Journal of New Materials for Electrochemical Systems 13, 15-20 (2010)
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Nanostructured CdS:Cu Formed by Chemical Doping in an Aqueous Bath

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Received: July 29, 2009, Accepted: August 4, 2009

Abstract: *Nanostructured CdS thin films doped with Cu were synthesized by chemical bath deposition. The structural, morphological, optical and opto-electronic properties of CdS were modified by Cu doping and resulted in the formation of nanostructured films. No compounds other than CdS were formed in this process. The atomic force microscopy (AFM) studies showed that the particle morphology transformed from spherical to nanostructured or amorphous for un-doped to doped, caused by Cu doping. The optical absorption maxima was displaced for the doped films compared to the un-doped films, so also variation in the band gap energy (Eg) which may be attributed to the variation in the grain size of the films with doping. The intensity of photocurrent response of the doped CdS was reduced compared to the un-doped films, due to the increase in the minority carrier concentration by Cu doping.*

Keywords: CdS:Cu, nanostructure, chemical doping, photocurrent, p-type semiconductor

1. INTRODUCTION

It is well known that cadmium sulfide (CdS) thin films are widely studied and applied in thin film solar cells. It is commonly used as the window layer in CdTe and $CuInSe_2$ heterojunction solar cells due to its high photosensibility, wide band gap and the *n*-type conductivity [1-3]. CdS is naturally formed in the *n*-type conducting form [4,5]. During the past there have been efforts to change its conductivity type from intrinsic to *p*-type conducting [6].

Y. Kashiwaba et. al, [6] have reported the impurification of CdS with Cu by thermal evaporation in vacuum. They observed that the film resistivity increased with increase in Cu concentration until 0.5 atomic %. Above this concentration of Cu it started decreasing until 25 atomic %. By Seebeck effect it was observed a change in the conductivity type from negative to positive as the Cu concentration in the film was increased. By Hall effect measurement also it was observed a change in the conductivity type from *n*-type to *p*-type as the Cu concentration in the film was increased [6]. CdS has also been doped with Cu by electrochemical [7] and chemical processes [8,9]. In both these processes the doping effect influenced only the opto-electronic and structural properties. It was not reported the conductivity type or the rectification effect.

By spray pyrolytic [10] and laser ablation [11] methods CdS has been doped with Cu and the change in conductivity type has been observed. But, by laser ablation method the formation of Cu_2S was observed in the film, which was attributed as the reason for the change of conductivity type.

The CdS(*p*)/CdS(*n*) homojunction was formed by vacuum evaporation by depositing first a layer of Cu on SnO_2:F coated glass and then depositing two CdS layers over the Cu layer. After depositing each layer of CdS an annealing process was applied. A conversion efficiency of 6.3% was obtained for structures formed by this method [12]. This value was improved by thermal annealing of the films and applying up to four layers of CdS in total. The conversion efficiency was reached up to 8.3% by this method [13].

Another report on CdS homojunction formation has been given by the spray pyrolysis method [14,15]. In this case the CdS film was deposited by the spray pyrolysis technique. The Cu layer was deposited on CdS by thermal evaporation in vacuum. Cu was diffused into the CdS film by thermal annealing at different temperatures. The efficiency obtained for the CdS homojunction was about 0.73%. Later on, the efficiency was improved to 3 % by applying a second layer of Cu and annealing [15]. Doped CdS has been reported in the formation of a homojunction [16] and as photodiode [16,17].

In this work the CdS films were doped with Cu in a chemical

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*To whom correspondence should be addressed: Email: sjp@cie.unam.mx bath. It was done in a chemical bath containing 75 ml of 1 M $Cd(NO_3)_2$, 45 ml of 1 M $C_6H_5Na_3O_7$, 6 ml of 1 M NH_4OH, 15 ml of H_2NCSNH_2, and 6 to 30 ml of 0.0075 M $CuCl_2$ was added to the chemical bath depending on the level of doping needed. As-deposited films were annealed in nitrogen atmosphere at different temperatures.

2. EXPERIMENTAL

The CdS and CdS(Cu) thin films were prepared by the chemical bath deposition method. The chemical bath employed was already reported by other authors from our center [18,19]. The bath composition consisted of 75 ml of 0.1 M $Cd(NO_3)_2$, 45 ml of 1 M $Na_3C_6H_5O_7$, 6 ml of 14.4 M aqueous NH_3, 15 ml of 1 M $[SC(NH_2)_2]$ and the bath volume was adjusted to 300 ml by adding tri-distilled water. The chemical bath was prepared in a closed flask with multiple entrances. The Corning glass substrates of 75 mm × 25 mm × 1 mm dimensions were vertically immersed in the chemical bath. The bath temperature was maintained at 60°C using a flat-plate heater. The deposition time was programmed for 6 hrs. The films were withdrawn, washed in tri-distilled water and dried in hot air from blowing air heater. For the deposition of the Cu doped films the same bath composition was used with the addition of 0.0075 M $CuCl_2$ in quantities varying from 6 to 30 ml.

The CdS and CdS(Cu) films were subjected to a post-deposition heat treatment in nitrogen atmosphere in a closed chamber at different temperatures during one hour with the intention of improving its properties.

The film thickness was measured using an Alpha Step 100 perfilometer. The structural characterization was done by the x-ray diffraction technique with a Rigaku DMAX X-ray diffractometer using Cu - K_α radiation. Normally the XRD technique utilizes two modes of measurements, the powder diffraction for bulk materials (θ -2θ) and grazing incidence ($\theta < 1$ degree) for thin films.

The particle size was measured using the program Jade 6.5 available with the diffractomer. In this study we used the 2θ mode for the analysis of the films. The transmittance and specular reflectance of the films were studied, in the spectral region 0.19 – 2.5 µm, with a Shimadzu uv 3101 PC spectrophotometer. The photocurrent response of the films was studied using a programmable voltage source Keithley 230 and a digital multimeter Keithley 619. Once the film resistance got stabilized in the dark the current in the dark was measured for 100 seconds, then the sample was illuminated and the photocurrent was measured under illumination for another 100 seconds and finally the falling photocurrent was measured for 100 seconds once the illumination was cut off. A tungsten-halogen lamp of 2.5 kWm^{-2} intensity was used for the illumination of the samples. The measurements were done at different applied voltages varying from 10 to 100 V.

The morphological characterization of the films was done with an atomic force microscope (AFM) utilizing a Scanning Probe Microscope Controller (di-Digital Instruments), which analyzes the sample surface in the tapping mode employing a SiN_4 tip. The sample conductivity was measured by the hot probe method which involves heating the point on the simple where the positive terminal of the multimeter is connected and the voltage measurement is done. The change of conductivity type is manifested by the variation and change of sign of voltage (positive to negative and vice versa).

3. RESULTS AND DISCUSSION

3.1. The Structural Properties of CdS Thin Films

The structural properties of the films were studied by x-ray diffraction (XRD). The results for different cases are given in figures 1 and 2. Figure 1 shows the XRD patterns for as-deposited CdS films without and with different quantities of $CuCl_2$ in the chemical bath. It is observed in the figure that as-deposited film crystallizes in the hexagonal form, the modification is Greenockite (PDF# 41-1049). The diffraction peaks approximate the (100), (002) and (101), with a slight preferred orientation along the (100) plane. It is observed that there is a decrease in the peak intensity as the quantity of CuCl2 (0.0075 M) in the chemical bath is increased. The XRD peaks become broader in shape indicating the formation of nanocrystalline structure. This behavior may be attributed to the decrease in grain size of CdS, which showed a grain size of about 14 nm which after CuCl2 addition decreased to about 12 nm. This phenomenon is possible by the substitution of Cd (ionic radius of Cd2+ is 0.97 Å) by Cu (ionic radius of Cu is 0.96 Å) rather than Cu occupying interstitial sites of CdS.

Regarding the heat treated films as shown in figure 2, the CdS

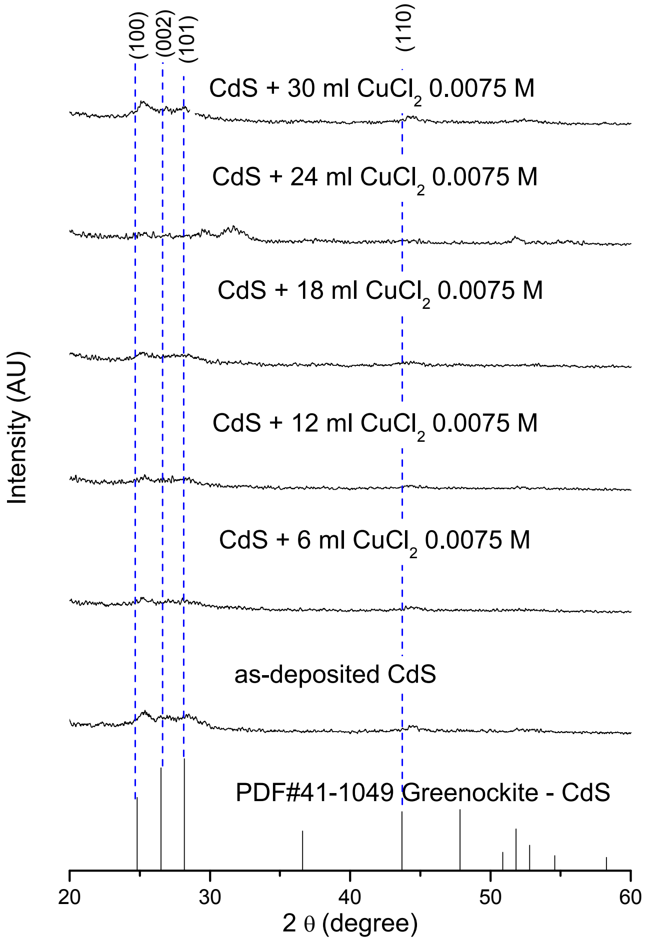

Figure 1. The XRD patterns of as-deposited CdS and CdS(Cu) thin films with different concentration of CuCl2 in the chemical bath.

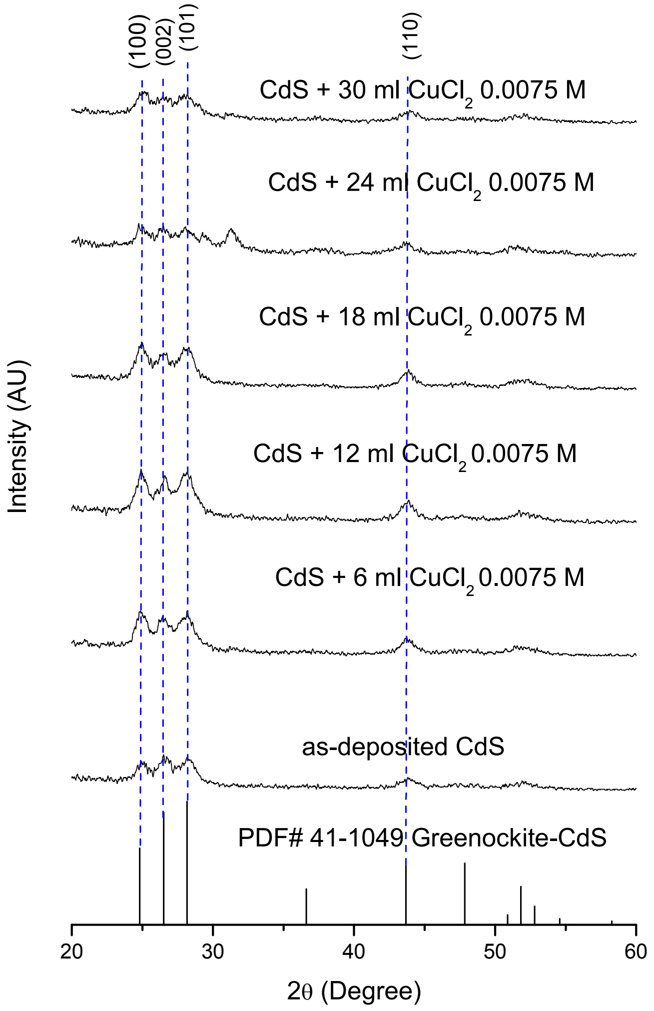

Figure 2. The XRD spectra for CdS and CdS(Cu) films annealed at 400 ºC.

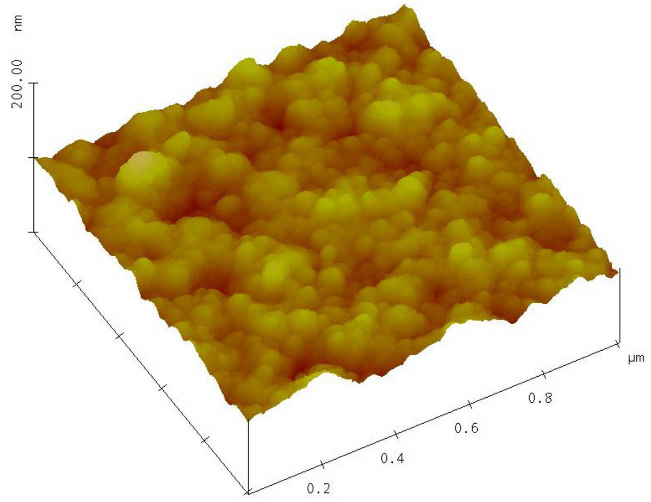

Figure 3. The AFM picture for a CdS film annealed at 350 ºC.

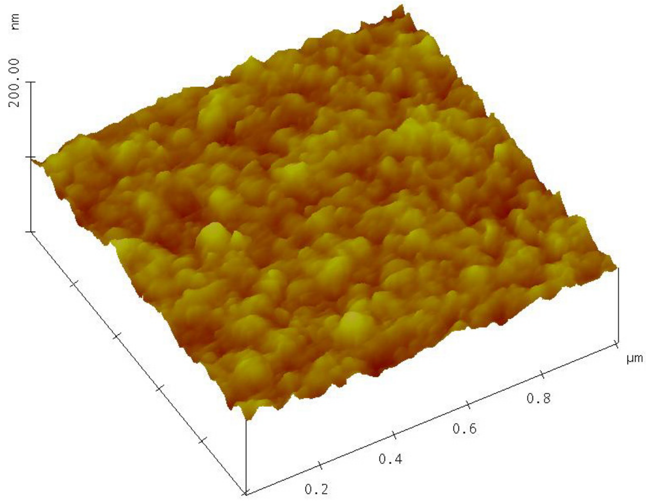

Figure 4. The AFM picture for a CdS(Cu) doped with 6 ml of 0.0075 M CuCl$_2$) annealed at 350 ºC.

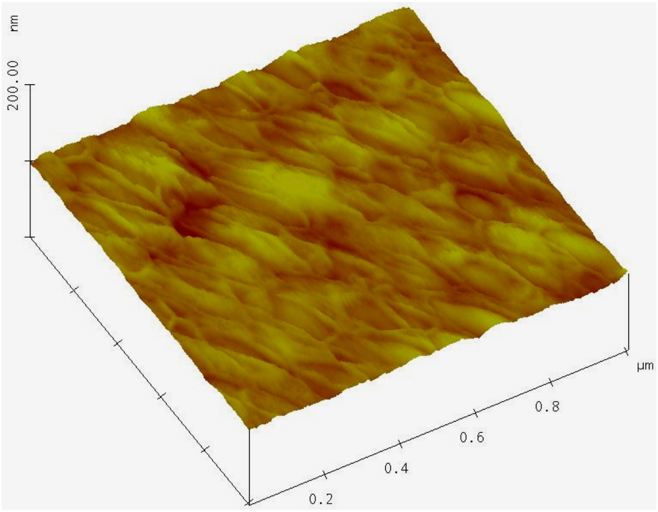

Figure 5. The AFM picture for a CdS(Cu) (18 ml of 0.0075 M CuCl$_2$) annealed at 350 ºC.

(pure) annealed at 400 ºC showed an increase in XRD peak intensity compared to the un-annealed film, indicating an increase in grain size and better crystallinity. But, this trend is reversed when CdS is doped with Cu where the grain size decreased by a few nanometers with the addition of CuCl$_2$.

3.2. Morphological Characteristics

As-deposited, annealed and doped CdS films were studied using an atomic force microscope (AFM). All the films were subjected to a heat treatment at 350 ºC before doing the AFM analysis. Figure 3 displays the AFM of an un-doped film. The AFM shows that the film morphology is constituted by spherical particles of approximately 70 to 100 nm. The films grew approximately 230 nm thick. When the film was doped with low Cu concentration (6 ml of 0.0075 M CuCl$_2$ in the chemical bath) it is observed that the film starts loosing its spherical surface morphology (figure 4) and the

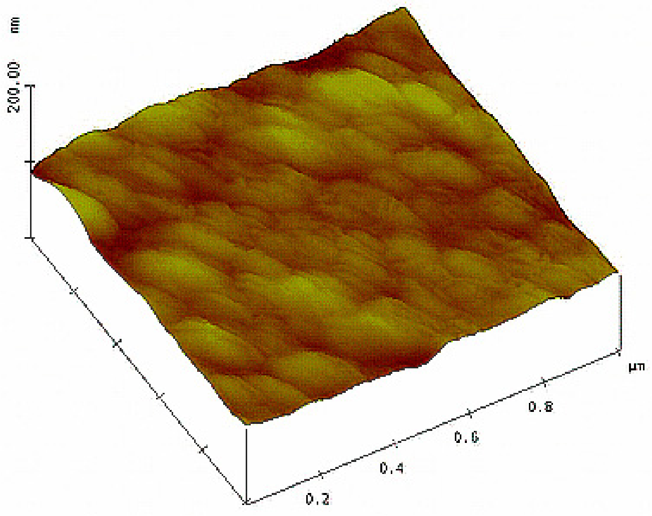

Figure 6. The AFM picture for a CdS(Cu) (30 ml of 0.0075 M $CuCl_2$) annealed at 350 ºC.

particle size gets diminished. In this case the film grew only about 200 nm. With the addition of more Cu in the film (24 ml of 0.0075 M $CuCl_2$ in the chemical bath) the surface morphology completely changed to amorphous particulate nature (figure 5). The film grew up to 150 nm only. With further addition Cu in the film (30 ml of 0.0075 M $CuCl_2$ in the chemical bath) the film grew up to 90 nm only and the film surface almost totally lost the particulate nature (figure 6). More than this much quantity of $CuCl_2$ in the solution it is difficult to grow the film with an appreciable thickness and it started to come off easily.

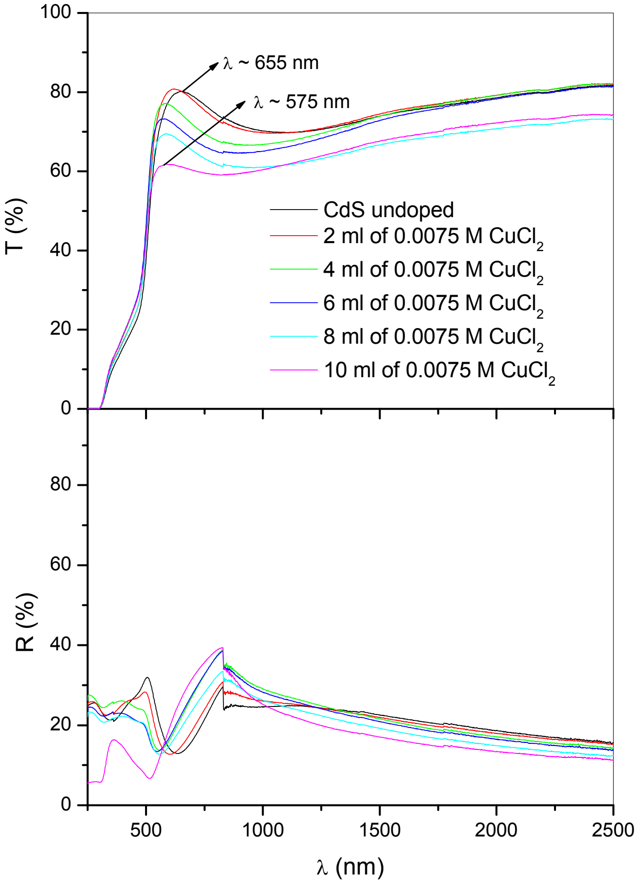

Figure 8. The optical transmittance and reflectance spectra for CdS films doped with different concentrations of 0.0075 M $CuCl_2$ and annealed at 400 ºC.

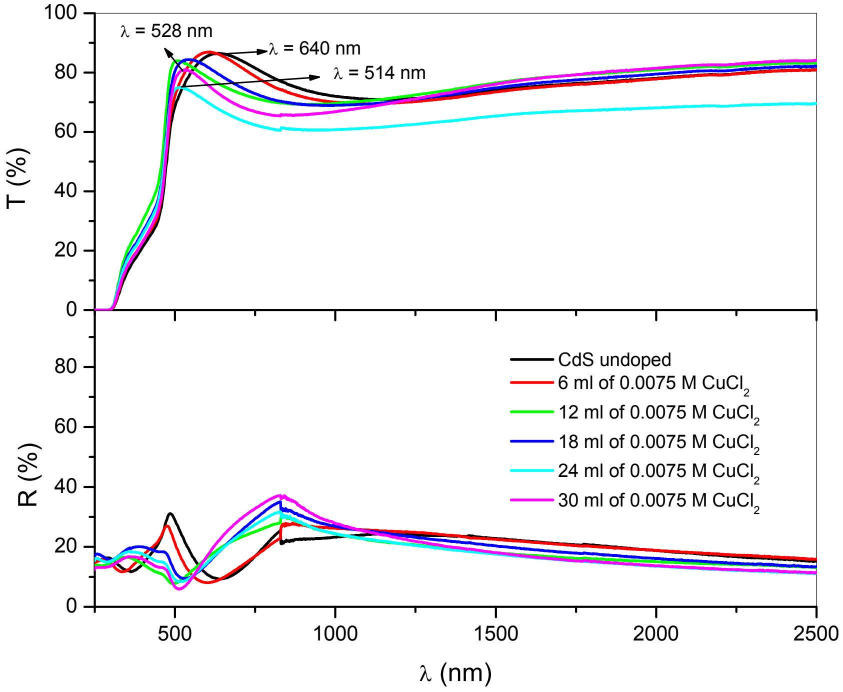

Figure 7. The optical transmittance and reflectance spectra for as-deposited Cu doped CdS films.

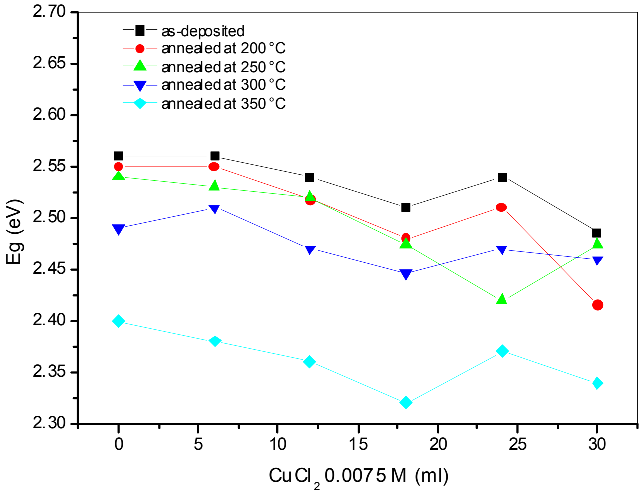

Figure 9. Variation in band gap energy for CdS and CdS(Cu) as a function of annealing temperature.

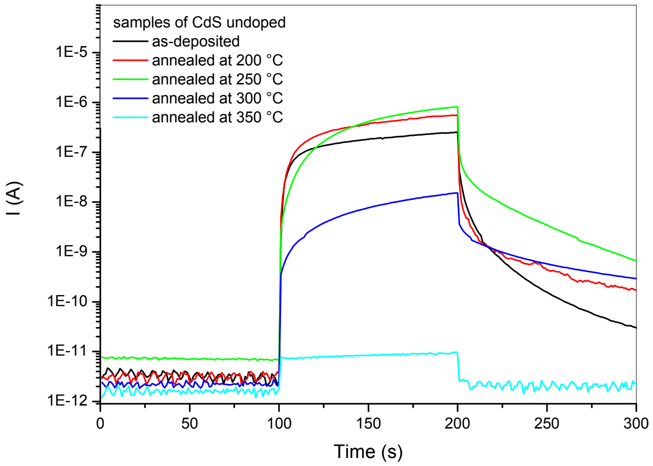

Figure 10. Photoresponse for the un-doped CdS films as a function of annealing temperature.

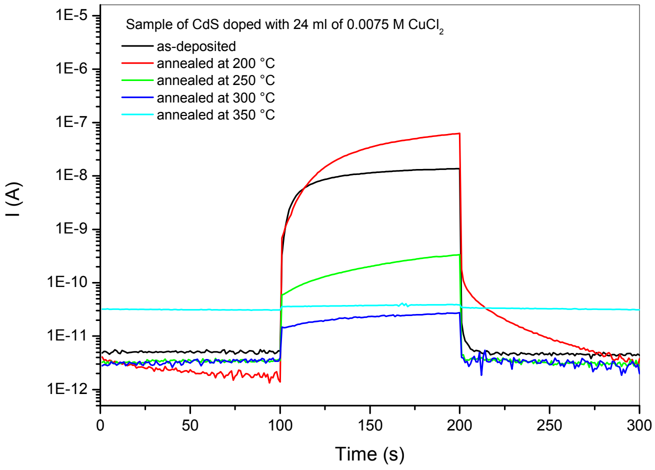

Figure 11. Photoresponse for the Cu-doped (24 ml of 0.0075 M) CdS films as a function of annealing temperature.

3.3. Optical Properties of the Films

The deposition period for all the films studied was 6 hours. The optical transmittance for the untreated CdS and CdS(Cu) films (figure 7) was about 60 to 80 % in the visible region. It is known that the optical transmittance is a function of film thickness and the absorption coefficient. A decrease in the optical transmittance and displacement of the absorption peak position to a lower wavelength region (515-650 nm) was observed for the doped films. This decrease was in accordance with the increase in the Cu concentration in the chemical bath. This phenomenon is attributed to the presence of Cu ions at the grain boundaries of CdS. These films were subjected to a heat treatment at 400 ºC. Changes in the absorption peak characteristics were observed for both CdS and CdS:Cu. A decrease in the optical transmittance was observed and the absorption peaks were fell in the 55 to 70 % transmittance range. More over a displacement in the peak position towards the longer wavelength region was observed. Upon comparison of the transmittance and the peak position, it is seen that CdS with higher doping concentration exhibited lower transmittance. This characteristic is due to the grain growth and introduction of Cu ions in the CdS crystalline lattice.

In the band gap (Eg) analysis, figure 9 displays a comparison of the band gap characteristics with respect to the Cu concentration in the bath and the annealing temperature. A decrease in the band gap was observed in accordance with the increase in the Cu concentration in the chemical bath. As the annealing temperature is increased this decrease in band gap is more pronounced. It is possible that this effect is caused by the grain growth, which was observed in the XRD analysis where higher annealing temperature resulted in the increase in the peak intensity. This effect can also be caused by the better Cu mobility in the film and hence more Cu doping in the CdS lattice with increase in annealing temperature

3.4. Electrical Properties

It is known that CdS is usually possesses high electrical resistance (10^{10}– 10^{12} Ω) and photosensitivity (~10^7). Photoresponse studies were carried out on CdS to analyze the influence of Cu doping and annealing effect (figures 10 and 11). Figure 10 displays the temperature dependence of the photocurrent response of the undoped CdS films annealed at different temperatures. The dark current of the films remained at $1x10^{-12}$ A. It is observed that with an external applied voltage of 10 V the photocurrent response was increased by an average of about five orders of magnitude. The average photocurrent was about 1×10^{-8} A. This trend was seen for the simples with annealing temperatures up to 250 ºC. As the annealing temperature increased above 250 ºC the photocurrent response started decreasing to reach until an order of magnitude. This decrease in photoresponse is attributed to the film grain growth and hence decrease in the life time of the charge carriers. This effect is caused also by the reduction in the number of recombination centers due to increase in annealing temperature.

Analyzing the photoresponse of the Cu doped CdS films (18 ml of 0.0075 M $CuCl_2$) annealed at different temperatures (Fig 11), it is observed that up to 200 ºC the doped films exhibit a photocurrent response of tour orders of magnitude with an average photocurrent of 1×10^{-8} A. The dark current remained at 1×10^{-12} A. With further increase in annealing temperature the photoresponse decreased further to reach 2 orders of magnitude for the films annealed at 250

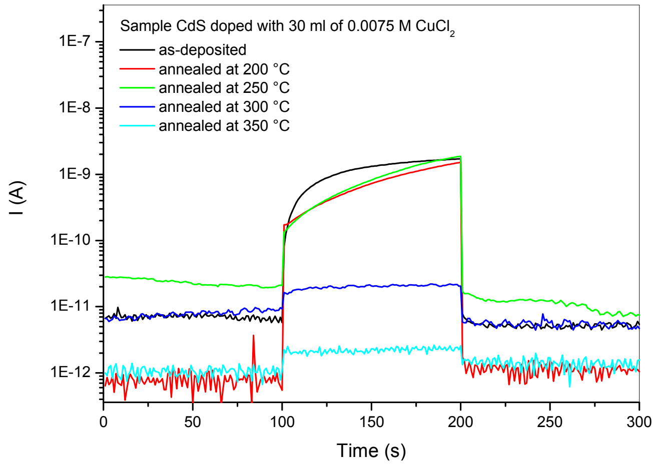

Figure 12. Photoresponse for the Cu-doped (30 ml of 0.0075 M) CdS films as a function of annealing temperature.

and 300 ºC and one order of magnitude for the films annealed at 350 ºC. This notable difference in photoresponse and photocurrent values for the Cu doped films compared to the undoped films is caused by the introduction of the Cu ions in the crystal lattice of CdS, causing an increase in the acceptor centers in the electronic structure.

A similar trend was observed Cu doped films with still higher concentrations of Cu in the chemical bath as shown in figure 12 where the photoresponse is shown for a film doped with 30 ml of 0.0075 M $CuCl_2$ in the chemical bath and annealed at different temperatures. In this case the effect of Cu doping is more pronounced on the photoresponse and photocurrent characteristics.

In the conductivity type analysis it was founds that as-deposited films were intrinsic in nature. The annealing treatment converted the films to n-type conducting. Cu doped and annealed films showed high resistivity and very feeble p-type conductivity.

4. CONCLUSIONS

CdS thin films were prepared in the nanostructured form by chemical deposition and doping with different concentrations of Cu using 0.0075 M $CuCl_2$. Structural and morphological changes were observed in doped films compared to the un-doped films. A noticeable decrease in particle size was observed for the doped films which varied as a function of the doping concentration. No other compound except CdS was formed in the case of un-doped and doped films. By AFM analysis a noticeable change in the morphology was observed for the doped films, the particle shape varied from well defined spherical (un-doped) to nanocrystalline or near-amorphous. The optical absorption edge for the doped film was displaced towards longer wavelength region due to the decrease in the grain size of the film. A variation in the optical band gap was observed for the doped film compared to the un-doped film (30 ml of $CuCl_2$). It indicated that there is a decrease in the grain size and variation in the band gap due to Cu incorporation in CdS. With respect to the opto-electronic properties a decrease in the photoresponse was observed for the doped film, which is attributed to the increase in the minority carrier concentration caused by the Cu incorporation in CdS.

5. ACKNOWLEDGEMENTS

The authors acknowledge the technical assistance received from Gildardo Casarubias and Maria Luisa Ramon in the characterization of the materials. The financial support for the project was received from DGAPA-UNAM through the project IN113107.

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