Structural transition of chemically deposited CdS films on thermal annealing

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Abstract. CdS films were grown by chemical bath deposition. The as-grown films had the cubic CdS crystalline structure. As-grown films were thermally annealed in a controlled $Ar + S_2$ atmosphere. The annealing temperature was varied from 200 to 400 °C. The annealing process produces a gradual structural transition from cubic for the as-grown CdS film to hexagonal for the CdS film annealed at 400 °C. The CdS structural transition is studied by x-ray diffraction spectroscopy, atomic force microscopy and by optical absorption measurements. The changes in surface morphology, as observed from atomic force three-dimensional images of the as-grown and annealed film surfaces, provide a direct indication of the structural transition performed by the CdS annealed films.

1. Introduction

Cadmium sulphide (CdS) is a II–VI semiconductor material with appropriate properties for application in the fabrication of optoelectronic devices. Thin films of this compound can be easily obtained by several techniques such as r.f. sputtering, evaporation, spray pyrolysis and chemical bath deposition. In particular, chemical bath deposition is one of the simplest and most economic techniques to grow hard, adherent, specularly reflecting and stoichiometric CdS thin films [1, 2]. In this method the CdS film is deposited on a substrate immersed in an aqueous solution where CdS molecules are formed as the result of chemical reactions among the ions in the solution. The physical properties of the deposited films depend mainly on parameters such as the pH and temperature of the aqueous solution, the kind of substrate and the relative concentration in the solution of the substances providing the Cd^{2+} and S^{2-} ions for the chemical reactions. It has been found that depending on the growth kinetic, the crystalline structure of the chemically deposited CdS films can be hexagonal (wurtzite) or cubic (sphalerite) [2]. The hexagonal structure is obtained when deposition is achieved by means of an ion by ion gradual condensation on the substrate. On the other hand, cubic structure is the result of adsorption of cubic CdS clusters formed in the aqueous solution. Thus, CdS films having either cubic or hexagonal structure can be obtained by chemical bath deposition.

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The cubic to hexagonal structural transition in chemically deposited CdS thin films has been recently investigated [3–6]. The transition from as-grown polycrystalline CdS films with the metastable cubic structure to CdS films with the stable hexagonal structure is produced by thermal annealing in a controlled $Ar + S_2$ atmosphere. The structural transition of the cubic CdS films is accompanied by changes in the energy band gap of the annealed films. At lower annealing temperatures, the value of the band gap of the CdS films decreases from the value for cubic CdS to a minimum value at a critical temperature. Then, at higher annealing temperatures the energy band gap of the films increases to the value of hexagonal CdS, which is very similar to that of cubic CdS. The structural transition temperature for CdS films annealed in similar conditions to those used in this work has been reported to be between 250 and 300 °C [3–6].

In this work we study the cubic to hexagonal structural transition of chemically deposited CdS thin films by means of atomic force microscopy (AFM). We report for the first time direct evidence of the systematic change of structure of CdS films by means of the surface morphology as measured by atomic force microscopy. The structural transition was induced by thermal annealing of as-grown cubic CdS films in a flux of Ar plus S_2 gases. The sequence of three-dimensional AFM images of the surface of CdS films annealed at temperatures from 200 to 400 °C shows the gradual transition from the cubic to hexagonal crystalline structure of CdS. The study is completed by x-ray analysis and optical absorption measurements on the as-grown and thermally annealed CdS films.

2. Experimental details

CdS layers were deposited on glass slide substrates by the chemical bath technique. The reactive substances KOH, $CdCl_2$, NH_4NO_3 and $CS(NH_2)_2$ (thiourea) were dissolved in an aqueous solution. The initial pH of the solution was 10. During the deposition process the temperature of the solution was kept at 80 °C ± 3 °C and it was continuously stirred. The time of deposition was 20 minutes. The resulting CdS films were homogeneous, hard, transparent, yellowish and with a good adherence to the substrate. The crystalline structure of the films was cubic as shown by x-ray spectroscopy. The average thickness of the films was 120 nm. The thermal annealing of as-grown CdS films was simultaneously performed in a hot-wall furnace with a quartz tube. During the annealing process, a flow of argon plus sulphur was passed through the tube. The annealing temperature was varied from 200 to 400 °C, with an error of ±5 °C, taking advantage of the temperature profile of the furnace. The duration of the annealing process was 24 h. The AFM images of the film surfaces were obtained with a Park Instruments nanoscope operating in the constant-force mode. X-ray diffraction patterns of the films were obtained with a D500 Siemens diffractometer using the Cu Kα radiation line. The absorption spectra were measured by a Perkin–Elmer Lambda 9 spectrophotometer.

3. Results and discussion

Figure 1 shows the x-ray diffraction spectra of as-grown and thermally annealed CdS films. At the bottom, the spectrum of the as-grown film shows a broad peak at 2θ about 26.5° overlapped by a broad diffraction band produced by the amorphous glass substrate. This diffraction peak is produced by the (111) crystalline planes of the cubic CdS structure or the (002) crystalline planes of the hexagonal CdS one. It has been reported that both lines coincide within one per cent. From previous reports [3–5, 7] we can be assured that the
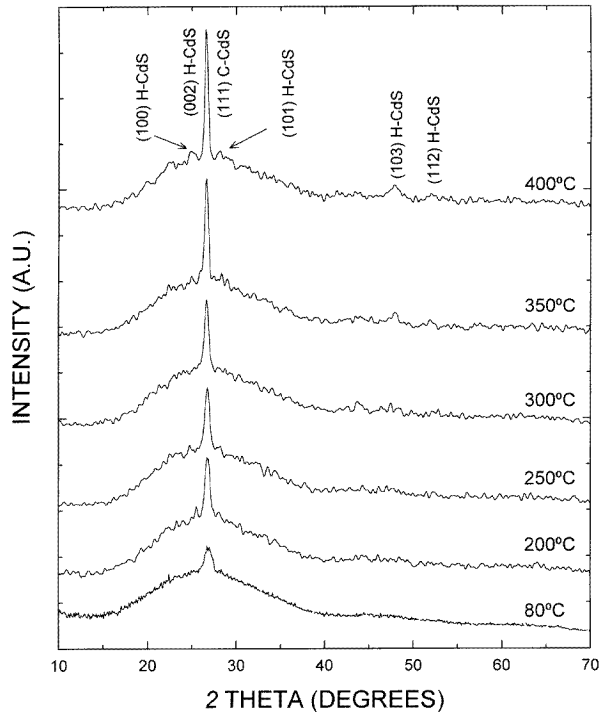
Figure 1. X-ray diffraction patterns of as-grown (80 °C) and thermally annealed CdS films.

crystalline structure of the as-grown sample is the zincblende one, by noting the presence of other diffraction peaks corresponding to this crystalline phase. The high orientation of the CdS crystallites along the [111] direction reduces considerably the intensity of other diffraction peaks. In this case, the presence of an isolated peak associated with the (111) crystalline planes of the cubic CdS phase may be due to a small averaged grain size or to the small thickness of the sample. This peak is also dominant in the spectra of the annealed samples and it is also overlapped by the diffraction signal of the substrate. The effects of the thermal annealing are the narrowing of the dominant peak, indicating an increase of the size of the CdS crystallites in the films. It can be also observed the formation of additional peaks at 2θ equal to 24.81, 28.18, 47.84 and 51.82°. These peaks are related to the (100), (101), (103) and (112) crystalline planes of the CdS hexagonal structure respectively and can be seen more clearly in the spectrum of the CdS sample annealed at 400 °C. Thus, the formation of the diffraction peaks associated with the hexagonal CdS structure in the spectra of the annealed CdS films indicates an evolution of the sample structure from the as-grown cubic phase to the hexagonal one.

In figure 2 are plotted the interplanar distances between the (111) crystalline planes of the CdS cubic phase or the (002) crystalline planes of the CdS hexagonal phase. These distances were obtained from the x-ray diffraction patterns in figure 1. The increase in the interplanar distance from the as-grown sample to the sample annealed at 200 °C may be produced by a reduction of sulphur vacancies in the cubic CdS lattice as a consequence of the annealing process in the sulphur rich atmosphere. As-grown cubic CdS samples prepared by this method present sulphur vacancy defects which produce a red broad-band (1.8 eV) photoluminescence emission [7]. Sulphur vacancies in the CdS lattice reduce the lattice
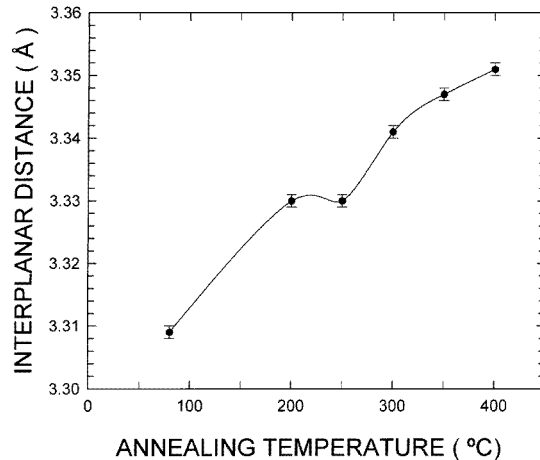
Figure 2. Interplanar distances between planes (111) from the CdS cubic phase or (002) from the hexagonal CdS phase, given by the x-ray diffraction spectra from figure 1.

constant. It has been established that thermal annealing at low temperatures ($\sim$200 °C) in a sulphur atmosphere suppresses the red band in the photoluminescence spectra, indicating that this process contributes to reduce the number of sulphur vacancies and then to expand the CdS lattice. From 200 to 300 °C, figure 2 shows a transition which can be associated with the crystalline structure transition of CdS. At higher temperatures the interplanar distance increases up to the distance between (002) crystalline planes of the CdS hexagonal structure.

The AFM three-dimensional (3D) images of the surface samples confirm the x-ray measurement results. Figure 3 shows a 3D surface image sequence from the as-grown cubic CdS film to the hexagonal CdS film annealed at 400 °C. The 3D surface image of the as-grown CdS film shows the polycrystalline character of the sample with pyramidal shaped crystallites, typical of cubic crystallites oriented in the [111] crystalline direction [8, 9]. The roughness surface and mean height of the area in this image are 5 and 19 nm respectively. The shape of the crystallites of the CdS sample annealed at 200 °C is similar to that of the as-grown CdS sample, indicating the cubic structure of this film. This result is in agreement with the discussion in the preceding paragraph. The effect of the annealing process, at higher temperatures, is observed in this image sequence as a gradual flattening in the shape of the crystallites with the increasing of annealing temperature, on passing from a pyramidal geometry to a well defined prism geometry. The flat and rounded top and flat faces of the crystallites observed in the image of the film annealed at 400 °C resemble the hexagonal prism shape of hexagonal crystallites oriented in the (002) crystalline direction. The structural transition begins at 250 °C as shown by the image in (c). This sample along with the sample annealed at 300 °C present CdS crystallites with shapes that do not correspond exactly to the cubic phase or to the hexagonal one. The CdS crystallites in these samples are composed by a mixture of both crystalline phases. This result show that the critical temperature for the structural transition is between 250 and 300 °C.

The structural changes in the CdS films induced by the thermal annealing produce changes in their energy band gaps, as observed in the optical absorption measurements. Figure 4 shows the spectra $(\alpha h\nu)^2$ versus energy ($h\nu$) of the as-grown and some annealed CdS samples. From the model for direct allowed transitions [10], the value of the energy band gap is given by the intercept of the straight line with the energy axis. The energy band
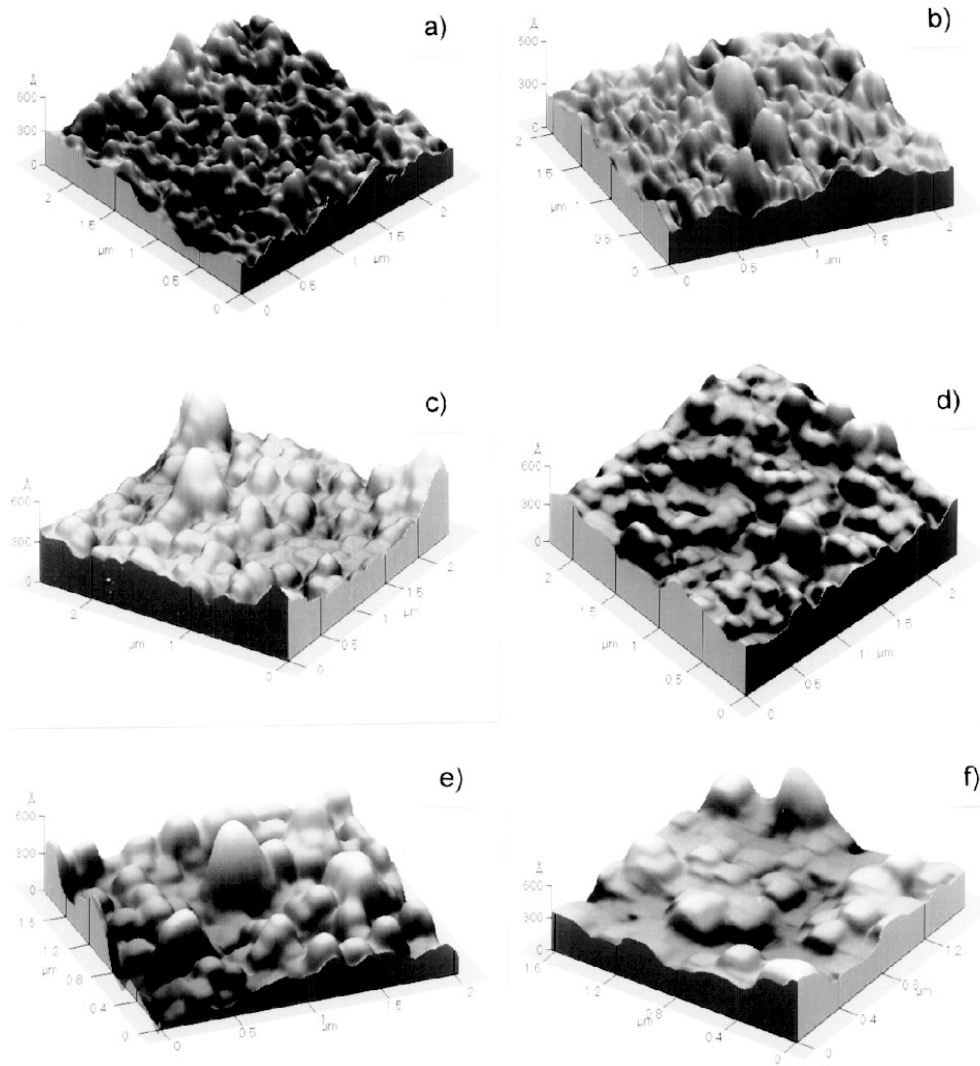
Figure 3. Three-dimensional surface images of the (a) as-grown CdS film and CdS films annealed at (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C and (f) 400 °C.

gap of the as-grown sample is 2.48 ± 0.005 eV, which is higher than the 2.40 ± 0.005 eV value previously reported [3–5] for CdS films prepared by the same method. This shift could be explained by a quantum confinement effect due to the small size of the crystallites of the as-grown film [11]. An estimation of the lower limit for the size of these crystallites is about 9 nm, as calculated from the x-ray measurements by using the Debye–Scherrer broadening formula.

Figure 4 clearly shows a shift of the energy band gap of the annealed films to lower energy values. The CdS sample annealed at 300 °C has the minimum energy band gap. For higher annealing temperatures the energy band gaps of the films increase up to 2.40 eV, which corresponds to the energy band gap of hexagonal CdS films. The evolution of the
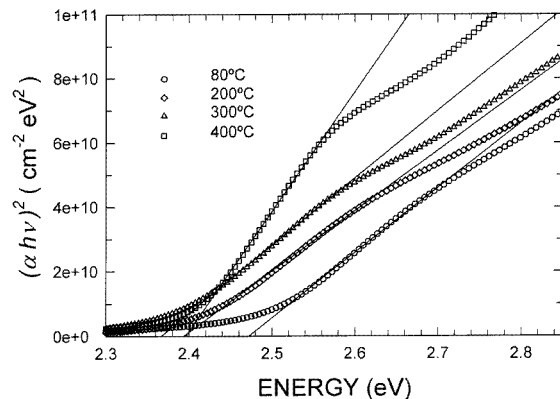
Figure 4. Square of the absorption coefficient times the photon energy as a function of the photon energy for the as-grown (80 °C) CdS film and three CdS films annealed at 200, 300 and 400 °C. The solid lines represent the best fit to the linear portion of the curves and it is used to obtain the energy band gap of the films.
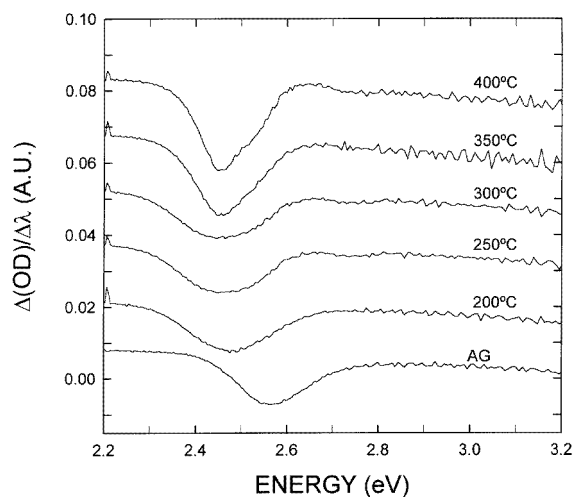

Figure 5. First numerical derivative of the absorption spectra as a function of the photon energy of the as-grown (80 °C) and annealed CdS films.

energy band gap is more evident in the plot given by the derivative of the absorption spectra, as can be observed in figure 5. In this figure, the fundamental absorption edge of the CdS films appears as a broad band. The centre of this band gives an estimation of the energy band gap value of the films [3, 12]. In figure 6 are shown the energy band gaps of the CdS films as a function of annealing temperature, given by the allowed direct transition model and by the absorption edge estimation from the derivative of the absorption spectra. It is clear that both criteria predict the same behaviour.

The annealing temperature at which the energy band gap of the films is a minimum has been considered as a critical temperature associated with the structural transition. The origin of the alteration in the energy band gap of annealed CdS films has not been fully
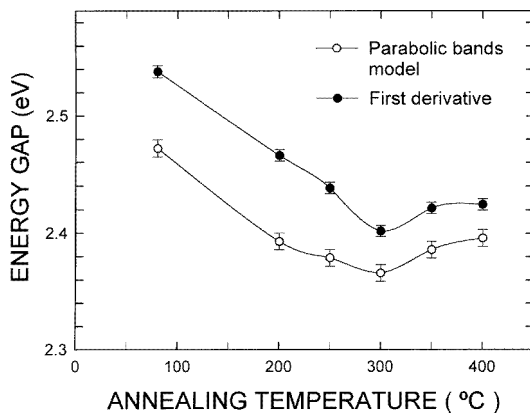
Figure 6. Energy band gap of as-grown and thermally annealed CdS films obtained from figures 3 and 4.

understood. The decrease of the energy band gap of the CdS film annealed at 200 °C can be produced by the expansion of the cubic CdS lattice. Our results suggest that the structural transition observed at higher annealing temperatures may be an order–disorder transition [13]. From this point of view, the decrease of the energy band gap of the CdS films annealed at 250 and 300 °C is produced by an increase in the structural disorder induced by the change from cubic to hexagonal phase of CdS. That is, the resulting crystalline structure of the annealed samples contain a mixture of cubic and hexagonal regions. The maximum disorder corresponds to the CdS film with minimum energy band gap and indicates that both crystalline phases are contained in similar proportions in the film. In the present case this explanation is supported by the AFM surface images which show that at this annealing temperature the CdS film is composed by a mixture of both crystalline phases of CdS.

In conclusion, direct evidence of the structural transition demonstrated by chemically deposited CdS films upon thermal annealing has been reported in this paper. A gradual change in the shape of the crystallites is observed in a sequence of three-dimensional images of the film surfaces, measured by atomic force microscopy. The pyramidal shape is observed in the as-grown cubic CdS films, while a well defined prism shape is observed in the hexagonal CdS film annealed at 400 °C. X-ray diffraction measurements show that the as-grown CdS film has a cubic structure with a (111) growing preferential orientation, and that the CdS film annealed at 400 °C has the hexagonal structure with a (002) growth preferential orientation, both results in agreement with the surface morphology as observed with AFM. The changes in the energy band gap of annealed CdS films could be produced by the structural disorder induced by the gradual change of structure of the CdS annealed films.

Acknowledgments

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