

Cd(S_(1-x) + CO_{3(x)}) thin films by chemical synthesis

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A microcrystalline mixture of cadmium carbonate (CdCO₃) and cadmium sulfide (CdS) were grown in the thin film format onto glass substrates by means of chemical bath. The temperature of the bath (T_d) was selected in the interval 23–80°C. At low temperatures, CdCO₃ is the compound predominant in the layers. At high temperatures CdS is the compound deposited on the substrate. At intermediate T_d -values a mixture of both materials are present, i.e., the gradual transition from an insulator (CdCO₃) to a semiconductor (CdS) growth occurs when T_d increases. Physical properties of films were studied by means of X-ray diffraction and optical absorption. The forbidden energy band gap of direct electronic transitions (E_g) was calculated by applying the $\alpha^2 \propto (h\nu - E_g)$ relation to the optical absorption spectra. © 2005 Springer Science + Business Media, Inc.

1. Introduction

In the preparation of CdS or Cu(In,Ga)Se₂ thin films by chemical bath (CB), cadmium carbonate (CdCO₃: Otavite) is introduced as impurity into the semiconductor materials [1, 2], however this oxide is present alike a stable precipitate [2] until temperatures $\geq 300^\circ\text{C}$ [3]. As far as we know, CdCO₃ has not been reported to be prepared in the thin film format. The physical properties of this oxide have been scarcely studied and, to a lesser degree, mixed with a semiconductor. The material can be useful in applications such as insulator, composite, electrode, sensor, microcapsule, among other devices. Some physical properties of CdCO₃, reported by other authors, are birefringence [4], lattice energy [5], entropy [6], phase transformations [3, 7], (Cd_{1-x}Ca_x)CO₃ solid solutions [8, 9], etc. On the other hand, physical properties and applications of CdS have been widely studied and until now abundant work on them continues being reported. This work has been focused to analyze the gradual pass from CdS (semiconductor) to CdCO₃ (insulator) when the films are grown by the chemical bath (CB) technique, and the temperature of the bath (T_d) is chosen between 80 and 23°C. X-ray diffraction patterns show the thin films evolution from cubic (zincblende) CdS for $T_d = 80^\circ\text{C}$, to hexagonal (rhombohedral) CdCO₃ for $T_d = 23^\circ\text{C}$, with mixed crystalline structures at intermediate T_d values. Fur-

thermore, optical absorption allows to observe how the energy band gap (E_g) of layers changes from 2.41 eV for CdS to 3.87 eV for CdCO₃. As both chemical compounds seem do not form solid solutions between them, the study of embedded CdS particles into the transparent CdCO₃ material looks as an interesting subject for research. It is important to remark that nanocapsules of CdCO₃ are valuable for applications related to drug delivery, functional properties of adsorption of proteins and other biologically relevant molecules. These nanocapsules have been prepared by layer-by-layer deposition of alternative charged pyroelectrolytes [10]. In this way, CB could represent a simpler alternative to grow the CdCO₃-nanocapsules.

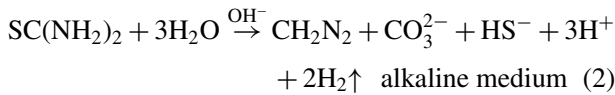
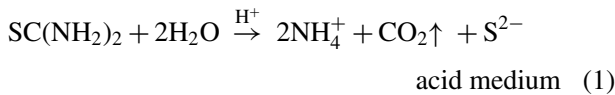
2. Experimental

The substrates used were commercial glass slides, which were subjected to a strong-clean process. For CB growth aqueous solutions of CdCl₂ (0.02 M), KOH (0.5 M), NH₄NO₃ (1.5 M), and SC(NH₂)₂ (0.2 M) were prepared using deionized water. These solutions have been usually employed by us to grow CdS films on glass substrates [11, 12]. After deposition the layer were rinsed in deionized water and dried at $\sim 50^\circ\text{C}$. The relative concentrations, volume proportions, deposition temperature, and pH (≈ 8.3) were kept constant during

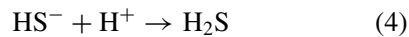
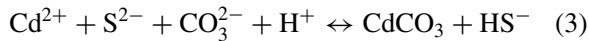
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all the growth processes. Different growing temperatures were chosen in the interval 23–80°C, and each T_d was controlled within $\pm 1^\circ\text{C}$. T_d -values used were 23, 40, 50, 60, 70, and 80°C. X-ray diffraction (XRD) patterns of samples were registered using the $\text{Cu K}\alpha$ line of a D5000 Siemens diffractometer. Optical absorption spectra measurements, carried out in the range 1.4–4.2 eV of photon energy, were obtained by means of a Unicam 8700 spectrophotometer. Measurements of stoichiometry, within an error bar of $\pm 1\%$, were achieved utilizing a Voyager II X-ray quantitative microanalysis in an 1100/1110 EDX system from Noran Instruments, which was employed to record scanning electron microscopy (SEM) images of the CdCO_3 microcrystals. All the characterization analyses were carried out at room temperature (RT).

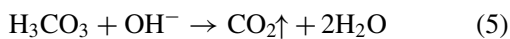
The chemical reactions and growth conditions for the CdS layers deposition by CB have been widely studied and reported. Nevertheless, the growth conditions for CdCO_3 thin films have still not been reported. In this way the chemical reactions (at RT) are:



The CO_3^{2-} ion arises in an alkaline medium because the thiourea decomposes according to reaction 2. This ion is soluble at temperatures lower than 75°C [13]. Then, if the temperature decreases, the CdCO_3 proportion increases [13]. This behavior indicates that the CO_3^{2-} ion, in an alkaline environment, gradually substitutes the S^{2-} ion. Shortly, the equilibrium reactions present for $T \leq 70^\circ\text{C}$ are:



In the temperature range 75–23°C, the reactions 3 and 4 are favored toward the right side, because the CO_3^{2-} is more soluble and, therefore, more reactive than the S^{2-} ion in that interval of temperatures. The ion S^{2-} is lesser reactive as the temperature decreases. On the other hand, when the solution containing the CO_3^{2-} ion is heated to 80°C gives place to the spontaneous formation of CO_2 (gas), which leaves the solution according the following reaction:



3. Results and discussion

As-grown $\text{Cd}(\text{S}_{1-x}) + \text{CO}_{3(x)}$ samples are strongly attached to the substrate and hard to be scratched. The different parameters involved to grow thin films by any technique are determinant to change the physical properties of materials prepared. In the chemical bath (CB) method it is well known that by changing the way and rate of stirring, different crystalline structures of

TABLE I Growing temperature, color and concentrations of cadmium (Cd), sulfur (S), carbon (C), and oxygen (O), in atomic percent

Growing temperature ($^\circ\text{C}$)	Color	Concentration (%)			
		Cd	S	C	O
80	Yellow	49.0	51.0	–	–
70	Pale-yellow	28.2	18.4	35.4	18.0
60	Pale-yellow	24.5	17.6	39.6	18.3
50	Pale-yellow	24.8	14.6	34.3	26.4
40	Pale-yellow	19.4	3.7	35.8	40.1
23	Green-yellow	12.8	0.3	20.0	66.9

a same material can arise [14]. Other important growing parameter in CB, beside concentrations and type of substrate, is temperature, which has large influence in the sticking of material, composition, specularity, and color; e.g., CdS prepared at $T_d = 80^\circ\text{C}$ looks, at naked-eye, intense-yellow, but when $T_d = 70^\circ\text{C}$ the appearance is pale-yellow. In this work, when $T_d = 23^\circ\text{C}$ the color of the layers is green-yellowish. The stoichiometry of CdS grown at $T_d = 80^\circ\text{C}$ is Cd: $(51.0 \pm 1.0)\%$ and S: $(49.0 \pm 1.0)\%$. When T_d diminishes from 80 to 23°C these values diminish and carbon (C) and oxygen (O) start to increase their presence up to that S practically vanishes at $T_d = 23^\circ\text{C}$. See experimental section for the processes of reaction involved in the CdCO_3 formation. In Table I are listed the color and composition of the samples studied.

XRD patterns are illustrated in Fig. 1 for each T_d -value. The sample with $T_d = 80^\circ\text{C}$ is CdS in cubic zincblende (ZB) phase with an XRD maximum peak located at $2\theta = 26.5^\circ$ (100% intensity in XRD of cubic CdS). For $T_d = 70^\circ\text{C}$, the XRD maximum peak is also located at $2\theta = 26.5^\circ$, however, other small XRD lines begin to appear at $2\theta = 23.5^\circ$ and 30.3° . This last line corresponds to line with 100% intensity of XRD- CdCO_3 . The experimental result indicates that already for $T_d = 70^\circ\text{C}$, an important contribution of CdCO_3 is present into the CdS layers. As T_d goes down, the crystalline structure of layers gradually shows a larger contribution of XRD- CdCO_3 peaks, with the respective diminution in the intensity of the XRD-CdS lines. For $T_d \leq 40^\circ\text{C}$, the intensity of the main XRD-CdS peak is abruptly reduced. The critical point of the growth, i.e., that on which CdS and CdCO_3 are at the same proportions, was not clearly defined here and it will be subject

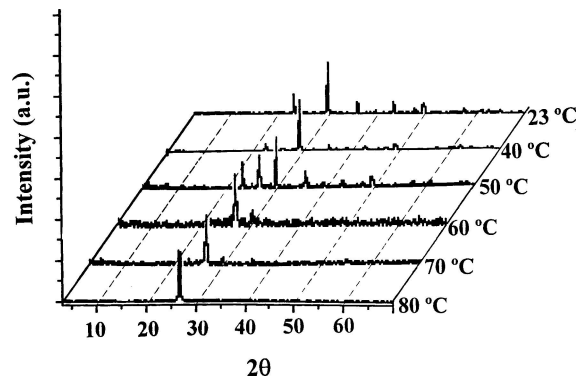


Figure 1 X-ray diffraction patterns of CdS- CdCO_3 layers, for different deposition temperatures.

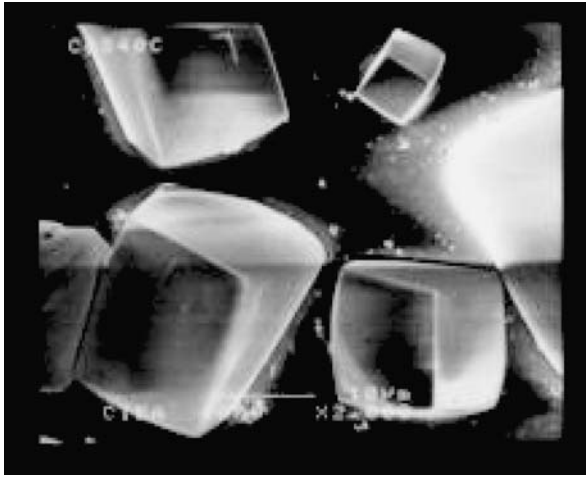


Figure 2 SEM picture of the CdCO₃ microcrystals. The bar depicted in the bottom of the picture represents 10 μm.

of a future work. For $T_d = 23^\circ\text{C}$, the XRD peaks at $2\theta = \{23.5, 30.3, 36.4, 43.8\}$ have been identified with CdCO₃ which has rhombohedral crystalline structure [15]. This rhombohedral phase of CdCO₃ has the same aspect of the rhombohedral phase of calcite (CaCO₃), i.e., SEM images of both types of microcrystalline materials show similar structures (they look cubic at first glance). See Fig. 2 for CdCO₃. The reader can check Ref. 16 for CaCO₃. Actually, (Cd_{1-x}Ca_x)CO₃ solid solutions have the same rhombohedral crystalline structure in the entire range $0 \leq x \leq 1$ (the otavite-calcite series). The transition from the CdS-semiconductor to CdCO₃-oxide observed by the XRD analysis when T_d decreases is, in some way, supported by measurements of atomic compositions (See Table I).

Optical absorption spectra allow to calculate E_g for all the films studied. The relation for semiconductors of direct band gap employed [17] is $\alpha^2 = (\text{cte})(h\nu - E_g)$, where α is the optical absorption coefficient and $h\nu$ the photon energy. In Table II are compiled the values of E_g calculated for all the samples analyzed. Fig. 3a exhibits the α^2 versus $h\nu$ plot for the CdCO₃ film. The extrapolation of the linear part of the curve intercepts the $h\nu$ -axis at 3.87 eV, which equals E_g of CdCO₃. In the inset of Fig. 3a, the same procedure is illustrated for the E_g value of CdS, which is in agreement with the reported value (2.42 eV) for cubic CdS at RT [11]. In Fig. 3b is displayed the calculation of E_g for the sample grown with $T_d = 50^\circ\text{C}$. In the inset of Fig. 3b, the obtaining of E_g for $T_d = 40^\circ\text{C}$ is included. The region where the curve is a straight line and its extrapolation until the energy axis for the determination of E_g in the stoichio-

TABLE II Temperature of deposition and forbidden energy band gap (E_g) of layers

Growing temperature ($^\circ\text{C}$)	E_g (eV)
80	2.41
70	2.50
60	2.50
50	2.47–3.60
40	2.42–3.63
23	3.87

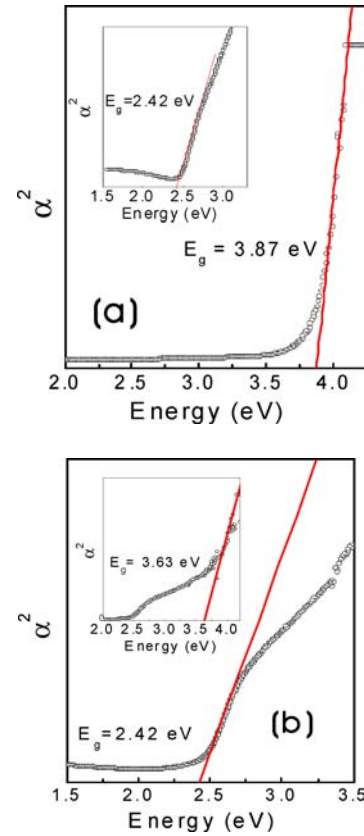


Figure 3 (a) α^2 versus $h\nu$ plot for $T_d = 23^\circ\text{C}$. The material deposited has been identified as CdCO₃ with $E_g = 3.87$ eV. The inset exhibits the same type of plot for CdS ($T_d = 80^\circ\text{C}$) with $E_g = 2.42$ eV. (b) α^2 versus $h\nu$ plot for $T_d = 50^\circ\text{C}$. The material is a mixture of CdS and CdCO₃. The inset displays the same type of plot for $T_d = 40^\circ\text{C}$. In these case two values of E_g are obtained.

metric films of CdCO₃ and CdS, shown in Fig. 3a and in its inset, respectively, are clearly defined. However for samples with $T_d = 40$ and 50°C , whose fitting for E_g determination are depicted in Fig. 3b, the linear region for extrapolation is not unique as in Fig. 3a. According with the inset of this figure, at $T_d = 40^\circ\text{C}$, for instance, two linear parts can be extrapolated and two values of direct E_g are defined. All this behavior is an indication that for $T_d \leq 50^\circ\text{C}$, both materials are segregated one from the another one. Each crystalline phase can include some small density of impurities taken from the aqueous ambient, as it can be deduced from the variation of the corresponding E_g values, when T_d is different from 80 or 23°C . In Table II, for $T_d = 40$ and 50°C , two values of E_g are listed.

4. Conclusions

Supported by our experimental results, we can ensure that the growth of thin films from a semiconductor material (CdS) to a dielectric one (CdCO₃) has been obtained. The band gap of this oxide is direct and has a value of $E_g = 3.87$ eV. For low CdCO₃ concentrations, CdS films show an increase of the band gap energy. CdCO₃, which is useful for many applications, become interesting because the physical properties in the form of thin film, also to study the properties of nanocrystals of CdS embedded inside of the volume.

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