 illumination. The efficiency of the nanocrystalline solar cell is limited by the poor fill factor of

26%. Recent studies show that group VII elements such as Cl and Br added as dopants would help to reduce the high resistivity associated with  $\text{Cu}_2\text{O}$  films [25]. Our current work shows that the above parameters can be further improved using Cl doped  $\text{Cu}_2\text{O}$  films for sulfidation. However, the efficiency value we report here, to our knowledge, is the highest reported efficiency for a thin film solar cell made with electrodeposited  $\text{Cu}_2\text{O}$  films.

#### 4. Conclusion

In conclusion, this investigation has demonstrated that polycrystalline n-type cuprous oxide thin films having small crystals of the size of 100 nm could be electrodeposited. An acetate bath of pH 7.5 was used to obtain crystal size of 100 nm and the resulted films were used as templates to grow thicker n-type nanocrystalline films in a bath of pH 6.2. A thin film solar cell was made by the sulfidation of the nanocrystalline films and the resulted solar cell produced an efficiency of 0.54%, the highest efficiency reported for the electrodeposited  $\text{Cu}_2\text{O}$ -based thin film solar cells. For this solar cell, an open-circuit voltage,  $V_{oc} = 610$  mV and a short-circuit current,  $J_{sc} = 3.4$  mA cm $^{-2}$ , were obtained at AM 1.5 illumination. This is a significant enhancement compared to the solar cell structures based on microcrystalline  $\text{Cu}_2\text{O}$  films that resulted in an efficiency of only 0.11%. The observed enhancement of the efficiency of the n- $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$  junction solar cell device is attributed to the increase in the active junction area of the cell due to the nanocrystalline nature of the  $\text{Cu}_2\text{O}$  film.

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