

Influence of thermal annealings in different atmospheres on the band-gap shift and resistivity of CdS thin films

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We study by photoacoustic spectroscopy the band-gap shift effect of CdS films. The CdS films were grown by chemical bath deposition and exposed to different annealing atmospheres over a range of temperature in which the sample structure changes. We show the band-gap evolution and resistivity as a function of temperature of thermal annealing and determine the process that produces the best combination of high band-gap energy and low resistivity. © 1995 American Institute of Physics.

I. INTRODUCTION

The study of heterojunctions has become a subject of intense activity in solid state research. Apart from their utility in the fabrication of transistors and diodes, heterojunctions play an important role in the development of solar cell technology. In particular, CdS/CdTe heterojunctions represent one of the principal candidates for low-cost and high conversion-efficiency solar cells.¹ In this type of solar cell, fabrication of CdS films with low resistivity is very important because it helps to diminish the dispositive sheet resistance and to obtain the space charge region in the active zone, i.e., in the CdTe film.

It is known that CdS exists in either of two different structural phases, namely, a highly stable hexagonal phase and a metastable cubic phase. Cardona *et al.* have demonstrated by means of room-temperature reflectivity measurements that such phases have a band-gap energy differing by less than 0.1 eV.² Cubic phase CdS films display a band-gap shift (BGS) effect that is dependent on the temperature and annealing atmosphere. The influence of temperature on Si films was first reported by Balkanski *et al.*³ Subsequently, because of its technological importance in optoelectronic design, the BGS effect of intrinsic and extrinsic semiconductors has been extensively investigated.⁴⁻⁸ Recently, Zelaya-Angel *et al.*⁹ have reported the first study of the influence of the annealing atmosphere on the BGS effect in CdS films. However, it is worth noting that such a BGS effect, as well as the growth procedures to obtain CdS films in either of the phases, are not well understood up to now.

In this article, we study the influence of the temperature of thermal annealing (TTA), in different annealing atmospheres, on the band-gap shift and resistivity in CdS thin films. The annealing atmospheres include Ar, Ar+S₂,

H₂+In, H₂, and air, in the temperature range 200–450 °C. We show the interesting and technologically important combination of low resistivity CdS thin films with high-energy gap. The band-gap shift is studied by photoacoustic spectroscopy (PAS) because this technique allows us to obtain spectra that clearly show the BGS effect.⁹⁻¹²

II. EXPERIMENT

Cadmium sulfide thin films of approximately 0.25 μm thickness were prepared by the chemical bath deposition (CBD) method. The chemical bath was an aqueous solution of CdCl₂, KOH, NH₄NO₃, and CS[NH₂]₂ (thiourea). The solution was maintained at (80±3) °C and continuously stirred in order to ensure a homogeneous distribution of the chemical compounds.¹³

Postdeposition thermal treatments of the samples were performed in a quartz tube placed into a hot wall furnace. Using the furnace temperature profile, CdS samples were heated simultaneously in the temperature range 200–450 °C. For the Ar gas and Ar gas+S₂ vapor flux annealings, the CdS samples were heated for 28 h at 208, 260, 296, 353, 398, and 447 °C (for Ar+S₂, the last TTA was 418 °C). The S₂ vapor flux was obtained by placing a boat containing sulfur at 190 °C. For the H₂ gas, H₂ gas+In vapor flux, and air annealings, the CdS samples were kept at 200, 250, 300, 350, 400, and 450 °C for 1 h. For H₂+In, a boat containing In was placed at 330 °C, whereas for the H₂ annealing, a flow of H₂ gas was kept for 30 min before placing the samples. The pressure for all the treatments was about 1 atm.

Photoacoustic absorption spectra of the films were obtained in the region 400–700 nm by the use of a standard photoacoustic spectrometer fitted with a 1000 W Xenon lamp (Oriol). The radiation from the lamp was focused onto a variable-frequency light chopper held at 17 Hz and placed at the entrance slit of a monochromator. The monochromatic light was focused onto the samples placed into a closed pho-

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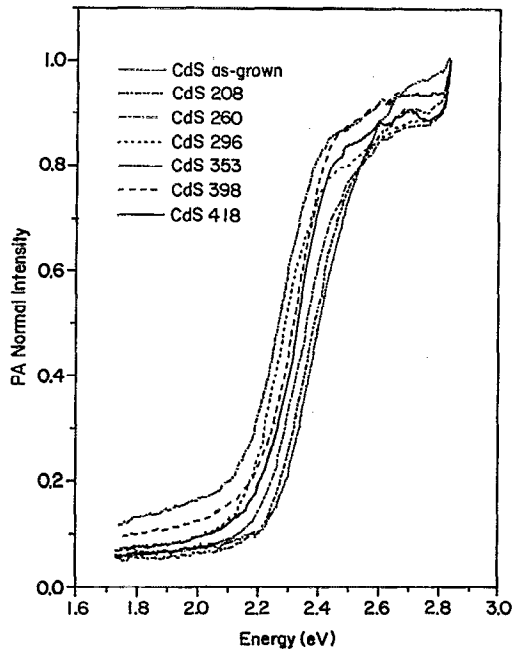


FIG. 1. PA normal intensity as a function of energy for CdS films annealed in Ar+S₂ atmosphere for different TTA.

toacoustic cell. The photoacoustic signal was preamplified and, subsequently, sent to a lock-in amplifier.

Resistivity measurements were performed at room temperature by the two probe method for high resistivity films and the four probe method for low resistivity films. The four probe technique was not satisfactory for high resistivity films because the order of magnitude of the film resistance and the electrometer input impedance was the same. Ohmic contacts were evaporated on the film surface in order to measure the lateral resistivity.

III. RESULTS AND DISCUSSION

In Fig. 1, we show the photoacoustic (PA) spectra for the as-grown CdS sample and the set of CdS films annealed in the Ar+S₂ atmosphere. We assume that the band-gap energy is given by the inflexion point in the spectrum. The values of the band-gap energy (BGE) for samples annealed in the Ar and Ar+S₂ atmospheres are displayed in Table I. The results

TABLE I. Values of the band-gap energy E_g and band-gap shift ΔE_g as a function of temperature of thermal annealing for Ar and Ar+S₂ annealings.

TTA (°C)	Ar		Ar+S ₂	
	E_g (eV)	ΔE_g (eV)	E_g (eV)	ΔE_g (eV)
80 (as-grown)	2.42	...	2.42	...
208	2.40	0.02	2.40	0.02
260	2.36	0.06	2.37	0.05
296	2.35	0.07	2.29	0.13
353	2.30	0.12	2.28	0.14
398	2.29	0.13	2.33	0.09
418			2.34	0.08
447	2.31	0.11		

TABLE II. Values of the band-gap energy E_g and band-gap shift ΔE_g as a function of temperature of thermal annealing for H₂, H₂+In, and air annealings.

TTA (°C)	H ₂		H ₂ +In		Air	
	E_g (eV)	ΔE_g (eV)	E_g (eV)	ΔE_g (eV)	E_g (eV)	ΔE_g (eV)
80 (as-grown)	2.42	...	2.42	...	2.42	...
200	2.40	0.02	2.40	0.02	2.37	0.05
250	2.39	0.03	2.37	0.05	2.34	0.08
300	2.37	0.05	2.34	0.08	2.27	0.15
350	2.31	0.11	2.28	0.14	2.25	0.17
400	2.27	0.15	2.27	0.15	2.26	0.16
450	2.27	0.15	2.28	0.14	2.26	0.16

for samples annealed in the H₂, H₂+In, and air atmospheres are given in Table II.

In Fig. 2, we show the BGE as a function of TTA for the samples annealed in the Ar+S₂ atmosphere. Note that the BGE decreases as the TTA increases for the temperature range 80–350 °C. At roughly 350 °C, we find that the BGE reaches a minimum. This effect carries down the BGE from its 2.42 eV initial value to 2.28 eV. For temperatures above 350 °C, the BGE increases up to 2.35 eV at 418 °C. This narrowing-widening-like behavior presented by CBD-CdS films annealed in an Ar+S₂ atmosphere has been attributed to the transition from the cubic to the hexagonal phase, which is assumed to occur at the temperature corresponding to the minimum BGE.⁹ TTA coefficients of the BGE have been found to have values of approximately 10⁻⁴ eV/TTA (K) in the linear region of the data.¹⁴ The magnitude of these coefficients generally agree with those reported for other materials, e.g., Si, Ge, GaAs, and MgI₂.^{14,15}

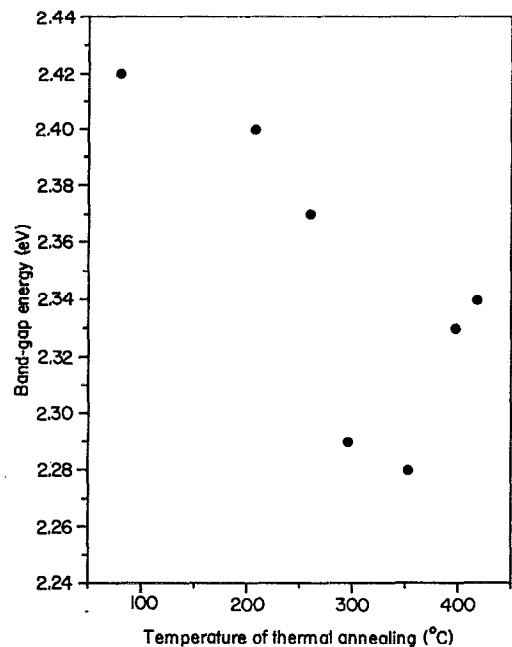


FIG. 2. TTA dependence of band-gap energy for CdS annealed in Ar+S₂ atmosphere.

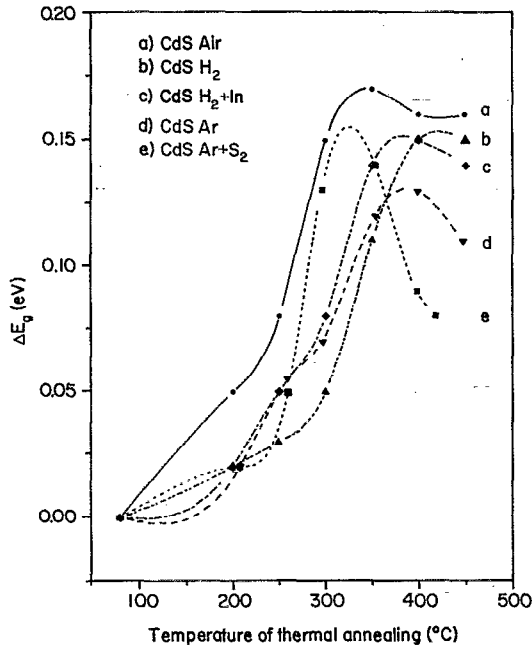


FIG. 3. TTA dependence of band-gap shift for CdS annealed in different atmospheres.

With respect to the other annealing atmospheres, we found that samples display only a narrowing-like behavior (see Tables I and II). For some of these annealings, the decrease in the BGE is faster or slower and the samples reach a higher or lower minimum value than when exposed to Ar+S₂. However, it is very important to point out that none of the atmospheres produce a clear widening-like behavior as Ar+S₂ does. On the contrary, all of them cause a stable tendency above the temperature corresponding to the minimum BGE. These results are shown in Fig. 3, where the BGS, given by

$$\Delta E_g(\text{TTA}) = E_g(80^\circ\text{C}) - E_g(\text{TTA}), \quad (1)$$

is plotted as a function of TTA. Here, $E_g(80^\circ\text{C})$ is the band-gap energy of the as-grown samples. Notice that, among the investigated annealing procedures, air produces the highest ΔE_g values. Its maximum value $\Delta E_g = 0.17$ eV occurs at approximately 350 °C. Also, note that only the Ar+S₂ annealing produces a considerable diminution of the BGS, ΔE_g , after having reached the maximum value.

In view of our interest in finding the thermal process that produces CBD-CdS films with the best combination of high band-gap energy and low resistivity, let us turn our attention to the electrical resistivity as a function of TTA. We describe only the typical behavior displayed by the samples because all of the annealing atmospheres have produced similar effects in them. The resistivity of as-grown samples measured $\rho = 2.3 \times 10^7 \Omega \text{ cm}$. For the annealed samples, the increase in the TTA caused a decrease in the resistivity until it reached a minimum value (as we can see in Table III, this minimum value becomes nine orders of magnitude smaller for H₂+In samples than for as-grown samples). For temperatures above

TABLE III. Minimum resistivity and corresponding E_g as a function of temperature for thermal annealing in different atmospheres.

Annealing	Minimum ρ ($\Omega \text{ cm}$)	E_g (eV)	TTA (°C)
Air	1.0×10^3	2.27	300
Ar+S ₂	1.9×10^3	2.29	296
Ar	2.5×10^2	2.30	353
H ₂	0.15	2.37	300
H ₂ +In	0.05	2.37	250

this region, the resistivity increased again. As shown in Table III, $\rho(\text{TTA})$ assumes a minimum value dependent on the annealing atmosphere.

The Ar+S₂ annealing diminishes the resistivity by increasing the grain size, therefore the number of grain boundaries decreased in the films. On the other hand, the Ar annealing increases the grain size and produces a large amount of sulfur vacancies as a consequence of the nonequilibrium conditions. In the air annealing, the presence of oxygen creates both CdO and CdSO₄ layers on the surface, increasing slightly the resistivity of the films compared to the Ar case.¹⁶ The thermal treatments in H₂ and H₂+In have the advantage of containing H₂, which is a strong agent for grain boundary passivation by oxygen chemisorption.^{17,18} The presence of H₂ causes the resistivity to decrease by 4 and 5 orders of magnitude, respectively, compared to the Ar+S₂ case.

In order to simultaneously consider the band-gap energy and the resistivity, we define

$$\xi(\text{TTA}) = \frac{\Delta\rho(\text{TTA})}{\Delta E_g(\text{TTA})} = \frac{\rho(80^\circ\text{C}) - \rho(\text{TTA})}{E_g(80^\circ\text{C}) - E_g(\text{TTA})}. \quad (2)$$

Since $E_g(80^\circ\text{C})$ is larger than $E_g(\text{TTA})$, a large band-gap energy $E_g(\text{TTA})$ is equivalent to a small value for $\Delta E_g(\text{TTA})$. Similarly, a low resistivity $\rho(\text{TTA})$ implies a high value for $\Delta\rho(\text{TTA})$. It follows from Eq. (2) that the higher the value of $\xi(\text{TTA})$, the better the combination of high $E_g(\text{TTA})$ and low $\rho(\text{TTA})$. Accordingly, $\xi(\text{TTA})$ characterizes the annealed samples and allows us to identify both the atmosphere and the TTA that produce optimum conditions of high band-gap energy and low resistivity. We should observe that $\xi(\text{TTA})$ is basically governed by $\Delta\rho(\text{TTA})$ [because of its high values compared to the values of $\Delta E_g(\text{TTA})$]. This gives us insight into the TTA that should be investigated first, namely, those which produce high $\Delta\rho(\text{TTA})$ values in the samples.

We have calculated $\xi(\text{TTA})$ for all of the annealing atmospheres. With the highest values, shown in Table IV, we

TABLE IV. Maximum value of $\xi(\text{TTA})$ in different annealing atmospheres.

Annealing	Highest ξ ($10^8 \Omega \text{ cm/eV}$)	TTA (°C)
Air	1.53	300
Ar+S ₂	1.76	296
Ar	2.09	447
H ₂	4.59	300
H ₂ +In	4.60	250

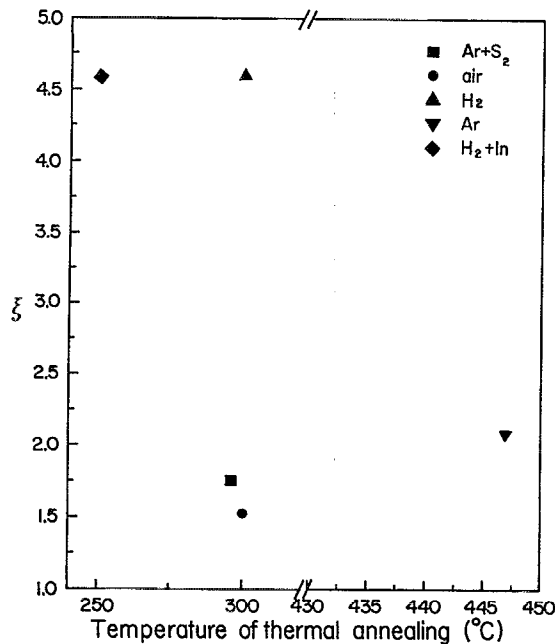


FIG. 4. Maximum value of ξ (TTA) for different annealing atmospheres.

found the figure of merit illustrated in Fig. 4. This figure shows that, among the analyzed annealings, the H₂ and H₂+In atmospheres produce the best combination of low resistivity and high band-gap energy. In particular, the H₂+In annealing is slightly better than the H₂ annealing. Its maximum value for $\xi=4.6 \times 10^6 \Omega \text{ cm/eV}$ occurs at 250 °C. The measured resistivity for this sample was $\rho=5 \times 10^{-2} \Omega \text{ cm}$. A similar value has been reported¹⁹ for a CdS crystal grown by the melt, using the Tamman method in Ar gas at around 110 atm of pressure. Moreover, for the Ar+S₂ atmosphere, the minimum resistivity is $\rho=1.9 \times 10^3 \Omega \text{ cm}$. This resistivity is roughly reproduced ($2.3 \times 10^3 \Omega \text{ cm}$) for a normal CdS crystal only at 4.2 K.¹⁹

X-ray diffraction patterns show that all the annealed samples present a slight interplanar-distance increase compared to the as-grown samples, but only the samples exposed to the Ar and Ar+S₂ annealings undergo a cubic to hexagonal phase transition. On the other hand, the samples annealed in the H₂, H₂+In and air atmospheres preserve the same structural phase along the complete thermal process.¹⁷ The mechanism that explains this microstructural behavior is under study at present.

Photoluminescence (PL) spectra of CdS samples an-

nealed in Ar and Ar+S₂ atmospheres present a shift of the luminescent peaks as a function of TTA. This shift has been interpreted as an evidence of evolution from S₂ vacancies to interstitial S₂ formation.¹⁷ For these annealing atmospheres, interstitial S₂ becomes part of the hexagonal structure itself. Thus far, PL spectra of CBD-CdS samples annealed in H₂, H₂+In, and air atmospheres have not been obtained.

In summary, we have found that CBD-CdS thin films display low resistivity and high band-gap energy when exposed to an H₂+In annealing atmosphere at 250 °C. CdS films with these characteristics play an important role because they are used in the development of low resistivity CdS/CdTe solar cells with high quantum efficiency. Thus, they are real candidates for high conversion-efficiency solar cells.

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