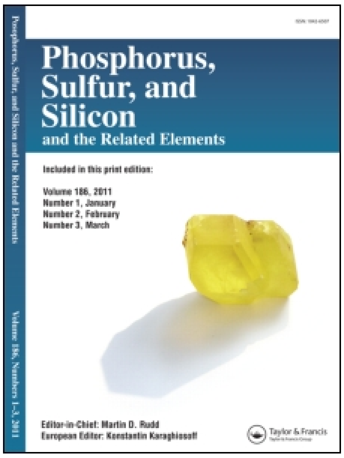

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THEN FILM CELLS BASED ON $CuInSe_2$

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THIN FILM CELLS BASED ON $CuInSe_2$

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ABSTRACT Using thin film devices of the form CdS(n)/$CuInSe_2$(p) fabricated on electrodeposited $CuInSe_2$, electrical and optical measurements have been made. From temperature-dependent I-V measurements, it was observed that the recombination current became progressively more important as the temperature was decreased. Results of dark C-V measurements indicated that $CuInSe_2$ films with carrier concentrations in the range from 10^{15} to 10^{17} cm^{-3} can be easily prepared using the electrodeposition method. Photoresponse of the devices was also measured, giving an essentially flat region in the range from 0.6 to 1.0 micron. At wavelengths beyond 1 micron, the quantum efficiency decreased continuously with the increase in the wavelength. This continuous decrease in the quantum efficiency could be due to the presence of interface states as suggested by the photo capacitance measurements.

INTRODUCTION

Thin film devices of the forms CdS(n)/$CuInSe_2$(p) and CdS/$CuInSe_2$ are very promising and interesting for photovoltaic application due to the following advantages: 1) large optical absorption coefficients of $CuInSe_2$ (direct gap, E_g=1 eV) for photons in the solar spectral range, therefore a large conversion efficiency of the devices even with a small film thickness, 2) good thermal stability of $CuInSe_2$ and CdS, and hence good thermal stability of the fabricated devices, and 3) a small lattice mismatch between $CuInSe_2$ and CdS (the mismatch can be further reduced by adopting CdZnS). For the CdZnS/$CuInSe_2$ cells, an energy conversion efficiency of more than 12% has already been achieved recently by researchers using vacuum evaporated $CuInSe_2$ films[1], suggesting that thin film $CuInSe_2$ to be a potential candidate for large scale terrestrial applications. For such large-scale applications, low cost and large area $CuInSe_2$ thin films with uniform mechanical and electrical properties are needed. These requirements can not be easily met by using vacuum methods because of the expensive equipments and large power consumption during the fabrication. Furthermore, it is relatively difficult to increase the throughput of the film deposition using the vacuum methods. In the present work, we have adopted thin films of $CuInSe_2$ deposited by a low cost electrodeposition method for device fabrication. The properties of the devices have been investigated in an attempt to determine whether the electrodeposited $CuInSe_2$ films are useful for terrestrial solar cell production. For the fabricated devices, dark and illuminated current-voltage characteristics were first measured. Dark and illuminated differential capacitance-voltage measurements were then carried out to obtain information about the carrier concentration and interface states in the devices. Such data are important for the improvement of cell efficiency.

EXPERIMENTAL

$CuInSe_2$ Thin Films

Thin films of $CuInSe_2$ with a thickness of about 1.5 microns were deposited from a solution containing Cu, In and Se ions using a simple electrodeposition method[2]. During the deposition, Mo and Mo coated glass plates were used as substrates. The deposited films were found to be polycrystalline with a chalcopyrite crystal structure, which can be further improved by a post deposition heat treatment[3]. After such heat treatment at temperatures above 300^oC for a period of 30 minutes, magnitude of the characteristic X-ray peaks was found to increase significantly[3]. The compositional uniformity of the films were examined by electron probe micro analysis (EPMA) and it was found that all of the deposited films had essentially a constant distribution for the three elements both across and along the sample. This uniform concentration distribution is important for films with uniform electrical resistivity which is required for high quality devices. The concentrational depth profile of the deposits was determined using secondary ion mass spectroscopy (SIMS). Results from the SIMS analysis showed essentially flat Cu, In and Se profiles throughout the complete film thickness. For the electrodeposited $CuInSe_2$ films, the elemental concentration can be easily controlled by controlling the depositing conditions. The morphology of the film was examined by taking SEM photographs for both the top and the side views of the films deposited on Mo coated glass substrates. Fig. 1 is a side view of a fractured $CuInSe_2$ film showing the uniform thickness and smooth surface. This figure also shows the columnar film structure which also has been found in high quality vacuum-deposited $CuInSe_2$ films. The direction of the columnar grains of the deposited films was found from X-ray diffraction to coincide roughly with the direction of (112). This columnar structure, having the long axis perpendicular to the substrate surface, is important for devices involving CdS which are described in the next sections.

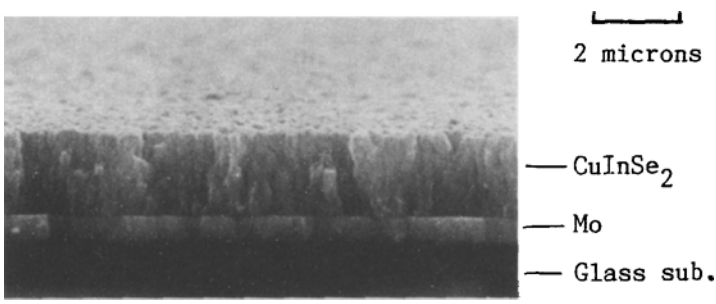


FIGURE 1 A cross sectional view of the electrodeposited $CuInSe_2$ film.

CdS Thin Films

The semiconductor CdS has a relatively large band gap (E_g = 2.4 eV) and therefore has large optical transmission coefficients in most part of the solar spectral region. This material has long been used with Cu_2S for photovoltaic devices due to the good thermal stability and the attainable low electrical resistivity. Thin films of CdS used in the present study were prepared in a vacuum system by a single source thermal evaporation technique[4]. The evaporation source was prepared by mixing weighed amounts of high purity CdS and In_2S_3 powder (about 2% In_2S_3). Indium was introduced in order to reduce the electrical resistivity of the CdS films. For the films with a thickness of about 4 microns, typical resistivity was about 10^{-3} ohm cm when deposited at a substrates temperature of 180°C and a rate of 0.7 micron/min. Using the above conditions, the CdS films also showed a columnar structure with the long axis perpendicular to the substrate (see Fig. 2). The direction of the long axis was confirmed to be that of the (002) plane from X-ray diffraction. When deposited on a $CuInSe_2$ film with the (112) preferred orientation, the lattice mismatch between the two materials amounts to about 1%. This small lattice mismatch is required in order to reduce interface states density and thus improved device performance.

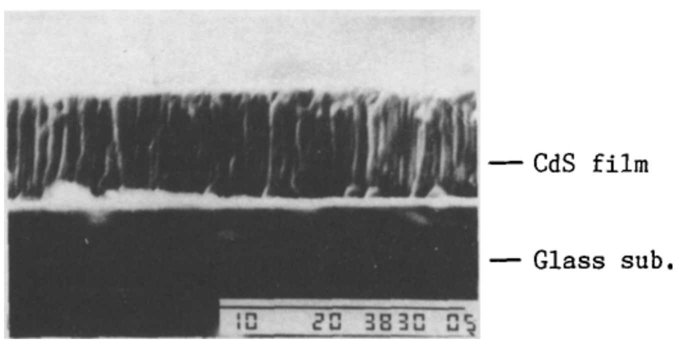


FIGURE 2 A cross sectional view of the vacuum deposited CdS film (horizontal bar is 10 microns).

For actual device fabrication, the CdS films were deposited on the $CuInSe_2$ surface through an aluminum mask with a window area of 0.9 cm^2. The cross section of the CdS/$CuInSe_2$ assembly is shown in Fig. 3. Here it is seen that the long axis of CdS is aligned along that of the $CuInSe_2$, with a small inclination resulting from a nonvertical angle of incidence of the source material during the deposition[4]. After the CdS deposition, aluminum grids with a thickness about 2 microns were evaporated through a second mask for electrical contacts.

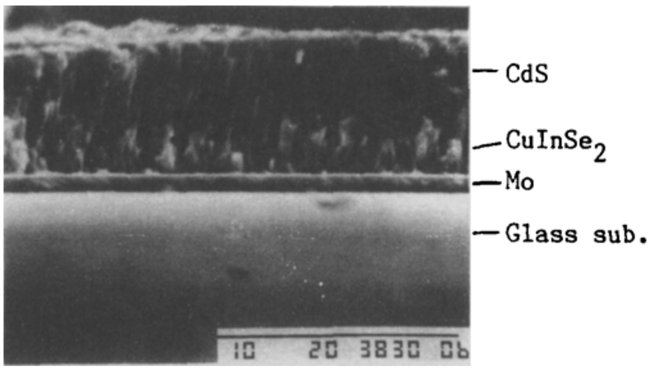


FIGURE 3 A photomicrograph of the CdS/$CuInSe_2$ assembly.

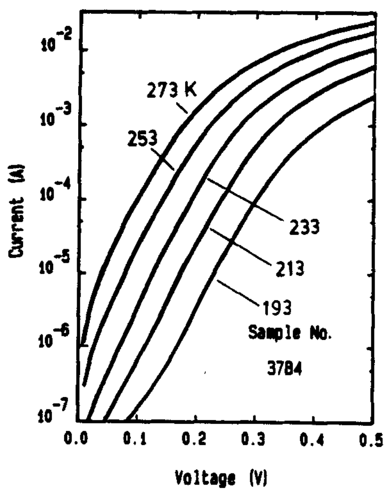
RESULTS

Dark current-voltage characteristics of the devices were measured in a range from room temperature to about -100 ^oC using an HP model 4145A semiconductor parameter analyzer controlled by a microcomputer. Fig. 4 shows the I-V results for one of the devices under forward bias taken at 5 different temperatures. In the low voltage region, the curves of log(I) versus V show a linear region with an ideality factor very close to 1 at room temperature. In order to understand further the junction behavior, saturation current (I_s) and recombination current (I_r)

of the devices were determined by using a program established according to the method proposed by McLean[5]. The fitted results showed an I_s value of 7×10^{-7} amp and an I_r of about 4×10^{-6} amp at a temperature of 273 K. A series resistance of about 7 ohm was also obtained for this device at 273 K. From the fitting results, it was further found that the I_s/I_r ratio decreased as the temperature was decreased, indicating that the recombination process became relatively more important at lower temperatures.

Illuminated I-V characteristics of the devices were measured under a simulated AM1 condition. Results for one of the cells with an active area of 0.71 cm^2 are shown in Fig. 5. Here, the energy conversion efficiency is 4%. Photoresponse measurements of the devices were also carried out in the wavelength range from 0.5 to 1.2 microns (results not shown). It was found that as the wavelength was increased, the quantum efficiency increased rapidly and reached a maximum at about 0.6 micron wavelength. The value remained essentially unchanged as the wavelength was continued to increase to about 1 micron. As the wavelength was further increased to beyond 1 micron, the quantum efficiency started to decrease linearly with the increase of wavelength. This behavior appears to be different from the one for vacuum-deposited high efficiency $CdS/CuInSe_2$ thin film cells, where the constant quantum efficiency region extends to about 1.2 micron. In order to investigate the possible causes for this difference, photo capacitance measurements were carried out on several selected devices.

The photo capacitance measurements were carried out using an HP model 4274A LCR meter at several frequencies in the range from 1 kHz to 100 kHz. Measurements were first made in a small forward and reverse voltage region under a constant illumination condition. The light intensity was measured to be about 30 mW/cm^2 using a calibrated silicon detector. When the $1/C^2$ value (here C is the measured capacitance) was plotted versus the



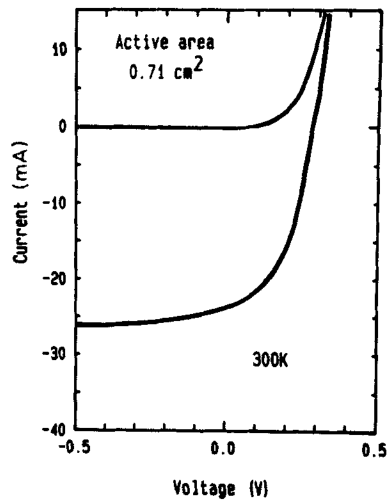


FIGURE 4 Temperature-dependent dark I-V characteristics of a $CdS/CuInSe_2$ cell.

FIGURE 5 Dark and illuminated I-V characteristics of a 4% cell.

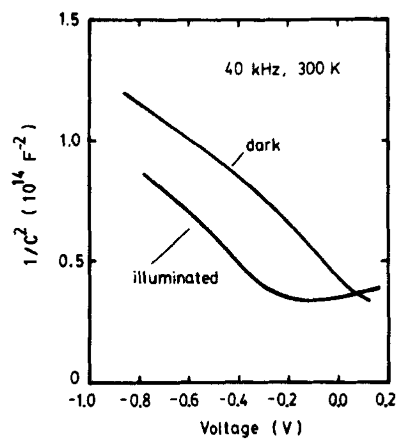


FIGURE 6 Dark and illuminated C-V characteristics of a cell.

voltage, a straight line was usually obtained where the slope of the curve was inversely proportional to the carrier concentration in the depletion edge of the $CuInSe_2$ and the intercept gave the diffusion potential of the junction. The concentration for the p-type $CuInSe_2$ from the dark C-V curve given in Fig. 6 was about 10^{17} cm^{-3}. From other samples, it was found that concentration values in the 10^{15} to 10^{17} cm^{-3} range can be easily achieved in the electrodeposited $CuInSe_2$ films. A charge carrier concentration in this range is required for high efficiency $CdS/CuInSe_2$ devices. Under the illumination condition, the $1/C^2$ curve was found to shift to the reverse voltage side, yielding a reduced diffusion potential. Here, the slope of the illuminated $1/C^2$ curve is essentially unchanged, indicating that the density of energy states, which are charged under the illumination, in the depletion region is small as compared to the total density of the shallow energy levels. The shift of $1/C^2$ curve with the illumination, which is expected for conventional photovoltaic devices, was found to be greater than that for a 10.2% device reported by R.A. Ahrenkiel[6]. The relatively large shift with the illumination is believed to be due to the presence of interface states with a large density. The interface states are charged under the external illumination and give rise to an additional reduction in the diffusion potential.

DISCUSSION

Using photovoltaic devices fabricated on electrodeposited $CuInSe_2$ thin films, investigation has been carried out. The dark differential capacitance-voltage measurements showed that the carrier concentration of the electrodeposited films can be controlled to the 10^{15}-10^{17} range, which is needed for high efficiency devices. Furthermore, the X-ray diffraction and scanning electron microscopy showed that the electrodeposited $CuInSe_2$ films have a preferred (112) orientation with a lattice constant very well matched to the vacuum deposited CdS films. However, the subsequent photo capacitance measurements showed a large density of interface states which resulted in a relatively small open circuit voltage for the devices. From the above results, it is clear that further research experiments are needed in order to reduce the interface state density and to increase the conversion efficiency.

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