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Ion-beam Sputtering Deposited Cu-doped CdS Thin Film

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Abstract. Cu-doped CdS thin film has been successfully deposited by ion-beam sputtering deposition. The structural, morphology, optical and electrical properties of as-deposited and annealed Cu-doped CdS thin films were investigated. The heavily Cu-doped CdS films annealed at 400 °C was demonstrated to be improved in structural, morphology, electrical and optical properties. X-ray diffraction (XRD) analysis indicated the formation of polycrystalline CdS film with the structure of hexagonal wurtzite phase. No distinct impurity of Cu and Cu-S phase was detected in Cu-doped CdS thin films. Atomic force microscopy (AFM) revealed that the grain size was increased after annealed. Optical transmission and absorption spectroscopy measurement revealed a high absorption and energy band gap was of about 2.40 eV. The CdS thin film was of p-type conductivity and the resistivity was found to be $1.28\times10^{-1}\Omega$cm.

Introduction

Of the Ⅱ-Ⅵ semi-conducting materials, cadmium sulfide (CdS) is the leading candidate to be an excellent heterojunction partner for p-type cadmium telluride (CdTe) and p-type copper indium gallium diselenide (CIGS), due to its wide band gap (E_g = 2.42 eV), photoconductivity, and high electron affinity[1]. It is an interesting crystal material in the area of optoelectronic devices including thin solar cells, photodetectors, window glass coating, flat panel diodes, transistors and high emitting diodes. CdS is an n-type photosensitive material and can be changed to p-type by proper Cu doping, greatly influencing its photo-response characteristics. It has generally been considered that the formation of p-type CdS is very difficult because of strong self-compensation effect due to sulfur vacancies and the depth of the acceptor level in CdS(～1 eV)[2]. Various techniques for preparation of Cu-doped CdS thin films have been employed, such as vacuum evaporation, ultrasonic spray pyrolysis and chemical bath deposition technique [3-5], however, it was difficult to control the concentration of Cu in CdS thin film through the methods mentioned above. Little attention has been paid on the growth of Cu-doped CdS thin films by ion beam sputtering deposition (IBSD). Actually, IBSD has several advantages such as excellent stoichiometry transfer of the target material, good uniformity and simple setup required for the film formation.

In this work, the doping Cu in CdS thin film process was achieved by ion beam sputtering a fan-shaped Cu and CdS target plate, as needed of its area ratio easily adjust the Cu concentration in CdS thin film. The structural, surface morphology, electrical and optical properties of Cu-doped CdS thin film were investigated.

Experimental Procedures

The IBSD apparatus [6] was used for the CdS thin films preparation. The fan-shaped ceramic target with certain area ratio of Cu (99.99% purity) and CdS (99.99% purity) of were fixed at target holder. Using the IBSD technique, Cu-doped CdS thin films were deposited onto BK7 glass substrates at room temperature and after in-situ annealing at 400 °C for one hour. Prior to deposition, the substrates were ultrasonically cleaned in acetone and alcohol for 10 min respectively. The vacuum chamber was evacuated to base pressure of 6.0×10^{-4} Pa. High-purity (99.99%) Ar of 8 sccm was introduced and deposition was carried out at working pressure of 6.0×10^{-2} Pa after presputtering for about 20 min to remove contaminants from the target. More details on sample preparation are given in Table 1.

Table 1. The ion-beam sputtering parameters used for preparing Cu doped CdS thin films

	Voltage (V)	Current (A)	Plasma energy (keV)
Screen	-	-	1.3
Anode	80	0.3	-
Acceleration	250	-	-
Cathode	8	12	-
Beam	-	0.02	-
Neutral	-	3.5	-

The crystallinity and crystal orientation of the films was determined by x-ray diffraction (XRD) (ax5-D8-ADVANCE, BRUKER) with CuKα radiation ($\lambda = 0.15406nm$). The surface morphology and root-mean-square (RMS) surface roughness were characterized using an atomic force microscopy (AFM, CSPM5500) in contact mode. CdS thin film thicknesses of as-deposited and annealed at 400°C measured using a DEKTAK 150 profilometer was about 500 nm, respectively. Optical transmittance was obtained at room temperature by ultraviolet (UV)/visible (VIS)/near-infrared (NIR) spectrophotometer (Lambda 950, Perkin Elemer). Thermo electric power measurement (TEP) was carried out for determination of origin of conductivity. In the TEP measurements the open circuit thermo voltage was generated by film sample when a temperature gradient was applied across a length of the sample and was measured by Keithely 2400. The electrical sheet resistance Rs was determined using the four-point probe method, and the resistivity ρ was obtained using $\rho = R_s d$ where d is the film thickness.

Results and discussions

The physical examination of as-deposited and annealed Cu-doped CdS thin films prepared by ion-beam sputtering deposition indicates that the films are uniform and brownwish different from undoped CdS thin film with yellow in color. The prepared Cu-doped CdS films exhibit a good adhesion with no mechanical defects, such as cracks or peel-off. The elemental composition of Cu-doped CdS thin films is shown in Table 2.

Table 2. The composition of the Cu doped CdS thin films determined by EDS analysis.

Samples	Cd (at.%)	S (at.%)	Cu (at.%)	Ratio Cu / (Cd+S)
As-deposited	25.66	30.69	43.65	0.75
Annealed	32.53	35.30	32.17	0.47

It can be found that the two samples are of heavily doping Cu. After annealed, the Cu decrease and the Cd and S content increase correspondingly. Then the optimized properties of Cu-doped CdS films can be achieved after annealed process.

X-ray diffraction (XRD) patterns of Cu-doped CdS films are shown in Fig. 1, which indicated that the prepared films processed a CdS hexagonal structure with the (100), (002), (101), (110), (112) planes. No distinct impurity of Cu and Cu-S phase was dected in Cu-doped CdS thin films, which may have contributed for the formation of Cu interstitial and substitutional Cu at the Cd site. The highest reflection peak (002) of as-deposited films is at 26.42° with calculated lattice parameters of d=3.3708 Å. The average crystalline size was estimated by resolving the highest intense peak using Scherrer's formula. It is found to be 17.1 nm. After annealed at 400 °C, the corresponding peak (002) is fixed at slight higher angle with 26.72 ° and the calculated average crystalline size is 40.5 nm. The observed increasement of (002) preferred orientation after annealed is attributed to the enhancement in surface diffusion of the absorbed species resulting in an improvement in crystallinity of Cu-doped CdS films.

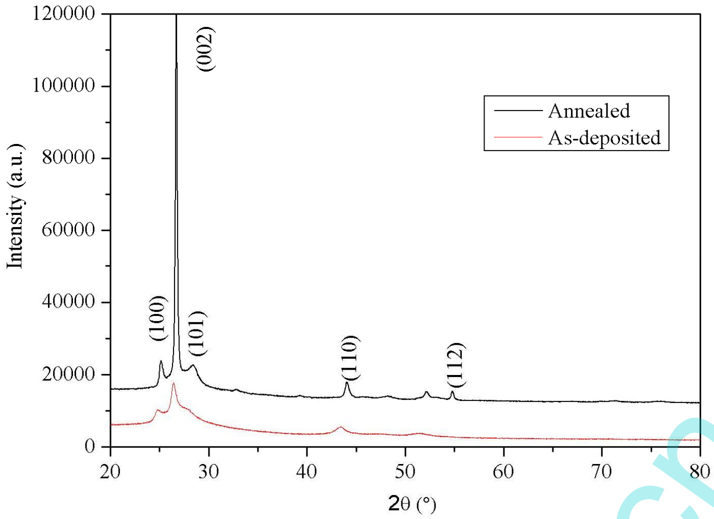

Fig. 1 XRD patterns of the as-deposited and annealed Cu doped CdS films

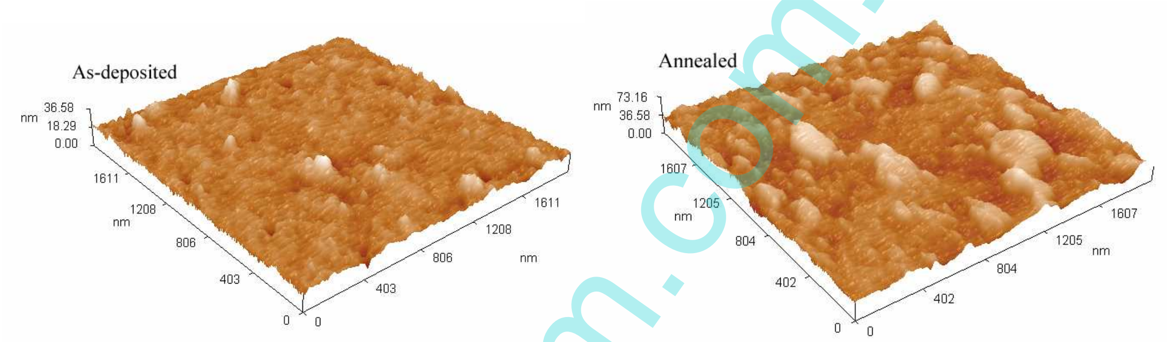

Fig. 2 AFM image of the as-deposited and annealed Cu doped CdS films

The surface morphology of CdS thin films are shown in Fig.2. The AFM image reveals that the as-deposited Cu-doped CdS film has a smooth surface and the detected room-mean-square (RMS) roughness is 2.29 nm. After annealed, the grain size increases and the RMS roughness is found to be 6.70 nm, which suggests that the improved diffusion and transfer ability of surface atoms lead to the accelerated crystallization of CdS film and hence the enhancement of surface roughness.

Figure 3 shows the transmittance spectra as a function of wavelength (200～1500 nm) for the as-deposited and annealed Cu-doped CdS films. The spectra shows the usual interference pattern of a high refractive index film in the range of low absorption with a sharp absorption edge due to the direct transition of electrons from the valence band to the conduction, which indicates that the good crystallinity of annealed Cu-doped CdS films is obtained. The fundamental absorption, corresponded to the electron excitation from valance band to conduction band, was usually used to determine the value of optical band gap (E_g). As a direct band gap semiconductor, CdS has an absorption coefficient (α) obeying the following relation for high photon energies ($h\upsilon$) [6]:

$$\alpha h\upsilon = C(h\upsilon - E_g)^{1/2} \tag{1}$$

here, C is a constant, the photon frequency and h the plank constant. As shown in Fig.4, the optical energy band gap (Eg) of CdS films was determined from Eq. (1) by extrapolating the linear part of the spectrum $(\alpha h\upsilon)^2 = f(h\upsilon)$ to zero. It can be seen that the annealed Cu-doped CdS films reveal high absorption coefficient of about 105 cm-1 and the calculated optical band gap of annealed films is 2.40 eV.

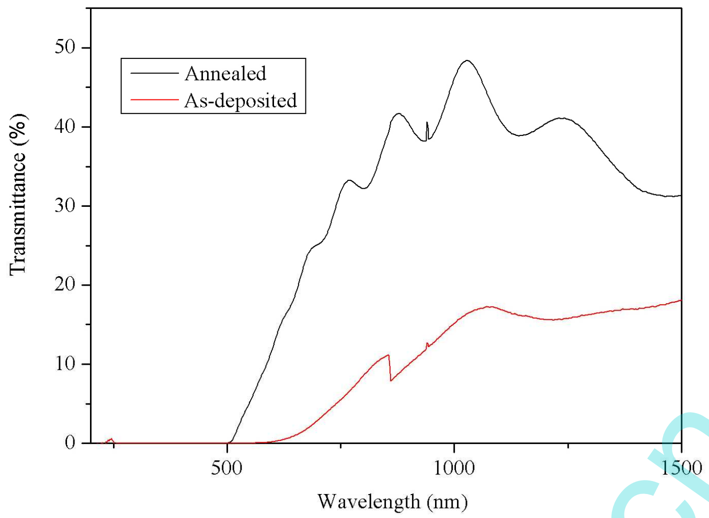

Figure 3 Transmittance spectra of the as-deposited and annealed Cu doped CdS films

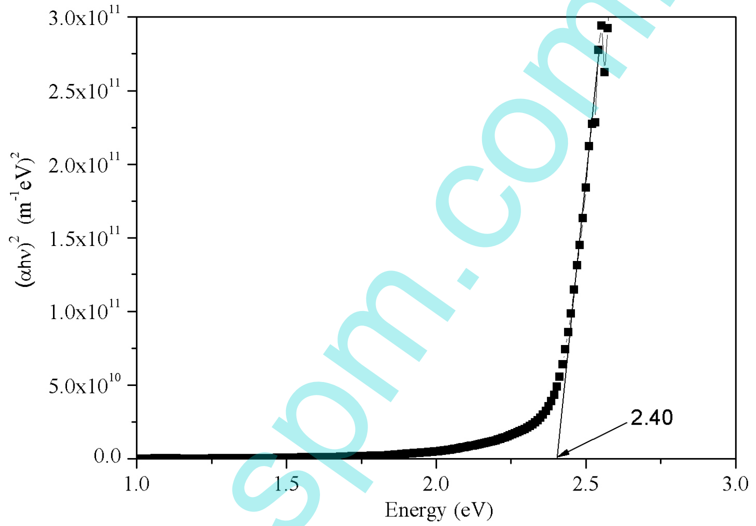

Figure 4 Plot of $(\alpha h\upsilon)^2$ vs. photo energy hυ for the annealed Cu doped CdS films

Thermo-electric power is used for determination of conduction origin. TEP is negative for n-type semi-conducting materials i.e. charge carriers are negatively charge particle electrons. From the sign of terminal connected to cold end of the sample, one can decide the sign of the predominant charge carrier [7]. In as-deposited Cu-doped CdS film, the negative sign indicates the n-type of conduction mechanism and the measured film resistivity is found to be 6.80×102 Ωcm. After annealed at 400 °C, film was converted to the p-type conductive characteristic and its measured film resistivity is 1.28×10-1 Ωcm, with the compensation mechanism explanation of native defect S vacancy primarily acting as an intrinsic compensation defect under p-type doping. Therefore, CdS films doped at a high concentration of Cu can be transformed into a p-type material at a certain temperature [2]. Further study in Cu concentration in CdS film and heating process with the critical properties should be necessary.

Conclusions

Cu-doped CdS thin film has been successfully deposited by ion-beam sputtering deposition. The structural, morphology, optical and electrical properties of as-deposited and annealed Cu-doped CdS thin films were investigated. The heavily Cu-doped CdS films annealed at 400 °C was demonstrated to be improved in structural, morphology, electrical and optical properties. XRD analysis indicated the formation of polycrystalline CdS film with the structure of hexagonal wurtzite phase. AFM revealed that the big grains were observed and the detected room-mean-square (RMS) roughness was 6.70nm. Optical transmission and absorption spectroscopy measurement revealed high absorption and energy band gap was of about 2.40 eV. The CdS thin film was of p-type conductivity and the resistivity was tested to be 1.28×10^{-1} Ωcm. Thus, a simplified fabrication of Cu-doped CdS thin film by ion beam sputtering was achieved.

Acknowledgments

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