

Thermal annealing of bilayers of evaporated In on chemically deposited CdS thin films

S. J. Castillo¹, M. Sotelo Lerma², R. Ramírez-Bon^{1,3} and F. J. Espinoza-Beltrán³

¹*Centro de Investigación en Física. Universidad de Sonora.
Apdo. Postal 5-88, 83190. Hermosillo, Son., MEXICO.*

²*Depto. de Investigación en Polímeros y Materiales, Universidad de Sonora.
Apdo. Postal 130. Hermosillo, Son., MEXICO.*

³*Laboratorio de Investigación en Materiales, CINVESTAV-IPN - Qro.
Apdo. Postal 1-798, 76001, Querétaro, Qro., MEXICO.*

Abstract

In/CdS bilayers were prepared by evaporating In on CdS thin films deposited by the chemical bath technique. The thickness of the layers were about 50 and 150 nm for In and CdS respectively. In order to diffuse the In to the CdS layer, the bilayers were thermal annealed in air to temperatures from 250 to 450 °C. The obtained samples were characterized by X-ray diffraction (XRD) spectroscopy, optical absorption spectroscopy, photoluminescence (PL) spectroscopy and by scanning electron microscopy (SEM). The experimental results show that the thermal annealing produces a partial conversion of In into In₂O₃ and partial diffusion to the CdS layer. The In₂O₃ forms an external layer which does not allow the In outward diffusion or evaporation. The evidence of the In diffusion to the CdS lattice in the annealed samples is given by PL spectroscopy. The broad emission band in the red region, associated to vacancies, in the PL spectrum of the annealed samples has smaller intensity as compared to the same band in the spectrum of the sample without annealing.

INTRODUCTION

In the last few years, studies on doping of CdS have been the subject of active research, mainly n-type doping [1-4]. High efficiency solar cell structures have been reported based on heterojunction of n-CdS with p-CdTe [5-7] or p-CuInSe₂ [8]. CdS thin films can be deposited by several techniques. Among these techniques, the chemical bath deposition is considered one of the more convenient due to its simplicity [2-3]. This technique yields to hard, adherent, specularly reflecting, high resistivity and stoichiometric CdS thin films. Doping with impurity atoms can lower the resultant high resistivity of the CdS films. The n-doping of CdS has been done by introducing Indium atoms in the CdS lattice. Indium atoms can diffuse to the CdS lattice by thermal annealing of CdS thin films in a H₂+In flux [2], or by thermal annealing in air of In/CdS bilayers [3,4]. n-CdS thin films with electrical resistivity of about 10⁻³-10¹ Ωcm were obtained by either of these methods.

In this work we have prepared bilayers of evaporated In on chemically deposited CdS thin films. In order to diffuse In atoms to the CdS films, the In/CdS bilayers were thermal annealed in air to several temperatures from 250 to 450 °C. We studied the effects of the thermal annealing process on the structural and optical properties of the bilayer system. We also monitored by SEM the changes on the surface morphology produced by the annealing. In agreement with previous reports [3,4], we found that the thermal annealing produces an external layer of In₂O₃, which yields to a drop in the optical density of the samples. The indium diffuses to the CdS layer from an intermediate layer between the oxide and semiconductor layers. The PL spectroscopy evidences the composition changes in the CdS layers of the annealed

samples due to the In diffusion. The microscopy images shows the surface morphology of the studied samples.

EXPERIMENTAL DETAILS

The CdS thin films were deposited on glass slides substrates by means of the chemical bath technique. The reactive substances in the solution were: 0.1M CdCl₂, 1M C₆H₅O₇Na₃, 1M KOH, Buffer (NH₄Cl/NH₄OH) and 1M CS(NH₂)₂. The films were deposited by one hour in the solution at 80 °C. The obtained CdS films were flat homogeneous, green-yellowish, transparent and with very good adherence to the substrate. The energy gap was 2.6 eV, the thickness about 150 nm and the crystalline structure was hexagonal [9]. The In layer of about 50 nm was evaporated in a vacuum chamber (10⁻⁶ Torr) on the CdS films. Pieces of 1x2 cm of the In/CdS bilayers were thermal annealed in air in a Thermoline 30400 oven at temperatures: 250, 300, 350 and 450 °C. The X-ray diffraction measurements were performed by a D/Max-2100 Rigaku diffractometer. Optical absorption spectra of the bilayers were recorded by a Lambda 2 Perkin Elmer spectrometer. PL measurements were done in a S200 Ocean Optics spectrometer. Surface images of the samples were obtained by a JSM-5300 Jeol electronic microscope.

RESULTS AND DISCUSSION

In Fig. 1 are shown the X-ray diffraction patterns of several samples. At the bottom, the pattern of the In/CdS bilayer without annealing displays the diffraction lines of both hexagonal CdS (H-CdS) and tetragonal In (T-In). The strongest diffraction lines are the (002) at about 27° and the (101) at about 33° for CdS and In respectively.

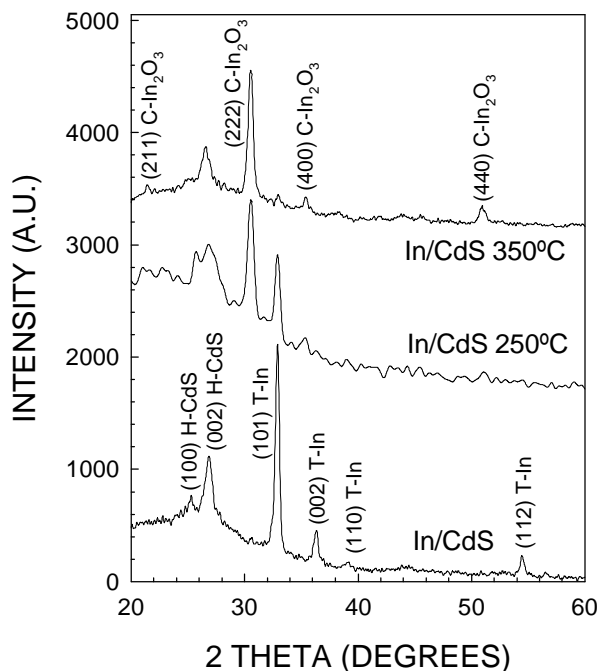


Fig. 1. XRD patterns of the In/CdS bilayer without annealing and of the bilayers annealed at 250 and 350 °C.

The effect of the thermal annealing is the oxidation of In as can be seen in the X-ray patterns of the bilayers annealed at 250 and 350 °C. In these patterns an intense diffraction line appears at about 30.6°, corresponding to the (222) crystalline planes of the cubic phase of In_2O_3 (C- In_2O_3). Meanwhile, the (101) diffraction line of In at about 33° decreases after the annealing at 250°C and almost disappears after the annealing at 350°C. These results can be explained in terms of the oxidation of the In layer surface exposed to the air during the annealing. A third external layer of In_2O_3 is formed during the annealing which grows from the In layer with annealing temperature. The intermediate In layer decreases with annealing temperature due to the partial conversion in oxide and to the partial diffusion into the CdS layer. The external oxide layer prevents from the outward In diffusion or evaporation and from the oxidation of the CdS layer. Thus, the In diffusion to the CdS layer is more efficient.

Fig. 2 shows the optical absorption spectra of the sample without annealing and of the samples annealed at 300 and 350°C. The optical density in the spectrum of the In/CdS bilayer without annealing is higher than one in the whole measurement range, due to the opaque In layer. However, in this spectrum can be observed the CdS absorption edge at about 480 nm. The drop in the optical density in the spectra of the annealed samples is due to the partial conversion of In into In_2O_3 , in agreement with X-ray diffraction measurements. This material is transparent in the visible region of the spectra. The

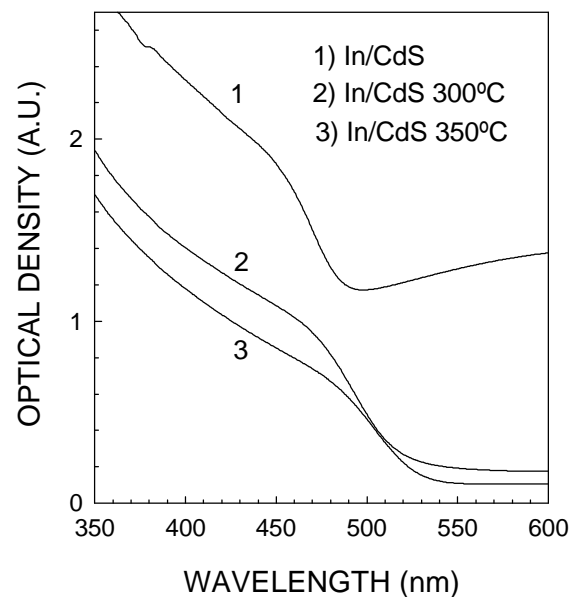


Fig. 2. Optical absorption spectra of the In/CdS bilayer without annealing and of the bilayers annealed at 300 and 350 °C.

values of the optical density of these samples are similar to those of pure CdS films in the whole measurement range [9]. It indicates that the intermediate In layer in these samples must be very thin. Another interesting feature in these spectra is the red shift in the CdS absorption edge to about 520 nm. The growth of the CdS grain, the relaxation of the CdS lattice constant or the composition changes in the samples as consequence of the thermal annealing could produce the red shift of the CdS absorption edge.

In Fig. 3 there are shown the photoluminescence spectra of the sample without annealing and of the sample annealed at 450 °C. The spectra were excited by the 454 nm line of an Argon laser at room temperature. The PL spectrum of the sample without annealing displays a red broad band that has been associated to sulfur vacancies or surface damages. In the spectrum of the annealed sample the intensity of this defect band has reduced considerably. This is an evidence of the composition changes in the CdS layer as consequence of the In thermal diffusion [2].

In Fig. 4 it is shown a sequence of surface images from the sample without annealing to the samples annealed at 300 and 450 °C. The surface image of the sample without annealing displays the surface morphology of the In layer. The surface of the sample annealed at 300 °C presents dark spots on a clear background. The spots have a round shape with size about 2.5 μm . The energy dispersion spectroscopy (EDS) analysis of both surface regions shows that the Cd and S peaks are more intense than the In peak in the dark spots.

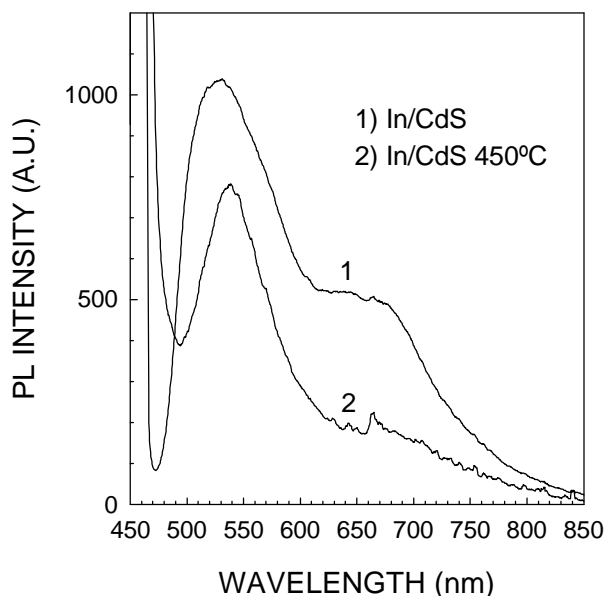


Fig. 3. PL spectra of the In/CdS bilayer without annealing and of the bilayer annealed at 450 °C.

In the clear background the opposite holds. Thus, the clear background can be identified with the external In_2O_3 layer and the dark spots with CdS covered by a thinner In_2O_3 layer. This identification can be supported by the different morphology of both regions. The morphology of the clear background is similar to that of the In layer, as while in the dark spots the thin In_2O_3 has the shape of the CdS layer. The surface of the sample annealed at 450 °C also shows the two regions. However, in this case the dark spots, covering a smaller relative area, are smaller with irregular shapes and the clear background has the shape of the CdS layer. At this annealing temperature, the surface is completely oxidized with the shape of the CdS layer.

CONCLUSIONS

We have reported the structural and optical changes of In/CdS bilayers under thermal annealing. The formation of an external In_2O_3 layer by partial oxidation of the In layer protects the CdS layer against oxidation and allows the In diffusion into CdS. The suppression of the red emission band in the CdS layer of the annealed samples indicates composition changes produced by the In diffusion. Actually, we are working on chemical etching of the oxide layer in order to measure the electrical properties of the isolated CdS layers.

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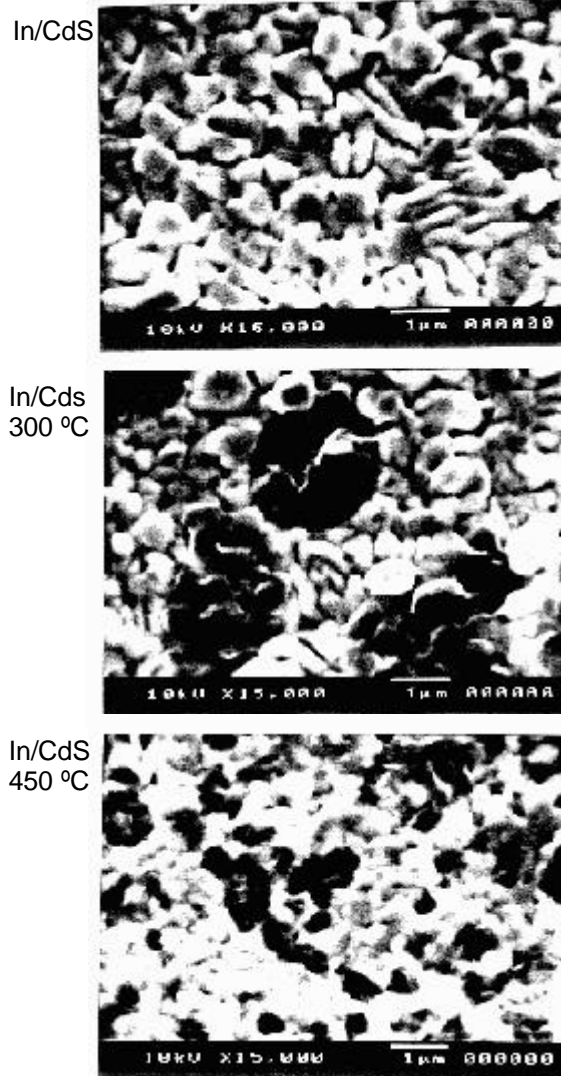


Fig. 4. SEM surface images of the In/CdS bilayer without annealing and of the bilayers annealed at 300 and 450 °C.

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