# Chemical bath deposited CdS films using magnetic treated solutions

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CdS thin films were obtained by chemical bath deposition onto corning glass slides using precursor solutions previously treated in a steady magnetic field. The kinetic growth was affected in dependence of the magnetic field intensity used in the solution treatments. The growth rate is slower when magnetized solutions are used; however, the reaction exhaustion is more delayed. The magnetic treatments improve the conversion of starting materials in thin films. Thus, the bath is more efficient and thicker films can be obtained.

## 1 Introduction

Chemical Bath Deposition (CBD) has been widely used, mainly by the low-cost and reproducibility, to grow thin films of a variety of compounds of technological interest. Particularly, CdS films growth by CBD are of special interest because of its wide range of applicability in solar cells, sensors, and other optoelectronic devices. Indeed, the more efficient CdTe/CdS solar cell is based on CdS films grown by CBD [1].

In CBD, the extent of the reaction on the substrate surface is limited by two major factors, the competing reaction in solution (which results in massive precipitation in solution) and deposition of material on the CBD reactor walls. Mostly, a chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. Thicker films can be obtained by successive growths in baths with fresh solutions. However, this procedure leads to films with several problems of homogeneity, due to the growth interruptions.

Several modifications to the CBD have been developed to overcome the inefficiency of the process, in terms of improve the conversion of starting materials in thin films. There are, deposition bath equipped with filtration and re-circulation systems [2]. Moreover, the influence on the film properties by the application of radiations [3], electric [4] and magnetic [5] fields during the growth has been recently reported. However, to the best of our knowledge, there is no information on the treatment of the precursor solutions with magnetic fields before the growth of CBD CdS.

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Barrett et al. [6] assessed the effects of magnetic treatment on calcium carbonate precipitate. They found that magnetic field used to treat the solutions retards nucleation rate and promotes existing crystal growth. The solutions maintained the effect of the magnetic treatment later of 60 hours. Madsen et al. [7, 8] have explained the influence of the field in the crystallization from the solutions assuming that the transfer of a proton takes place from the salt precursor to the water. However, in a relatively recent laboratory study it has been demonstrated that there is an effect only on diamagnetic salts of sufficiently weak acids. The aim of this work is to study the influence of the magnetic pre-treatment of the precursor solutions in the growth of CBD CdS.

## 2    Experimental details

Corning glass slides were used as substrates. Before the growth, these slides were washed with neutral detergent, rinsed with deionised water, and degreased successively in hexane, acetone and 2-propanol. The CdS thin films were deposited from $CdCl_2$, KOH, $NH_4NO_3$ and $CS(NH_2)_2$ solutions, which were magnetized separately in a Helmholtz coil. Static magnetic fields of 80, 110 and 140 G were applied for 40 min. The mixture of $CdCl_2$ + KOH + $NH_4NO_3$ solutions were put in the bath at 65 °C for the film growth. The substrates were introduced five minutes later and the thiourea solution was added when the solution mixture reached the thermal equilibrium with the bath. From this moment, the substrates were taken out at different times. At the same conditions, common CdS films were growth using non magnetic treated solutions. The grown films were extracted of the bath for times from 10 up to 360 minutes.

The CdS thin films were characterized by optical transmittance in a Lambda 40 UV-Vis Perkin Elmer spectrometer. The crystalline structure of the films was studied by X-ray diffraction in a Siemens D5000 diffractometer in the Bragg-Brentano geometry with Ni-filtered CuKa radiation.

## 3    Results and discussions

### 3.1    X-ray diffraction

Pale yellow, adherent and uniform CdS films were obtained. Figure 1 show a characteristic X-ray diffraction pattern of the samples. All the patterns have certain features in common: a main peak near 26.6° and two peaks of roughly equal intensity around 44.1° and 52.2°. Because the relative intensities of the diffraction peaks are incorrect with respect to reference and some major peaks are absent (hexagonal 102 peak near 36.5° and cubic 200 peak at about 31°), the texture and structure of the films are ambiguous. These patterns are often attributed to a polytype structure [9]. However, since the main peak does not have apparent structure (such as shoulders) in any sample, we consider that a cubic character is more accentuated.
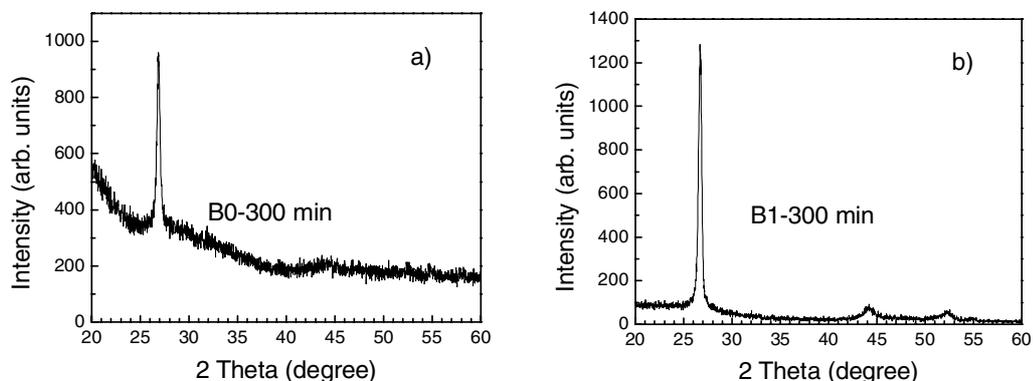


**Fig. 1**    X-ray diffraction pattern of CdS samples with 300 min, a) 0 G and b) 80 G.
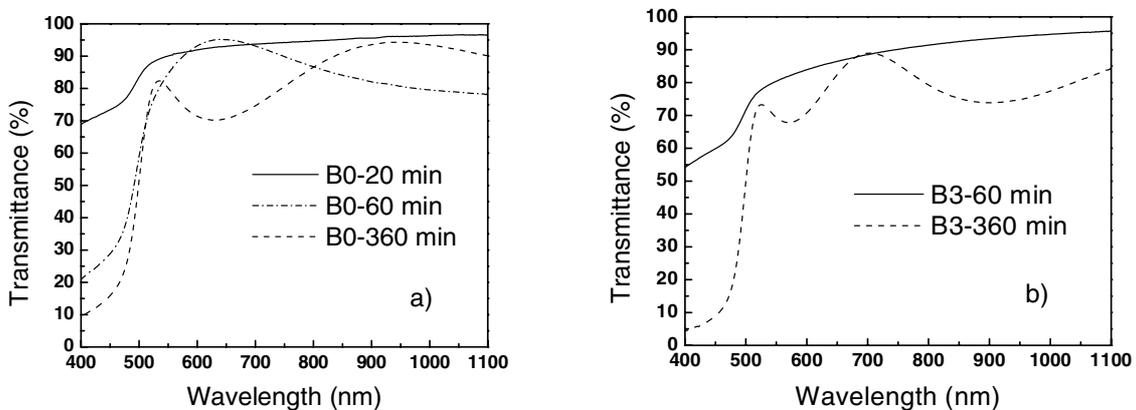
**Fig. 2** Transmittance changes in regard to the magnetic field strength. a) Precursors solutions without trying in the magnetic field, b) precursors solutions tried in a magnetic field of 140 G. The film grown during 20 minutes with solutions tried in the magnetic field of 140 G it was so thin that the thickness could not be determined.

### 3.2 Spectra simulation by dielectric modelling

In Fig. 2 are shown the transmittance spectra of the CdS thin films for different magnetic field strength: B0 – without field, B1 – 80 G, B2 – 110 G, B3 – 140 G and growth time in minutes.

The optical transmittance spectra were fitted with a computer model based on dielectric modeling [10] in order to calculate the thickness.

The optical properties of CdS thin films in the spectral range of interest, 400–1100 nm, were fitted by three types of electronic excitations: band gap transitions, interband transitions from the bulk of the valence band into the bulk of the conduction band, and intraband transitions of the electrons in the conduction band. These transitions were modelled with standard formulae available in the SCOUT 98 program. For the band gap transitions, we used the Tauc-Lorentz model [11] that has been proposed to model the band gap. The interband transitions into the upper half of the conduction band are represented by a harmonic oscillator. The Drude Model was used to calculate the contribution of free electrons to the susceptibility. All procedure used in the fitting are implemented in the SCOUT 98 program. The experimental data were fitted with a standard deviation better than 0.2.

In Fig. 3 are shown the values of the thickness calculated for by dielectric modelling method for samples growth at different times and magnetic field intensities. The solid lines are the bets fitting to the experimental data using Eq. (1):

$$d = d_\infty [1 - \exp(-t/t_c)][1 - \exp\{-k(t - t_c)\}]. \tag{1}$$
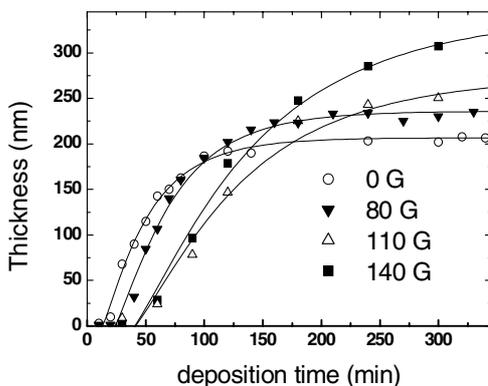


**Fig. 3** Samples thickness in function of the growth time and the magnetic field strength.
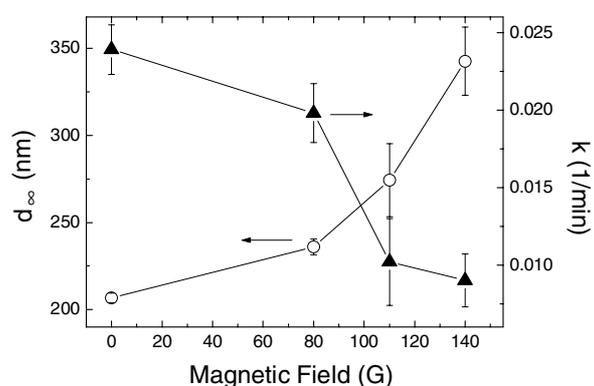


**Fig. 4** Influence of the field strength in the taking value of the constants used in the thickness fitting.

**Table 1**  Value of the constants used in the thickness fitting.

| $B$ (G) | $d_\infty$ (nm) | $k$ (1/min) | $t_c$ (min) |
|---|---|---|---|
| 0 | $207 \pm 3$ | $0.024 \pm 0.002$ | $13 \pm 1$ |
| 80 | $236 \pm 5$ | $0.020 \pm 0.002$ | $24 \pm 2$ |
| 110 | $274 \pm 21$ | $0.010 \pm 0.003$ | $41 \pm 7$ |
| 140 | $343 \pm 20$ | $0.009 \pm 0.002$ | $41 \pm 5$ |

In Eq. (1) the fitting parameters ar: $d_\infty$ (film thickness when the reaction is exhausted); $t_c$ (induction time, required time for the formation of a necessary catalytic surface); $k$ (velocity constant of the chemical reaction into the bath).

The first exponential term of Eq. (1) is related to the induction time for the nuclei formation on the substrate surface, whereas the second exponential term is related with the variation of the growth rate. It is easy to observe from the data fittings that the saturated thickness and the induction time increase with the strength of the magnetic field used in the precursor solutions treatment. However, the reaction velocity has an inverse behaviour; it decreases with the magnetic field strength. Due to this there is not film deposition at the initial times of growth when the strength of the field increases.

## 4    Conclusions

The magnetic treatment of the precursor solutions does not seem to have influence the crystalline phase of the CdS thin films. The results obtained indicate that the magnetic treatment of the precursor solutions before the growth of CdS thin films by CBD affect the growing process. The growth rate of the films is slower when magnetized precursor solutions are used; however, the reaction exhaustion is more delayed. In addition, the formation of nucleation centers on the substrate surface and clusters in the bulk of growth solution are modified. The inhibition of clusters formation into the bath enables that the reaction exhaustion is more delayed. Thus, thicker films can be grown using the same amount of precursor solutions. Our results are in good agreement with the results obtained by Barrett [6]; the action of the magnetic field retards nucleation rate and promotes existing crystal growth.

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