PHOTO-ELECTRONIC PROPERTIES OF CU-DOPED CDS THIN FILMS

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The effect of copper diffusion and electrodiffusion on structural, electrical, optical and photosensitivity characteristics of thin film Cu/CdS structures was investigated. The thermal diffusion of copper at 300-400^{o}C is accompanied by conversion of conductivity type of the films from n- to p-type, decrease of resistivity and origin the long-wave photosensitivity at $\lambda \geq 540$ nm.
XRD patterns of Cu/CdS structures exposed to thermal diffusion showed presence of Cu-S compounds. Diffusion under direct electrical field (electrodiffusion) of copper in Cu/CdS structures at room temperature results in increase or decrease the photosensitivity in depending on polarity of applied electric field.

1. Introduction

CdS thin films have been widely studied in the past 10 years due to their potential applications as windows in solar cells manufacturing. On the other hand, the Cu-CdS bilayer system is used for the preparation of metal-coated semiconductor nanocrystals which are of great interest for the fabrication of optical and electroluminescent devices [1]. As a rule, the as-grown CdS films has n-type conductivity, the high dark resistivity (about 10^5 -10^8 Ω cm) and exhibit a high photoconductivity (10^4 - 10^6). Donor centers which formed in CdS during growth, were attributed to the strong self-compensation effect due to the native point defects (vacancies of the sulfur sublattice, the interstitial cadmium atoms etc) caused by deviation of CdS composition from the stoichiometry. To make the as-grown CdS films useful in optoelectronic applications, the dark resistivity must be reduced from 10^5 - 10^8 Ω cm to almost 10 Ω cm. Moreover, on this view preparation of p-type CdS thin films is need. Growth of the p-type CdS by doping or conversion of n-type CdS into p-type and by thermal impurity diffusion is a hardly realized process [2,3]. Copper is substitutional acceptor impurity in CdS. Copper are reported to be incorporated also as interstitial donors, and mobility of interstitial Cu atoms is known to be very high [4]. Cu-diffusion doping was used for preparation of p-type CdS [5].

Here, we report the results of investigations of the effect of copper diffusion and electrodiffusion on structural, electrical, optical and photosensitivity properties of CdS thin films.

2. Experimental Procedure

The n-type CdS thin films with a thickness of 2-4 μm were fabricated on glass and SnO_2-coated glass substrates by spray-pyrolysis technique. The temperature of the substrates was 250^{o}C. The resistivity of as-grown n-type CdS films was about of ….Ω cm . The Cu films (about of 20 –30 nm) were deposited onto the upper surface of the CdS films by vacuum evaporation. Then, Cu diffusion in n-type CdS thin films was performed by annealing of Cu/nCdS structures at 300^{o}C for 10 min in vacuum. Moreover, the doping of CdS films was also carried out by electrodiffusion of Cu in CdS at room temperature under applying the accelerating or retarding electric field. Current-voltage characteristics of Cu-CdS structures were measured at room temperature in darkness and under an illumination of about 100 mW cm^{-2} from a solar simulator. The spectral distributions of photosensitivity were measured in the wavelength range 400-1100 nm at room temperature. Optical transmission spectra of films grown on glass substrates were measured in the range 400 – 1100 nm by using a “Lambda 2” Perkin-Elmer spectrometer.

The crystalline structure and composition of the undoped and Cu-doped films were analysed by the X-ray diffraction (XRD) technique using a Rigaku D/Max 111C diffractometer with CuK_α radiation. The surface morphology of films was studied using a JEOL JSM-6400 scanning electron microscope (SEM).

3. Results and discussion

The electrical measurement showed that resistivity of as-grown n-type CdS films was about of 10^9 Ω cm.

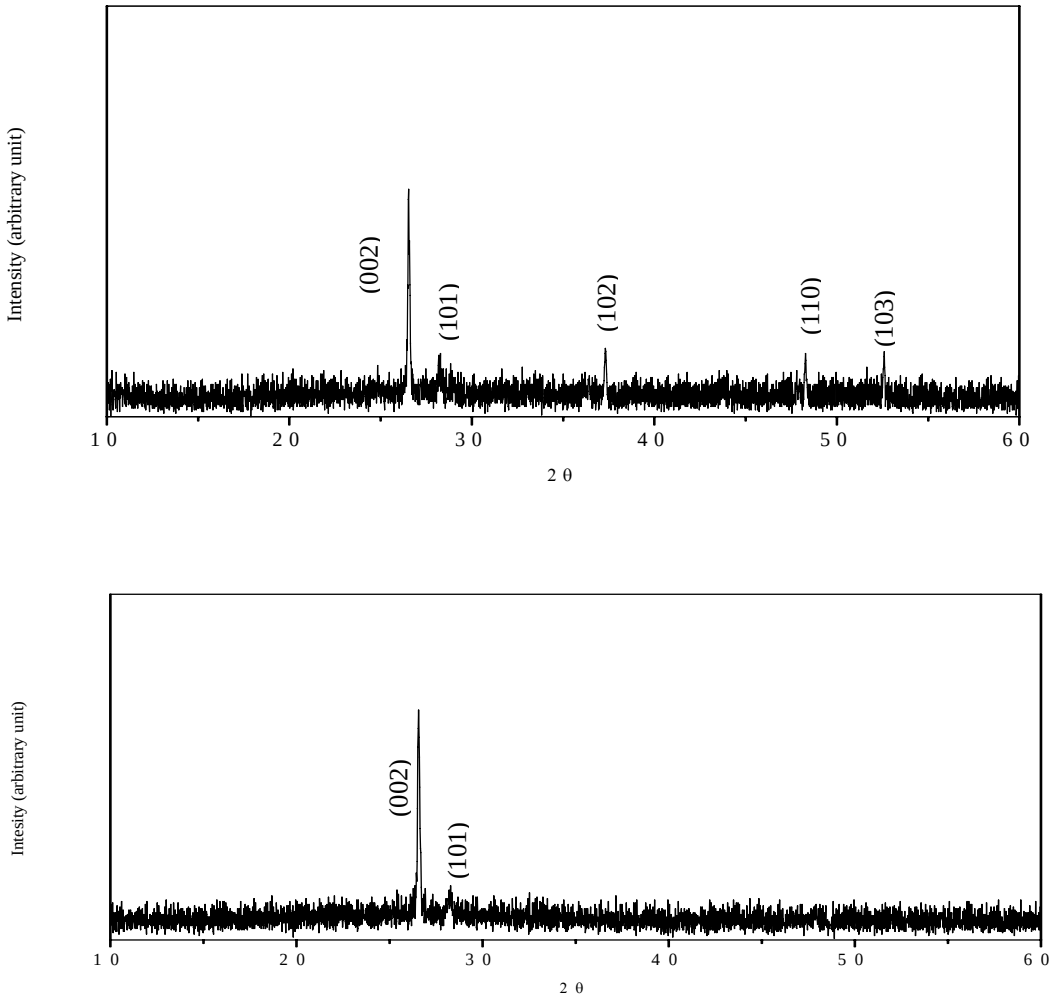

Fig 1. XRD patterns for (a) CdS film and (b) Cu/CdS structure (300^{o}C, 10 min).

Figure.1illustrate the XRD patterns of as-grown CdS film and Cu/CdS structure exposed to annealing at 300^{o}C for 10 min. The strong XRD peak at 2θ =26.6^{o} corresponds to diffraction angles of the (002) plane of hexagonal CdS [6]. Therefore, the CdS films deposited on a glass substrate by spray-pyrolysis were of a hexagonal structure and the c-axis of crystallites was mostly oriented perpendicular to the substrate. (102), (110) and (103) peaks Cu-S compounds (Cu_2S) in XRD patterns were additionally observed for the Cu/CdS structure exposed to copper diffusion at 300^{o}C. The morphology studies of CdS and Cu-doped CdS films reveal the existence of polycrystalline structure with crystallite dimension of …. and …μm (Figure 2).

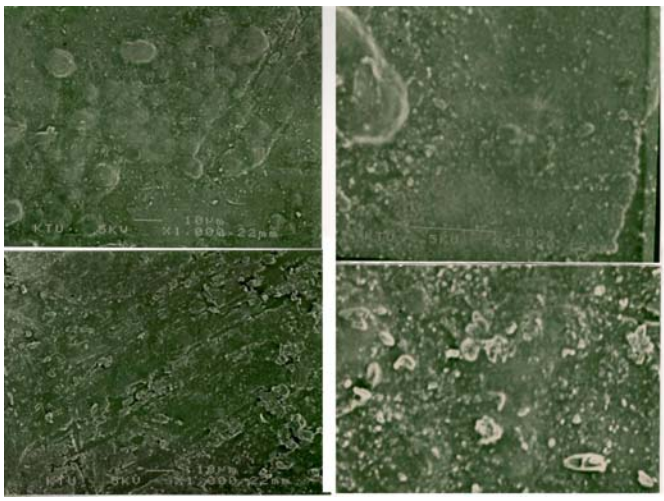

Fig 2. SEM micrographs for (a) CdS and (b) Cu-doped CdS films.

The conversion of conductivity type of CdS film from the n-type to the p-type, as result of Cu diffusion into CdS film at 300-400^{o}C is measured by thermoprobe. Herewith the resistivity of p-type film decreases from 10^{9}up to $2x10^{7}$ Ω cm.
Optical absorption coefficient spectra, depending on the duration of copper diffusion in bilayer Cu/CdS structure at 400^{o}C are presented in Figure 3.

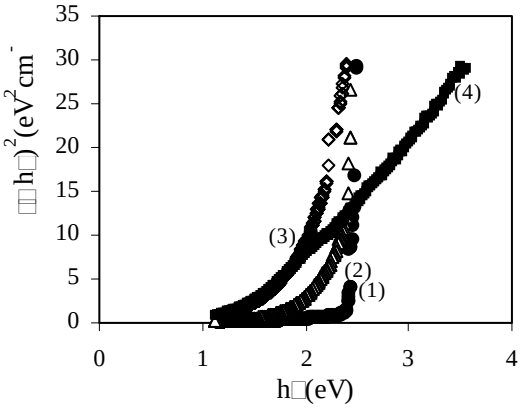

Fig 3. Optical absorption coefficient spectra of Cu/CdS structure (1) before and after annealing at 400^{o}C for (2) 15, (3) 30 and (4) 45 min.

Data on the absorption edge of films determined from $(\alpha h\nu)^2$ - $h\nu$ plots are presented in Figure 4.

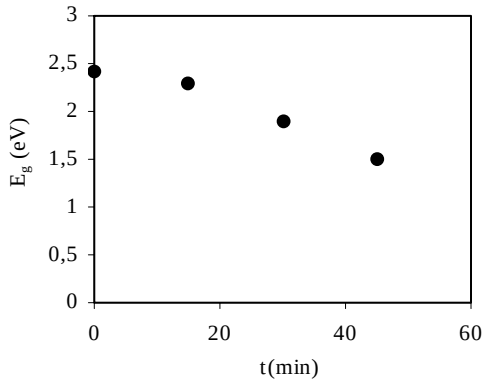

Fig 4. The energy band gap of Cu-doped CdS film in dependency on duration of annealing at 400^{o}C.

It is seen that the band gap of films decreases from 2.42 eV (CdS) to 1.5 eV ($Cu_{1.96}S$) as result of Cu diffusion in CdS film. These results can be explained by diffusion of Cu in CdS accompanied with formation a new Cu-S phases in CdS films.

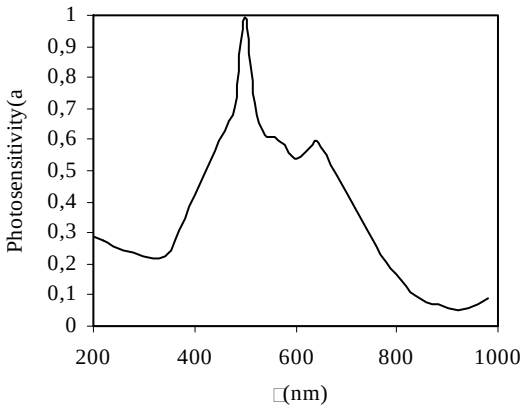

Fig 5. The spectral distribution of photosensitivity of Cu/CdS structure after annealing at 400^{o}C for 30 min.

Figure 5 shows the spectral distribution of photocurrent for Cu/CdS structure exposed to annealing at 400°C. It can be seen that the edge of photosensitivity begins at about of 800 nm (1.55 eV) and a peak of photosensitivity settles down at 510 nm (2.43 eV) corresponding to the band gap of CdS.
Thus the thermal diffusion of copper in Cu/nCdS structures at 300-400°C results in the conversion of conductivity type of the film from n-type to the p-type, decreases the resistivity from 10^9 to $2x10^7$ Ω cm and the band gap from 2.4 eV to 1.5 eV, and origins the long-wave photosensitivity at $\lambda \leq 800$ nm.

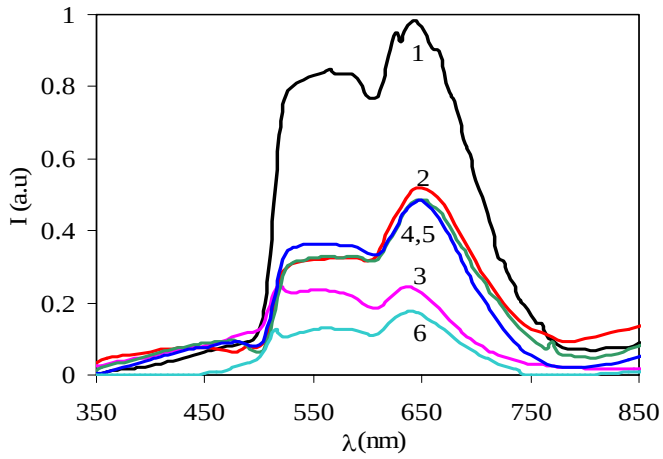

Fig 6. The spectral distribution of photosensitivity of Cu/CdS structure (1) before and after electrodiffusion for (2) 5, (3) 7, (4) 10, (5) 15 and (6) 20 min at 25°C ("+" on Cu).

Figure 6 shows normalized spectra of photocurrent of Cu/CdS structure in depending on duration of electrodiffusion at room temperature (+10V on Cu-side). Region of spectral photosensitivity for all spectra spreads from 500 to 780 nm and photosensitivity decreases with increase duration of electrodiffusion. In contrast, applying the negative polarity (-10V) on Cu-side of Cu/CdS structure results in increase of photosensitivity of Cu/CdS structure as a function of duration of electrodiffusion (Figure 7).

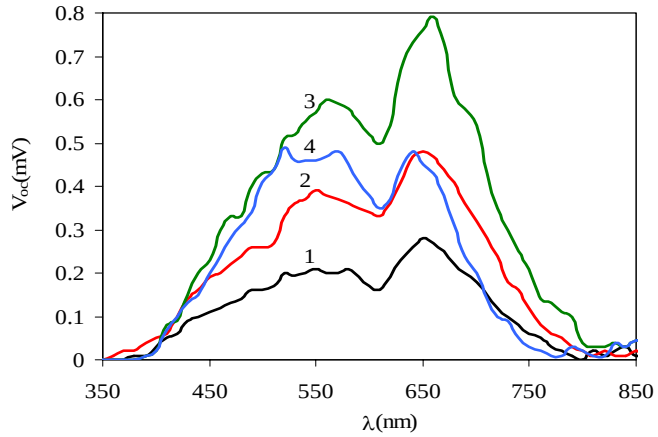

Fig 7. The spectral distribution of photosensitivity of Cu/CdS structure (1) before and after electrodiffusion for (2) 2, (3) 4 and (4) 6 min at 25°C ("-" on Cu).

Decrease of photosensitivity of Cu/CdS structure on accelerating action (for positive Cu ions) of applied electric field can be explained by the fast penetration of Cu^+ ions into CdS film accompanied by decrease of copper concentration at Cu/CdS interface. Applying the retarding electric field to Cu/CdS structure, on the one hand, prevents to penetration of Cu^+ ions inside of CdS film and the others hand, assists the out-electrodiffusion of S^+ ions to interface, accompanied by formation of Cu-S phases.

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