

Effects of annealing on the lattice parameter of polycrystalline CdS thin films

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Cubic CdS (β -CdS) polycrystalline thin films were prepared on glass substrates by chemical synthesis at 80 °C. Samples were subjected to thermal treatments (TT) in the range of temperatures (T) 180 – 500 °C during 30 hours in different ambients. Annealing in air and in H₂ produces in CdS larger lattice parameter enlargements ($\leq 2.5\%$) when T of TT increases up to T ≤ 500 °C. Whereas, annealing in Ar + S₂ and vacuum provokes intermediate ($\leq 1.2\%$) and smaller ($\leq 0.9\%$) maxima values of the lattice parameter increments, respectively. Energy band gap (E_g) as a function of T of TT and as a function of the lattice parameter has been also studied where it was observed that E_g behaves in very different manners depending on the ambient chosen for annealing.

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1 Introduction

Thermal treatments (TT) are common post-growth processes used to search the improvement of structural, optical, and electrical properties of semiconducting materials. Particularly, the effects of TT on CdS have been subject matter of numerous studies, alone or in heterostructures like CdS/CdInSe₂ or CdS/CdTe. Research on CdS is important because its applications in sensors [1], optoelectronic devices [2] and, mainly, in solar cells [3]. This work has been focused to the analysis of the changes on the lattice parameter (a) and of the forbidden energy band gap (E_g) as a function of the temperature (T) of TT, and the behavior of E_g versus the interplanar distances, of cubic zincblende CdS (β -CdS) polycrystalline thin films prepared on glass by chemical bath (CB), when TT is carried out in: (a) Ar + S₂, (b) vacuum, (c) H₂ and (d) air atmospheres.

2 Experimental

Polycrystalline layers of CdS in the cubic modification were grown on glass at 80 °C by CB during 45 min. Details of the growth process have been described in a previous work [4]. Thickness of films measured using a Dektak II profilometer was 200 ± 10 nm. Four series of as-grown (AG) samples -within 10 to 20 samples per series- of 0.5 cm x 1.0 cm of dimensions were cut from two different growing-batch prepared at the same conditions. Series (a) and (b) are from the first growth and series (c) and (d) from the second one. The nomenclature was chosen according to the atmosphere of TT used as indicated above. All the samples of each series were annealed at the same time in a tubular furnace at different temperatures in the range 150 – 500 °C

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taking advantage of the temperature profile along the tube. The effects of TT on virgin AG-CdS samples under each of the following atmospheres were studied: (a) Ar + S₂, (b) vacuum, (c) H₂, and (d) air. Lattice parameter values were calculated from X-ray diffraction (XRD) patterns achieved in a Siemens D5000 diffractometer. E_g values were calculated from optical absorption spectra taken at room temperature and registered in a uv/vis Unicam 8700 system over the 190-900 nm wavelength range with an accuracy of $\Delta\lambda = \pm 0.3$ nm, and employing the $(\alpha hv)^2 = A(hv - E_g)$ relationship, where α is the optical absorption coefficient, hv is the photon energy, and A is a constant.

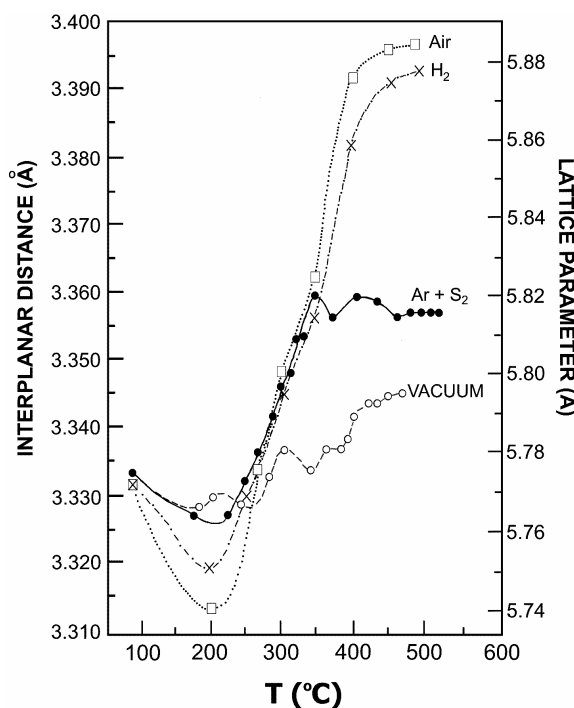


Fig. 1 Interplanar distance d and lattice parameter a versus T of TT. d equals d_{111} and $a = \sqrt{3} d_{111}$ for ambient (b), (c) and (d). For ambient (a) $d = d_{111}$ and $a = \sqrt{3} d_{111}$ when $T \leq 300$ °C; after $T = 300$ °C the interplanar distance changes from d_{111} to d_{002} , and the lattice parameter from $a = \sqrt{3} d_{111}$ to $c = 2d_{002}$. For samples in series (a) with W-phase, the numbers located on the vertical right axis should be multiplied by 1.15 to obtain the real values of c .

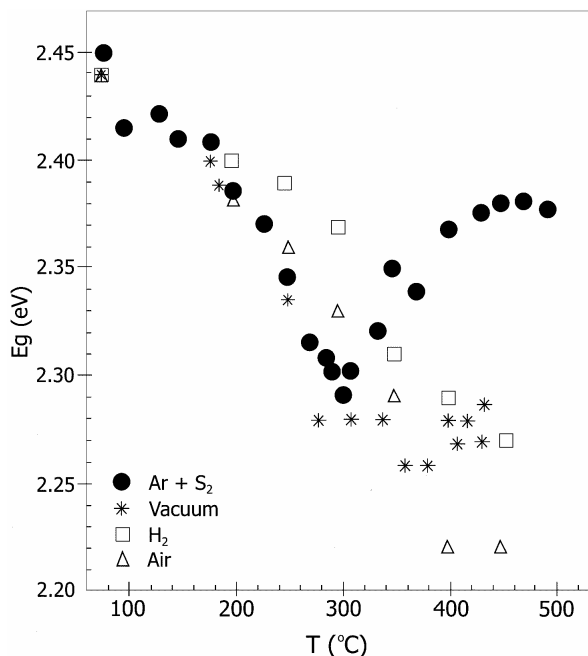


Fig. 2 The energy band gap versus the temperature of TT for the four ambients studied.

3 Results and discussion

AG-CdS samples have been grown in the metastable cubic zincblende (ZB) crystalline phase as determined from XRD patterns. These diffractograms show the peak corresponding to the (111) interplanar distance (d_{111}) of the ZB crystalline phase of CdS and to the (d_{002}) interplanar distance when CdS is in the stable hexagonal wurtzite (W). Fig. 1 illustrates d_{111} and the lattice parameter (a) versus T for the series of samples (b), (c) and (d). It is important to remark that AG-CdS cubic changes from ZB to the W crystalline phase only when TT is carried out in the (a)-atmosphere [5]. The critical point of the ZB-CdS \rightarrow W-CdS (α -CdS) transformation is $T_c = 300$ °C. Since the W crystalline structure has two lattice parameters: a and c , in series (a) of Fig. 1 we refer to the cubic lattice parameter a_{ZB} of the ZB-phase when $T \leq 300$ °C, and to c_W of the W-phase when $T > 300$ °C, but the real values of c_W are 1.15 times the values read on the axis of lattice parameter (vertical right axis of Fig. 1). There are two experimental points located at 80 °C (the growing temperature), one point indicates the

initial d_{111} and a values of the series (a) and (b), and the other point indicates the corresponding value for the series (c) and (d). This difference in both initial values of a gives an idea of the level of reproducibility of CdS samples grown by CB, in our case, under the same conditions. Here, the size of the points plotted in Fig. 1 represents the size of the error bar in the measurement of a and d by XRD. It is evident the difference of the effects on the CdS lattice originated by the different ambient employed in the TT's. The lattice parameter (a) of the cubic cell of the ZB phase equals $\sqrt{3} d_{111}$. In series (a), d_{111} changes to d_{002} after $T = 300$ °C, since the (111) direction of β -CdS is parallel to the (002) direction of α -CdS, which are the stacking direction of these phases, respectively, and the lattice parameter moves from $a = \sqrt{3} d_{111}$ to $c = 2d_{002}$. Lines through experimental points in Fig. 1 were outlined only for visual effects. Different effects of TT on CdS are due, basically, to either absorption or desorption of gases during TT and to the phase change when this last phenomenon happens. Series (b) annealed in vacuum displays the lower enlargement of the lattice parameter, which obeys to desorption of oxygen essentially, as it was reported in a previous work [6]. If this last process were acting isolated its contribution would be to reduce the lattice parameter value. The increase of a with TT is mainly caused by the rearrangement of ions of Cd and S inside the CdS lattice and to the diffusion of atoms or ions into its volume. In the case of series from (b) to (d), the metastable crystalline structure ZB of β -CdS tries to change with TT to the stable phase W of α -CdS, a fact that makes the ions move inside the lattice, and from here, the volume of unit cell has also a tendency to make itself equal to the unit cell of the phase W, and hence experiences an increasing. This movement in turn implies that a growth in the interplanar distances occurs. In CB-CdS, layers grow with an excess of Cd, i.e., the ratio $\text{Cd/S} > 1$, which is frequently attributed to the intrinsic error bar of EDS or Auger stoichiometry measurement techniques [7]. The presence of S^{2+} -vacancies in the CdS lattice impedes the complete $\text{ZB} \rightarrow \text{W}$ transition [8], however the movement of ions in this frustrated $\text{ZB} \rightarrow \text{W}$ structural transformation makes that the unit cell volume increases. With this in mind, one can conclude that the resultant rising value of lattice parameter observed in series (b) is owing to the oxygen desorption and the growth of the unit cell when CdS lattice tries to transform from the ZB to the W crystalline structure, where the second cause predominates in this case.

In series (a), the existence of sulfur in the ambient contributes mostly to reduce the density of S^{2-} -vacancies during TT. In this way the $\text{ZB} \rightarrow \text{W}$ transformation is favored, in such a manner that it is completed and the lattice parameter enlarges up to reach higher values than in the case of annealing in vacuum. For series (c) and (d), atoms and ions from the surroundings diffuse into the material occupying interstitial and/or vacancy positions and pushing out the lattice and, hence, giving place to an augment of the CdS lattice parameter to larger values than in the case of series (a). In this series diffusion of sulfur atoms reaches the saturation by equilibrium conditions at lower values of a , because S occupies chiefly vacancies of sulfur. In series (c) and (d), the expansion of the lattice have approximately the same characteristics. Fig. 2 displays E_g versus T for the four series of CdS layers studied. As previously reported [5], E_g of β -CdS in series (a) decreases when T rises, afterwards, it reaches a minimum value at the critical temperature $T_c = 300$ °C, and then turns back, when the material is already in a predominant α -CdS structure, until to reach values ~ 0.04 eV lower than initial values of E_g of β -CdS. The minimum value of E_g has been associated to the maximum disorder of the lattice at T_c where the lattice passes from a ZB-dominated to a W-dominated structure. When the transformation has been carried out—at larger T values—disorder disappears and E_g returns approximately to its initial (that of α -CdS) value. For series (b) to (d) the $\text{ZB} \rightarrow \text{W}$ transformation does not occurs because of disorder does not disappear and, in the range of T analyzed, E_g either always decreases or decreases and then reaches a temperature where it maintains a constant value, but it does not turn back. In these series E_g reaches lower values than in the case of (a)-series (see Fig. 2). One can appreciate that E_g as a function of T has more or less a similar behavior for $T \leq 300$ °C, but for $T \geq 300$ °C, the behavior of E_g with T is very different for each thermal annealing.

In Fig. 3 one can observe that the dependence of E_g with d is approximately linear for series (b), (c), and (d) and resembles a quadratic behavior for series (a). Although β -CdS in series (b) to (d) did not experience a complete phase transformation, it should be a certain component of the α -CdS phase, which can be neglected and, hence, to say that the variation of E_g is exclusively due to the changes on the lattice parameter. In the case

of solid solutions like $\text{CdS}_{1-x}\text{Se}_x$ the lattice parameter as a function of x ($0 \leq x \leq 1$) follows the Vegard law and the energy band gap in these solutions can be, in general, a linear or a quadratic function of x . When the β -CdS \rightarrow α -CdS transformation occurs, there is not a sudden transition but a gradual one from a ZB dominated lattice to a W dominated layer. For just $T = 300$ °C the lattice has both crystalline phases with equal proportions [9], even though, the minority phase decays exponentially with T by going through T_c . One can assume that, in this case, a solid solution of ZB and W structures exists and that the Vegard law is valid for the interplanar distance along the stacking direction as a function of the relative concentration parameter (x) of the W crystalline phase in CdS. The experimental proof of this assumption is not an easy task from XRD measurements because of the preferential orientation of the thin film CdS-growth does not permit the calculation of each crystalline component percentage value. However, if an inverse reasoning is used on the consequences derived from the Vegard law, i.e., by assuming that if a linear or quadratic dependence of E_g with a is fulfilled, then the Vegard law possibly rules the dependence of a with x in the solid solution of ZB and W structures in CdS thin films, as could be in series (a).

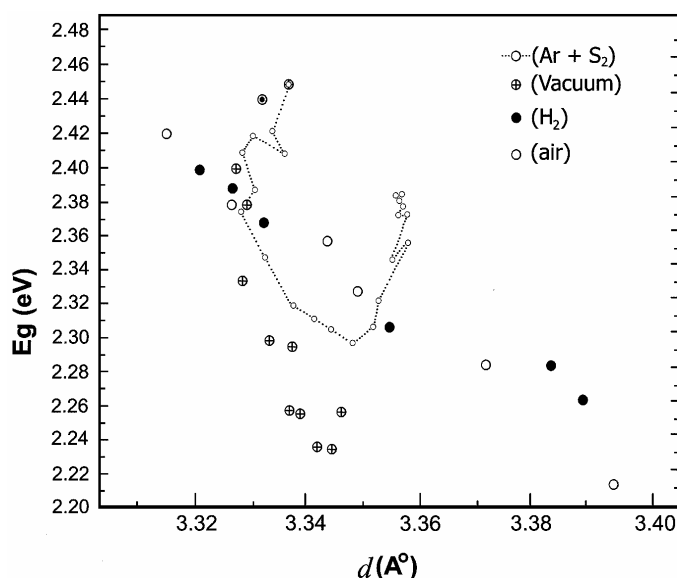


Fig. 3 The energy band gap as function of the interplanar distance for the four ambient studied.

4 Conclusions

The conclusive remarks are: (i) The experimental demonstration of the drastic difference on the lattice parameters changes carried out in polycrystalline CdS grown by CB when the thermal annealing is in the range 150-500 °C, depending on the type of ambient used and the T -value chosen. (ii) The variations in the energy band gap, which are roughly similar for all the ambients when $T < 300$ °C, and very different when $T \geq 300$ °C. And, (iii) the existence of a good probability that the Vegard law be valid for the “solid solution” of W and ZB crystalline phases in CdS, as observed in series (a). These facts deserve to be taken into account when solar cells for terrestrial use are designed.

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