Optik 148 (2017) 95–100

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Original research article

Study of ZnS/CdS structures for solar cells applications

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ARTICLE INFO

Article history:
Received 4 July 2017
Received in revised form 1 September 2017
Accepted 2 September 2017

Keywords:
ZnS/CdS thin films
CdTe solar cells
RF magnetron sputtering

ABSTRACT

ZnS/CdS bilayers were prepared by non-reactive RF magnetron sputtering. The bilayers were post-annealed from 100 °C to 500 °C. The films were characterized by X-ray diffraction analysis, atomic force microscopy, optical spectroscopy, and photoluminescence spectra. It was found that changing the annealing temperature for the multilayers ZnS/CdS is possible to promote the formation of $Zn_xCd_{1-x}S$ thin films. For CdTe/CdS solar cells this is an interesting route to improve the window layer.

1. Introduction

The fabrication of thin film solar cells is a promising approach for terrestrial and space photovoltaic devices [1]. Semiconductors of the II–VI group as ZnS, CdS, and ZnSe are wide use in the fabrication of solar cells, optical detectors, piezoelectric transducers, light emitting diodes, and transparent UV protection devices [2–4]. The CdS is *n*-type semiconductor used mainly as a window layer on CdTe and CuInSe solar cells. A CdS thick layer of 0.1 μm absorbs roughly 36% of the sun light [2,4–6]. However, CdS has disadvantages such as a lattice mismatch of about 10% with the CdTe [7], and a direct band gap of 2.42 eV, that introduces losses at shorter wavelengths in the UV range and therefore limits the performance of the CdTe solar cells [8,9]. A way to increase the transmittance of CdS and get better yields of the solar cell is decreasing its thickness, but this brings an excessive pinhole formation across the hetero junction. The pinholes adversely affect the device open-circuit voltage (V) and fill factor (FF); also shorts occur between grain boundaries [5,10,11].

Using other materials with a band gap greater than the CdS improve the efficiency of the CdTe solar cells. ZnS is a candidate because it has a wide band-gap energy of 3.6–3.9 eV, increasing the response in the short-wavelength region which allow the pass of more photons to the absorber layer. ZnS is also a low-cost, environmentally friendly and non-toxic material [12–15]. Disadvantages of ZnS include a lattice mismatch about 16% with CdTe, and is a highly resistive material. In despite of these reasons there are reports using ZnS/CdS bilayers or ternary $Zn_xCd_{1-x}S$ in solar cells devices [16,17]. With those configurations the absorption of photons in the window layer decreases and the short circuit current in the device increases [4].

Now the use of ternary and quaternary alloys of this group is studied because they have good performance in this field, for $Zn_xCd_{1-x}S$ there are Zn ions doping Cd ions in the CdS lattice that change its optical properties, enhancing the spectral response and increasing the band gap energy [4,18]. The preparation of these compounds can be made with the following techniques: epitaxial growth, electrodeposition, vacuum evaporation, metal organic chemical vapor deposition (MOCVD), spray pyrolysis, successive ionic absorption and reaction (SILAR), photochemical deposition, chemical bath deposition, co-

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http://dx.doi.org/10.1016/j.ijleo.2017.09.002
0030-4026/

Table 1
Interplanar distance for ZnS/CdS multilayers as a function of the annealing temperature.

Sample	2θ (002) peak	d (Å)
As-grown	26.48	3.275
100 °C	26.48	3.275
200 °C	26.48	3.275
300 °C	26.48	3.275
400 °C	26.86	3.229
500 °C	27.19	3.191

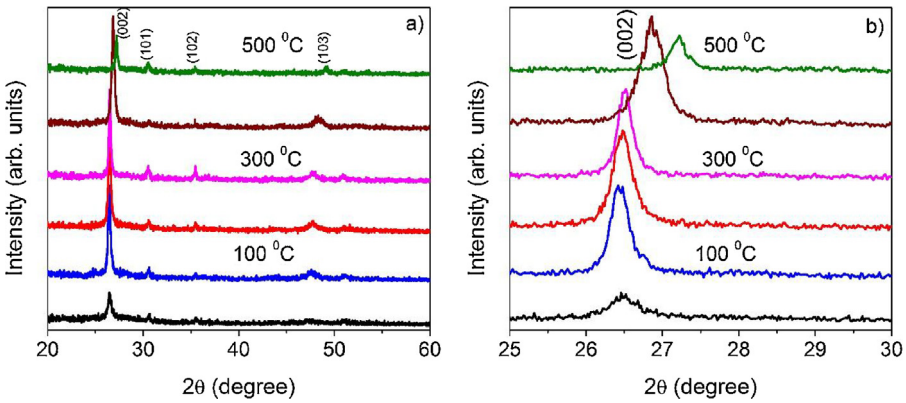

Fig. 1. a) XRD spectra in the 20–60 2theta range and b) details of the (002) peak for as-deposited and annealed films.

sputtering, etc. [18,19]. Among the ternary studied for application in CdTe solar cells we can find the following: $Zn_xCdS_{1-x}S$, $CdSe_{1-y}S_y$, $ZnO_{1-x}S_x$, $Zn_xCd_{1-x}O$, ZnS_xSe_{1-x}, because the Zn-based compounds can substitute the CdS as window layer in this solar cells [14,20–24].

In this work bilayers ZnS/CdS were grown and subsequently annealed at different temperatures. The main intention of studying the bilayer is that the ZnS film could be used as a buffer layer for the solar cell, and the CdS as the window layer. Hence, it is interesting to study the possible intermixing or diffusion processes across the ZnS/CdS bilayers as a function of the non-intentional annealing that resembles the grow of the absorber film in a solar cell. We reported the effect of changing the annealing temperature on the structural and optoelectronic properties of the bilayers. The method used in this work is an interesting route to improve the buffer-window layers for solar cells.

2. Experimental procedure

The ZnS/CdS thin films were deposited on Corning 1737 aluminosilicate glass, Indium Tin Oxide coated one surface, Rs = 4–8 Ω. The ZnS and CdS targets were Kurt J. Lesker 99.999% purity. Before each growth the substrates were cleaned in an ultrasonic bath for 10 min in three different solutions: distilled water and detergent, acetone and isopropyl alcohol, respectively. The ZnS/CdS bilayers were deposited using RF magnetron sputtering under pure argon gas at room temperature. The base pressure of the chamber was 9.0×10^{-5} Torr and the working pressure was 3.0×10^{-2} Torr; for the removal of any contaminants on the surface of the targets a pre sputtering was performed for 8 min.

The deposition of the ZnS thin film was under the conditions of RF power of 100 W and a time of 20 min. The CdS was grown during 10 min at 150 W of RF power. After obtaining the ZnS/CdS bilayer annealing treatments were performed at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C for 15 min, respectively, at atmospheric pressure.

Structural properties of films were obtained by X-ray diffraction (XRD), using a Siemens D500 diffractometer equipped with Cu Kα radiation (λ = 0.154 nm). Film morphology was determined with the help of a Nanosurf Atomic Force Microscopy (AFM) and using a NanoWorld Silicon probe in contact mode (constant force 0.18 N/m, resonance frequency 14 kHz). The mean roughness values reported in this work are arithmetic averages of the absolute surface height measured from the mean plane. These were provided by the Easy-Scan AFM analysis software. Film thicknesses were measured using a profiler Veeco Dektak 8 Stylus. The thicknesses were 100 nm for the ZnS thin film and 150 nm for the CdS thin film, so the bilayers ZnS/CdS had 250 nm of thickness. Transmittance spectra were recorded with the help of an Agilent 8453 UV–vis spectrophotometer. Low temperature PL measurements were carried out by exciting the sample with the 325 nm line of HeCd laser. All samples were measured at a temperature of 15 K.

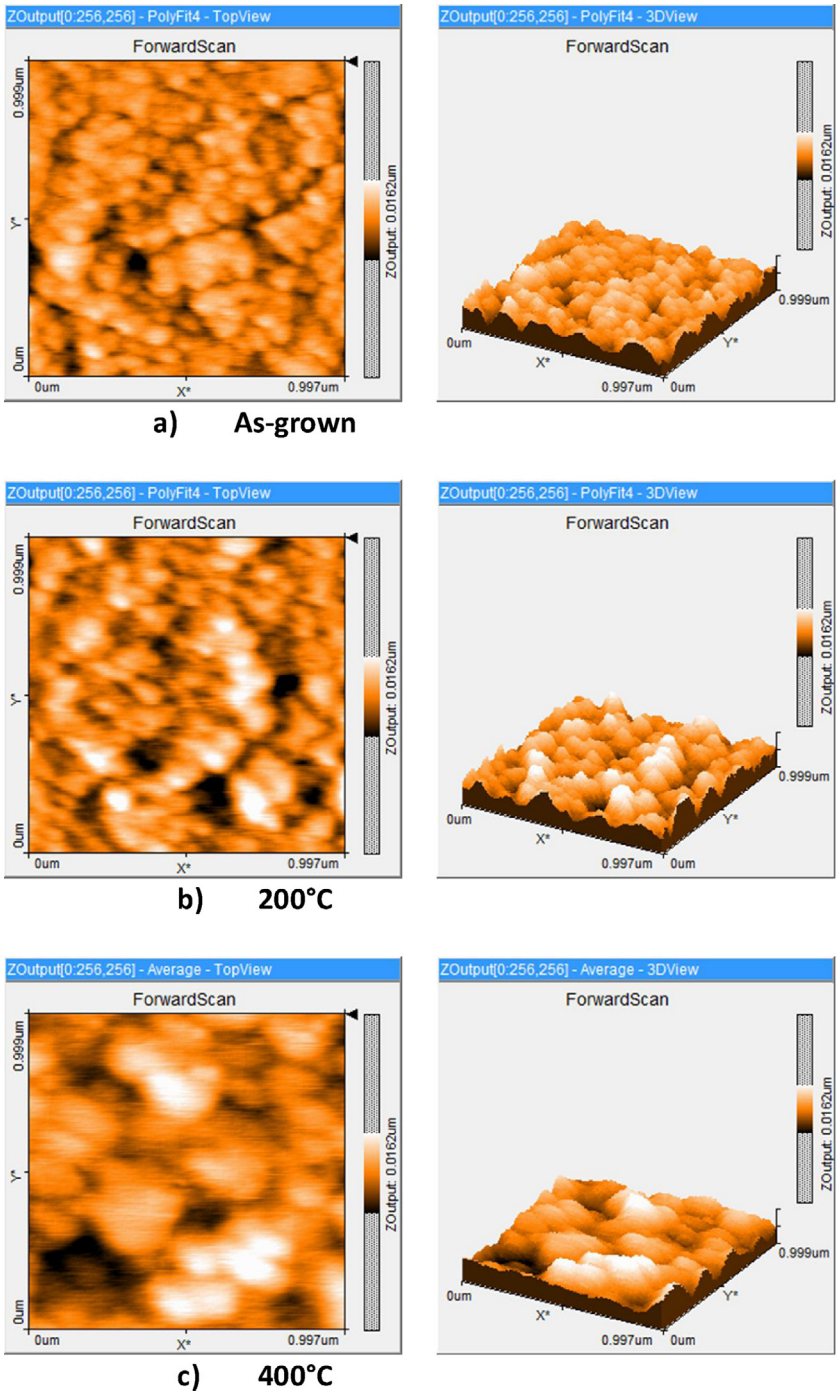

Fig. 2. AFM images of ZnS/CdS a) as-grown, and annealed b) at 200 °C, and c) at 400 °C. For all images z output is 16 nm.

3. Results and discussions

Fig. 1a shows XRD spectra for as-deposited and annealed multilayer ZnS/CdS films. For all samples there is a strong preferential orientation along the (002) planes. For annealed films some new weak peaks (101), (220) and (112) begin to appear. The intensity of (002) peak increases for films annealed from 100 to 400, see Fig. 1b. For annealing temperature 500 °C there is a decrease in the (002) peak intensity, and a remarkable shift in 2theta position.

Using Bragg's equation, $2d\sin\theta = n\lambda$, and calculating θ from the peaks of the XRD patterns in Fig. 1, we obtain the experimental d value, shown in Table 1. For as-grown and annealed films from 100 °C to 300 °C the (002) peak is located at 2theta

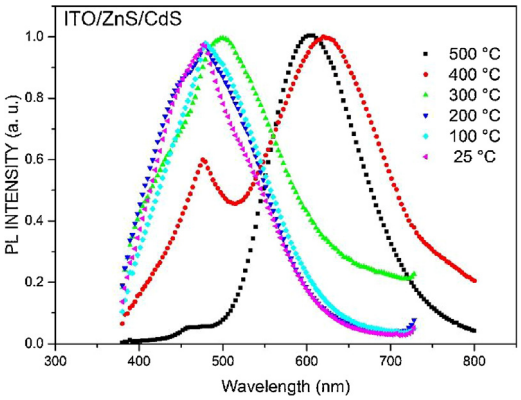

Fig. 3. PL spectra of as-grown and thermally annealed samples.

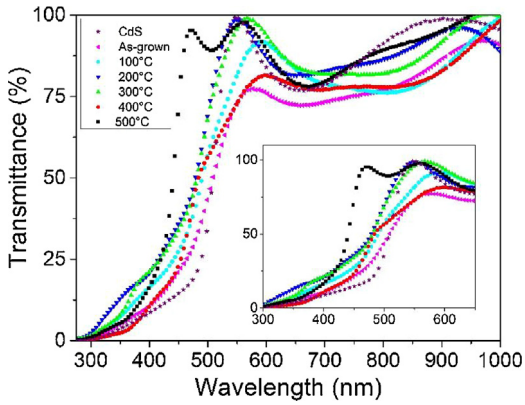

Fig. 4. Transmission spectra of ZnS/CdS bilayers annealed at different temperatures.

of 26.48. For 400 °C and 500 °C annealed films there is a strong shift in the 2theta values of (002) peak to 26.86 and 27.19 respectively. Hossain et al. reported $Zn_xCd_{1-x}S$ thin films ($0.0 \leq x \leq 1.0$) by RF co-sputtering using different RF-power ratios of CdS and ZnS [11]. They obtained d values from 3.3389 Å to 3.2035 Å as the x value increases. Our d values are distributed in this interval, see Table 1. Considering the data reported in the Hossain et al. paper [17], we interpolated a value of x = 0.11 for the bilayer annealed at 400 °C and x = 0.34 for 500 °C. Similar correspondence of x values with 2theta shifts are reported by Al-Douri et al. [25].

Changing the annealing temperature for the multilayers ZnS/CdS is possible to promote the formation of $Zn_xCd_{1-x}S$ thin films. For CdTe/CdS solar cells this is an interesting route to improve the window layer. In fact, an efficiency of 9.3% was obtained for the CdTe/CdS solar cells in the configuration Glass/ITO/a-ZnS/CdS/CdTe, as a result of the no intentional annealing at 530 °C during the CdTe deposition [26]. High performance cells using $Zn_xCd_{1-x}S$ have been reported by W. S. M. Brooks et al. [27] and A. J. Clayton et al. [28].

For as-deposited films the morphology was characterized by fine uniformly sized grains and smooth surfaces with an average roughness of 2.5 nm. Fig. 2a shows an AFM image of a typical as-deposited film. After post-annealing treatments at 200 °C and 400 °C, the morphology of the samples changed drastically due to the crystallization, see Fig. 2b and c. For the annealed samples the grains begin to clump together in clusters leading to a rearrangement to form crystals. This shows that thermal treatment has an important influence on the morphology of these films.

The photoluminescence spectrums of ZnS/CdS structures annealed at different temperatures under the excitation with a wavelength of 325 nm are shown in Fig. 3. The peak around 476 nm dominates the PL spectra in the range temperature from 25 to 200 °C. Further increase in the annealing temperature to 300 °C shifts this maximum to longer wavelengths. For sample annealed at 400 °C appears a second emission band at 624 nm, which dominate the spectra for sample annealed at 500 °C. We associate the change in the PL spectra after 300 °C annealing with two facts, the first one is the structure transition, as confirmed by XRD measurements. The other interpretation could be the appearance of defect band around 650 nm because of introduced stress in the CdS lattice as Zn content increase [16].

Fig. 4 shows the wavelength dependence of transmittance for ZnS/CdS bilayers annealed at different temperatures. It is important to notice that all bilayers had the same thickness (250 nm), so the variations in the optical properties were not related with thickness variations. All annealed films exhibited transmittances that exceeded 70% at wavelengths higher than 550 nm. Notice that the absorption edge shifts towards shorter wavelengths with the increasing of the annealing

temperature from 100 °C to 500 °C. Comparing with the CdS film, the annealed ZnS/CdS have a higher optical transmittance and consequently more photons of the short wavelength range can pass through the bilayers. This could contribute to a better performance of ZnS/CdS as effective buffer/window layer in photovoltaic applications.

4. Conclusions

ZnS/CdS bilayers were grown by RF magnetron sputtering and post-annealed at temperatures from 100 °C to 500 °C. From XRD data there are a significant shift in the 2theta position of (002) peaks as the annealing temperature increases, that can be correlated with the formation of the ternary compound $Zn_xCd_{1-x}S$. In PL spectra there is a transition from an emission band centered at 476 nm for samples annealed to 200 °C to a band emission centered around 624 nm for sample annealed at 400 and 500 °C. The change in the PL spectra would be explained by a structure transition, as confirmed by XRD measurements, or by the appearance of defect band around 650 nm as a consequence of introduced stress in the CdS lattice as Zn content increase. From optical measurements the absorption edge shifts towards shorter wavelengths with the increasing of the annealing temperature from 100 °C to 500 °C. Comparing with the CdS film, the annealed ZnS/CdS have a higher optical transmittance and consequently more photons of the short wavelength range can pass through the bilayers. This could contribute to a better performance of ZnS/CdS as effective buffer/window layer in photovoltaic applications.

Acknowledgments

The authors would like to thank to Patricia Quintana for the access to the National Laboratory for the Study of Nano and Biomaterials, to Daniel Aguilar Treviño for X-ray diffraction measurements, and to M.C. Willian Cauich for film thicknesses measurements.

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