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# AFM, XPS and RBS studies of the growth process of CdS thin films on ITO/glass substrates deposited using an ammonia-free chemical process

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### ARTICLE INFO

Article history: Received 21 August 2009 Received in revised form 3 February 2010 Accepted 4 February 2010 Available online 13 February 2010

Keywords: Chemical bath deposition Ammonia-free Cadmium sulphide Cadmium hydroxide X-ray photoelectron spectroscopy Semiconductor thin films

## ABSTRACT

This paper deals with a detailed study of the growth stages of CdS thin films on ITO/glass substrates by chemical bath deposition (CBD). The chemical and morphological characterization was done through X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and atomic force microscopy (AFM) techniques. On the other hand, optical transmission and X-ray diffraction (XRD) measurements were performed in order to study the optical and structural properties of the films. The time, the chemistry, and morphology of the different stages that form the growth process by CBD were identified through these results. Furthermore, clear evidence was obtained of the formation of Cd(OH)<sub>2</sub> as the first chemical species adhered to the substrate surface which forms the first nucleation centers for a good CdS formation and growth. On the other hand, the ITO coating caused growth stages to occur earlier than in just glass substrates, with which we can obtain a determined thickness in a shorter deposition time. We were able to prove that CBD is a good technique for the manufacture of thin films of semiconductor materials, since the CdS film does not have any impurities. Completely formed films were transparent, uniform, with good adherence to the substrate, of a polycrystalline nature with a hexagonal structure. These results indicate that films obtained by CBD are good candidates to be applied in different optoelectronic devices.

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# 1. Introduction

There is a wide variety of deposition methods that enable the synthesis of semiconductor thin films. Chemical bath deposition (CBD) has been recognized as an important route for the manufacture of these materials, since it is a fast, simple and low cost method that enables to obtain good quality films that can compete with films obtained by other more sophisticated methods. Currently, there are many semiconductor materials that can be deposited by CBD [1–4]. Cadmium sulphide (CdS) is one of them, which has shown great potential in the manufacture of different devices such as photovoltaic panels, optical sensors, light-emitting diodes, transistors, among others [5,6].

When it is stated that CBD is a simple and low cost method, this essentially refers to the fact that it does not required high purity raw materials and the equipment where the synthesis of the films takes place is very simple. For example, the reactor can be a glass beaker and the substrates can be any shape, size or material, provided the latter is insoluble in water, because of the deposition process takes place in an aqueous solution. The reaction occurs in the range of temperature from 10 to 90 °C. Nevertheless, the deposition of thin films by CBD is a process rather complex due to the series of chemical reactions, precipitation phenomena and surface chemistry in the reaction system.

The reaction solution for the synthesis of thin films of CdS, which is where the substrates will be immersed, is prepared by mixing aqueous solutions of the precursors. Thiourea, thiocetamide, sodium thiosulphate and sodium sulphide are the sources of sulphide ion. The sources of the cadmium ion are its water-soluble salts. Before adding the anion source, it is required for the cadmium ion to form complexes with the present ligand which, under the reaction conditions, are able to hydrolyze with the slow and gradual release of the cation. The sources of these ligands are ammonia solutions (the most used), sodium tartrate, sodium citrate, ethylenediamine, nitrilotriacetic acid [7–10], among others.

Quality control of the film thickness and the gradual precipitation process, by manipulating the pH of the solution, the temperature, the time and the concentration of the reactants, for instance, enable to cover large substrate areas by this deposition method, in addition to a good reproducibility of the films. In agreement with the principles of the precipitation theory, the homogeneity and stoichiometry of the reaction product is

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maintained in part, thanks to the solubility product  $(K_{sp})$ . The formation of the solid phase from the solution consists of at least three stages: nucleation, growth of the particle, and final growth. The nucleation is necessary for the formation of the precipitate on the substrate. Depending on the reaction conditions, the growth of the film may occur by condensation, called *ion-by-ion*, or by adsorption of colloidal particles, called *cluster-by-cluster*, or both, called *mixed* [11,12].

There is still too much to know about the way that the growth process occurs. Basically, we realize that the authors who have approached the subject show some differences about the kind of chemical species that determine the formation of the film on the substrate. Kitaev et al. and other authors [10-16] are in agreement about the necessary presence of cadmium hydroxide (Cd(OH)<sub>2</sub>), on which the CdS film grows and allows its adhesion to the substrate. Furthermore, there is a hypothesis that such Cd(OH)<sub>2</sub> layer is substituted by that of CdS once the thiourea hydrolyzes and the solution begins to have free sulphide ions. However, Kozhevnkova et al. [16], in a structural study by X-ray grazing incident diffraction of the early stage of CdS deposition, proved the presence of the Cd(OH)<sub>2</sub> layer after 3 min of reaction time. It is interesting that under different reaction conditions, results are similar to those we obtained, only that these were analyzed with other characterization techniques. Moreover, by studying the surface by AFM, we discovered that film growth occurs in a determined way, forming lines or bands. There are no indications thereof in any other paper that has been published to until now of our knowledge.

In this work, we studied the growth process of CdS thin films deposited on ITO/glass substrates from an ammonia-free reaction solution [4,17]. In order to know the growth process of CdS films, a study was conducted using atomic force microscopy, X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) of the surface of the films formed from very short periods of time until the time in which the film has reached all the features of CdS. The work was supplemented with the analysis of the structural properties through X-ray diffraction (XRD) and optical properties through transmission measurements (T).

## 2. Experimental details

CdS thin films were grown on glass substrates covered with 100 nm thick ITO ( $In_2O_3$ :Sn) coatings, with a sheet resistance of 50  $\Omega$ -square and a transmission of 90%. The substrates were

cleaned prior to deposition: initially they were immersed for 10 min in isopropanalol; thereafter, for 5 min in acetone; and lastly, for 10 min in distilled water. They were dried with hot air to eliminate any remaining humidity.

The reaction solution was formed by 12 ml of CdCl<sub>2</sub> (cadmium chloride) 0.05 M; 20 ml of  $C_6H_5O_7Na_3$  (sodium citrate) 0.5 M; 5 ml of KOH (potassium hydroxide) 0.5 M; 10 ml of CS(NH<sub>2</sub>)<sub>2</sub> (thiourea) 0.5 M; and 53 ml of distilled water. Each reagent was added sequentially and in that order into a 100 ml glass beaker. Samples were deposited at 70 °C without stirring. The substrates were immersed in the solution and with the aid of a holder, they were kept in a vertical position, at a distance of 2.5 mm from each other during the time of the deposition. Two series of 5 films each were deposited. The samples were withdrawn from the solution at different time periods: 15, 30, 60, 180, 240, 300, 360, 420, 720, 900 s.

Films were studied with different techniques. Optical properties were analyzed through transmission spectra on a Film Tek Trade Mark 3000 spectrophotometer at a 240 to 840 nm wavelength interval; structural properties, with a Rigaku D/Max-2000 X-ray diffractometer using K $\alpha$ -Cu ( $\lambda$  = 0.15406 nm) radiation; the surface morphology of the samples was studied with AFM using a Digital Instruments Dimension 3100 system. Film composition and distribution profiles were determined through RBS; measures were taken in a Pelletron accelerator. The samples were bombarded at a normal incidence with <sup>4</sup>He<sup>+2</sup> 2.0 MeV energy ions. Backscattering spectra were analyzed using the RUMP software [18]. On the other hand, XPS measurements were made on a VG-ESCALAB Surface Science Instrument using a monochromatic Mg (hv = 1253.6 eV) X-ray source. Spectra were obtained at a  $45^{\circ}$  angle with respect to the normal surface with a constant  $E_0 = 50 \text{ eV}$  energy step. The spectra deconvolution analysis was performed with SDPv4.1<sup>®</sup> software.

# 3. Results and discussion

To the naked eye, the presence of the film was undetected for very short periods of time, until 180 s, a pale yellow film can be appreciated. For the 300 s sample, a complete film can be observed which has the classical characteristics of CdS, that is, the film is bright yellow, uniform, and well-adhered to the substrate.

The morphology of CdS films was studied through AFM images, from the initial growth stages until a completely formed film was obtained [17]. The topography of the surface in two dimensions (2D) is shown for each image taken, with its corresponding *z*-axis at



Fig. 1. 2D topographical AFM images of the substrate (a) and the sample obtained at 180 s (b) in an area of 5  $\mu$ m  $\times$  5  $\mu$ m.



Fig. 2. 2D topographical AFM images of the sample obtained at 240 s in an area of  $50 \,\mu\text{m} \times 50 \,\mu\text{m}$  (a) and  $5 \,\mu\text{m} \times 5 \,\mu\text{m}$  (b).

the right side of the image. Fig. 1a shows the image obtained for the substrate surface; the ITO coating, in an area of  $5 \,\mu m \times 5 \,\mu m$ . The formation of a large number of particles, which form different-size "flakes" that are closely bound together can be seen, thus obtaining a homogeneous surface, a roughness average (RMS) of 2.7 nm being measured in this area.

Fig. 1b shows the sample deposited to 180 s. It can be seen the deposition of  $\sim$ 60 (±10) nm diameter particles that are homogeneously distributed on the "flakes", which cause the RMS to increase slightly to 3.1 nm, in the close-up of the area marked with a white box it can be seen more clearly. It is important to mention that a change in color occurs in the substrate surface as of this time; this can be due to the appearance of these particles on such substrate.

Fig. 2a shows the morphology of the sample obtained after 240 s in an area 50  $\mu$ m × 50  $\mu$ m. The growth of the material, which forms bands that run along the substrate, can be seen. These formations are in agreement with those reported by Mazón-Montijo et al. [4]. Fig. 2b corresponds to a close-up of the area pointed out in image (Fig. 2a), which provides a better image of the fact that the surface of the substrate still is not covered in full; the deposited particles continue growing forming bands without following the morphology of the ITO coating. It is interesting to note that according to previous work [4], the growth also occurs in a band-like manner. Considering this, it can be said that the ITO coating does not modify the morphology of the CdS. Nevertheless, this coating possibly stimulates a greater reactivity causing the earlier presence of growth stages in comparison to depositions on glass substrates. On the other hand, the RMS value obtained for this area increased, thus, obtaining a value of 8.19 nm which could have been due to the irregularities of islands formed on the substrate.

Fig. 3 shows the images obtained for the 300 s sample in two different scales. Image (Fig. 3a), taken in an area of  $5 \,\mu m \times 5 \,\mu m$ , shows how the substrate surface has been fully covered already. However, the contour of the "flakes" continues appearing slightly due to the very thin film at that time. Despite this, it is worthwhile mentioning that during this time of the deposition, the known yellow color of CdS will be visible to the naked eye. The average RMS for the image (Fig. 3a) was 3.6 nm, a lower value in comparison to the previous sample (Fig. 2b), since here the film already has been fully formed without there being any holes. Furthermore, the surface is formed by spherical-ellipsoidal particles, which can be seen better in (Fig. 3b) which shows the close-up of the compartment of (Fig. 3a), image which was taken in an area  $1 \,\mu m \times 1 \,\mu m$ . Particle size continues being around 60 nm.



Fig. 3. 2D topographical AFM images of the sample obtained at 300 s in an area 5  $\mu$ m  $\times$  5  $\mu$ m (a) and 1  $\mu$ m  $\times$  1  $\mu$ m (b).



Fig. 4. 2D topographical AFM images of the sample obtained at 720 s in an area  $500\,\mu m \times 500\,nm.$ 

For time periods above 300 s (figures not shown), sample thickness increases, this is visible to the naked eye due to the variation of the yellow color on the film. Particle shape is maintained and "flake" contour decreases until it disappears. Until that time of deposition, there is no cluster formation on the substrate; therefore, it could be stated that the *ion-by-ion* mechanism has prevailed. However, the following figure shows the image of the sample deposited at 720 s (Fig. 4); the measured area amounts to 500 nm  $\times$  500 nm. This image is very illustrative to observe the presence of clusters on the surface, that is, around this deposition time, the *cluster-by-cluster* mechanism prevails [17]. Thus, the formation of films occurs due to the combination of both mechanisms (*mixed* mechanism) [19].

Fig. 5 shows the optical spectrum of transmission for films deposited at different times. All films deposited up to 60 s present a transmission spectrum very similar to that of the substrate, that is, at this time there is no CdS formation on the substrate. For the samples that presented deposited material, a transmission percentage between 60% and 80% was observed; this value is a bit smaller than that of the substrate which had a transmission of about 90%. Once a time of 180 s was reached, a more noticeable transmission percent-



**Fig. 5.** Optical transmission spectra of the samples deposited at different times. The inset shows the  $(OD^*E)^2$  vs *E* spectra for films at 300, 360 and 720 s.



Fig. 6. X-ray diffraction patterns of the substrate and films obtained at 300, 360, and 720 s of deposition times.

age decrease can be observed, being more evident for the 240 and 300 s samples. In the corresponding graph at 360 s an absorption edge characteristic of CdS appears with a shift toward less energy for films with longer deposition times, as is shown in the figure. The inset shows the values of the band gap ( $E_g$ ) obtained for the 300, 360, and 720 s films. These values were determined from the transmission spectra of the respective samples, applying the model for direct transitions allowed between parabolic energy bands. The graph shows (OD\*E)<sup>2</sup> data against E, where OD is optical density and E is the energy of the photon. The value of  $E_g$  is obtained by extrapolating the straight portion of the line toward *x*-axis. The values obtained for CdS films are 2.38, 2.34 and 2.28 eV for 300, 360 and 720 s, respectively.

Fig. 6 shows the diffraction pattern of the substrate and of films obtained at 300, 360, and 720 s. Planes shown indicate the positions of the peaks for the substrate. As a result of increasing the thickness of the film, the peaks of the substrate begin to decrease in intensity, but do not disappear completely. The appearance of a small peak approximately at 26.0  $2\theta$  degrees is characteristic of the CdS diffraction pattern. For the 360 and 720 s films, the crystalline (hexagonal (H) or cubic (C)) phase of the deposited CdS cannot be defined, because some of the peaks that correspond to these phases overlap those of the substrate. Nevertheless, for the case of the 900 s sample (Fig. 7), the peak at 26.52  $2\theta$  degrees is more intense; furthermore other peaks occur at 25.2, 28.18, 37.6, 50.8, and 60.5  $2\theta$  degrees, all of them corresponding to planes (002), (100), (101), (102), (200), and (104), respectively, of phase H of the CdS [20]. As can be seen, the thickness of this sample is still not sufficient to eliminate



Fig. 7. X-ray diffraction pattern for the 900 s deposition film.



Fig. 8. RBS spectra corresponding to the substrate and the samples deposited at 180, 240, and 360 s.

the presence of the peaks of the substrate; however, the decrease of its intensity is evident (see Fig. 6). These diffraction patterns show that the films deposited in this work are of a polycrystalline nature, with hexagonal structure and preferential orientation in the (002) plane. It is important to mention that the use of a substrate with a crystalline structure, such as ITO, helped to improve the structural properties of the deposited material, because for only glass



**Fig. 9.** Typical RBS spectrum of the sample deposited at 360 s, together with a simulation of the film structure.

substrates, the peaks corresponding to CdS appeared less defined, with little intensity and it was more complicated to define the phase obtained for this deposit [4,17,19].

Fig. 8 shows the RBS spectra for the substrate and the 180, 240, and 360 s samples. Because the atomic mass of cadmium (Cd), indium (In) and tin (Sn) are very similar, it is difficult to observe the resolution of Cd for samples with less deposition time. In the case of times less than 180 s, the presence of sulphur (S) was not registered in the samples, which indicates that there is no CdS formation yet the substrate surface, such as was shown in previous analyses. Again, once the time of 180 s was reached, the appearance of a small S sign can be seen, as well as a small shift in the In and Sn signs, are indicative of the presence of a thin film on the substrate surface. Thus, we can state that the nucleation stage begins at



Fig. 10. XPS measurements of samples deposited at 60, 180, 240, 300, and 360 s. (a) Cd-3d region and (b) S-2p region.



Fig. 11. XPS measurements of samples deposited at 60, 180, 240, 300, and 360 s. (a) In-3d region and (b) Sn-3d region.

times shorter than 180 s. As the film thickness increases for times equal or grater than 240s, the Cd signal is clearly defined in the spectra. In the case of the 360s deposit, a film with a thickness of  $120 \times 10^{15} \pm 30 \times 10^{15}$  atoms/cm<sup>2</sup> can be found and considering a density of  $4.82 \text{ g/cm}^3$  (which is equal to  $4.02 \times 10^{22} \text{ atoms/cm}^3$ ) for CdS [21], a thickness of 29.8 (±7.5)nm is obtained. Hence, it was found that the thickness obtained for the films of equal or major thickness varies from 30 to 55 nm. Fig. 9 shows a typical RBS spectrum for the sample deposited at 360 s. The circles represent experimental data and the solid line, the best adjustment obtained through the RUMP software. In the case of the thicker films and wherever the Cd signal allowed it, the presence of two layers was observed in the deposition: first, an external layer formed by CdS on the surface with a 1:1 stoichiometry followed by a inner layer in contact with an approximately 10 nm thick ITO coating, with the presence of oxygen (O) and very little S concentration. Thus, the presence of oxides and hydroxides is suggested for this intermediate layer.

Fig. 10 shows the XPS spectra of Cd-3d (a) and S-2p (b). All XPS measurements were taken for the 60, 180, 240, 300, and 360s samples. Graph (a) shows how the presence of Cd occurs after short deposition times, despite that there is no obvious evidence of material deposited on the substrate. By increasing time, peaks start defining and their width decreases somewhat, which can be due to the fact that the growth of CdS on the surface is increasing in comparison to the other compounds that can be found. As of the 240 s sample, the position of the peaks in 405.3 eV for orbital  $3d_{5/2}$  and in 412 eV for that of  $3d_{3/2}$  correspond to CdS [22,23], whereas for the 60 s sample, the position is shifted to less energy around 405.1 eV for  $3d_{5/2}$  and 411.8 eV for  $3d_{3/2}$ , these positions being reported for the hydroxide or carbonate of the metal [24,25]. On the other hand, in graph (b), it has the spectrum for S, the peaks being positioned around 161.6 and 162.8 eV for  $2p_{3/2}$  and  $2p_{1/2}$ , respectively, which corresponds to the CdS [23]. There is no presence of other states of oxidation. It is also important to notice that for the 60 s sample there is no presence of S on the surface, which coincides with that



Fig. 12. XPS measurements of samples deposited at 60, 180, 240, 300, and 360 s for the O-1s region.

shown by RBS. Therefore, it is very possible that the detected Cd from this sample is bound to O, both as  $Cd(OH)_2$  or  $CdCO_3$ , according to the binding energy found for the Cd region. It can be stated that the formation of CdS on the substrate begins as of the 180s sample, as was mentioned already in the other analyses.

For the previous analysis to be more consistent, the following figure (Fig. 11) shows the spectra of XPS performed for the regions of In-3*d* and Sn-3*d*. The position of the peaks, in the case of In (a) are at 444.1 and 451.5 eV, and at 486.7 and 495.1 eV for Sn (b). These positions correspond to the ITO layer on the substrate [26–28]. It can be seen that as the deposition time increases, the peak intensity decreases, until almost disappearing around 300 s, time at which the film on the substrate already is completely formed (Fig. 3a and b). For the 180 and 240 s samples, it must be remembered that the formation of CdS occurs in form of particles and islands and therefore, the signals of the compounds that belong to the substrate are not detectable yet.

Fig. 12 shows the spectrum of O-1s. In this figure, the change of the oxidation state of the films at very short deposition times is more noticeable. The position of a peak appears in 529.9 eV for the 60 s sample, which corresponds to the ITO on the substrate [29]. Furthermore, with more energy, 531.6 eV, the appearance of a shoulder can be observed, which can belong to CdO, CdCO<sub>3</sub>, Cd(OH)<sub>2</sub> [24,30]. According to what has been reported by other authors [11,31–33] and the position found for the Cd region, Cd and O are linked as Cd(OH)<sub>2</sub>. In the 180 s sample, this shoulder increases in intensity and is found in a ratio of almost 50% with respect to the peak that belongs to the substrate. Despite the fact that at longer deposition times the formation of the film is clear, the peak that corresponds to hydroxide continues appearing. This indicates that a very thin layer of this material continues on the substrate and the CdS begins to deposit thereon, which is in accordance with what has been shown in RBS. With longer times, the peak that corresponds to the substrate disappears completely.

In order to appreciate more clearly the changes in oxidation stages that occur in deposited films, Fig. 13 shows the XPS spectra with the respective deconvolutions for each region of the deposited film at 360 s. In O-1s it can be observed that hydroxide is still present even with the formation of the CdS film, which can be seen also in the Cd-3d, where, in order to have a good fitness of the model, it was necessary to introduce a gaussian with its position corresponding to Cd bound to O as Cd(OH)<sub>2</sub>. On the other hand, it can be seen how for the S-2p region, it was sufficient only with models corresponding to CdS to have a very good adjustment, which indicates that there is no formation of other S compounds on the surface as was reported by Mazón-Montijo et al. and El Maliki et al. [4,31]. Moreover, in the C-1s and O-1s regions, there are signals of some compound formed by the binding of O-C. This is very probably due to chemically absorbed oxygen during the deposition process [31,34]; however, this had no influence on film quality.

The chemical analysis under discussion is consistent with the morphological, structural, and optical results obtained for these samples. Below, the results with respect to the stages that form part of the growth process by CBD are discussed. The chemical balance of the solution was attained and the surface of the substrate was modified during the incubation stage. According to the results, this must occur immediately after the reagents are added to the glass beaker, from the XPS analysis it was observed that the nucleation stage occurs at about 60 s of deposition, which is less time than that reported for glass substrates [4]. In this stage, the Cd(OH)<sub>2</sub> layer being formed on the substrate is clear, which in accordance with what has been reported previously by Ortega-Borges and Daniel Lincot [11]. At a deposition time of 180 s, the first CdS particles appear on the substrate, which corresponds to the growth stage.



Fig. 13. XPS spectra modeled for the Cd-3d, S-2p, O-1s, and C-1s regions of the film deposited at 360 s.

After some time has elapsed, islands forming bands (Fig. 2) appear, CdS continues forming until the substrate is fully covered and the CdS film continues growing (Figs. 3 and 4). The transition from *ion-by-ion* mechanism to the *cluster-by-cluster* mechanism was found for deposition times greater than (720 s), thus, the deposition of CdS layers for the times studied occurs by means of a *mixed* mechanism. The final stage (dust layer that is eliminated by washing with running water) was not shown in this study.

## 4. Conclusions

With our study of the substrate at different times of contact with the reaction solution, growth stages of films deposited by CBD become clearly evident, reporting changes in the morphology and chemical nature which occur in the formation and growth of CdS on ITO/glass. It was found that the ITO layer does not modify the morphology of the particles that have initially adhered to the surface, or of the CdS film which is finally formed. On the opposite; it favors the growth of this material, since the growth stages occur earlier than when using only glass substrates. Besides, there is evidence that its growth in lines and bands (as had been observed already on glass) is not affected on the ITO surface. On the other hand, it was shown that this method of manufacturing thin films is clean, since no contaminants were present on the CdS film.

Other than what has been reported by Kozhevnikova et al. [16] which assures that there are no cadmium compounds on the substrate prior to a 2 min time period, we found the presence of cadmium containing material on the surface of the substrate around the 60s of deposition time and this period can be taken as the nucleation stage. The formation of a  $Cd(OH)_2$  thin layer occurs during this stage in agreement with other reports [10-13,16] and the CdS layer grows on it. The CdS growth stage occurs as of 180s, where may be exist a mixture of Cd(OH)<sub>2</sub> and CdS on the surface. The *ion-by-ion* mechanism prevails at this moment. The complete formation of the CdS film took place at 300s. On the other hand, the transition to the *cluster-by-cluster* mechanism was identified at longer deposition times (720 s), thus, the deposit of CdS layers by CBD occurs by a mixed mechanism, a fact which agrees with what has been described by other authors [7,12]. Results obtained by optical and structural assessments indicate that the films deposited by this method in an ammonia-free system are good candidates to be applied in optical and optoelectronic devices.

### Acknowledgements

Our acknowledgment to J. C. Pineda, K. López, and F. J. Jaimes for their technical assistance in the operation of the IF-UNAM accelerator; M. C. María Luisa Ramón García for the measurements and support in the DRX analyses performed at CIE-UNAM; Dr. M. Quevedo López, for the XPS measurements performed at the University of Texas in Dallas; Dr. R. Ramírez Bon and Dr. F. J. Espinoza Beltrán for the access the use of the Film Tek Trade Mark 3000 and AFM equipment of the CINVESTAV-Querétaro. This work was partly supported by CONACyT, Mexico (Project 43570-Y).

#### References

- G. Hodes, Chemical Solution Deposition of Semiconductor Films, Marcel Dekker, Inc., Basel, New York, 2003.
- [2] A. Cortes, H. Gómez, R.E. Marotti, G. Riveros, E.A. Dalchiele, Solar Energy Materials & Solar Cells. 82 (2004) 21.
- [3] M. Kostoglou, N. Andristos, A.J. Karabelas, Journal of Colloid and Interface Science 236 (2003) 177.
- [4] D.A. Mazón-Montijo, M. Sotelo-Lerma, M. Quevedo-López, M. El-Bouanani, H.N. Alshareef, F.J. Espinoza-Beltrán, R. Ramírez-Bon, Applied Surface Science 254 (2007) 499.
- [5] L. Jae-Heyeong, Thin Solid Films 515 (2007) 6089.
- [6] B. Pradhan, A.K. Sharma, A.K. Ray, Journal of Crystal Growth 304 (2007) 388.
- [7] P.K. Nair, M.T.S. Nair, V.M. Garcia, O.L. Arenas, Y. Peña, A. Castillo, I.T. Ayala, O. Gomezdaza, A. Sánchez, J. Campos, H. Hu, R. Suárez, M.E. Rincón, Solar Energy Materials & Solar Cells. 52 (1998) 313.
- [8] M.B. Ortuño-López, J.J. Valenzuela-Jáuregui, M. Sotelo-Lerma, A. Mendoza-Galván, R. Ramírez-Bon, Thin Solid Films 429 (2003) 34.
  - [9] P. OĭBrien, T. Sabed, Journal of Cristal Growth 158 (1996) 497.
  - [10] G. Sasikala, P. Thilakan, C. Subramanian, Solar Energy Materials & Solar Cells 62 (2000) 275.
  - [11] R. Ortega-Borges, Daniel Lincot, Journal of the Electrochemical Society 140–12 (1993) 3464.
  - [12] P. OĭBrien, J. McAleese, Journal of Materials Chemistry 8 (1998) 2309.
  - [13] G.A. Kitaev, A.A. Uritskaya, S.G. Mokrushin, Russian Journal of Physical Chemistry 39 (1965) 1101.
  - [14] K.L. Chopra, S.R. Das, Thin Films Solar Cells, Plenum Press, NY, 1983, pp. 221–240.
  - [15] J.M. Doña, J. Herrero, Journal of the Electrochemical Society 144–11 (1997) 4081.
  - [16] N.S. Kozhevnikova, A.A. Rempel, F. Hergert, A. Magerl, Thin Solid Films 517 (2009) 2586.
  - [17] M.B. Ortuño-López, M. Sotelo-Lerma, A. Mendoza-Galván, R. Ramírez-Bon, Thin Solid Films 457 (2004) 278.
  - [18] L.R. Doolittle, Nuclear Instruments and Methods B 15 (1986) 227, http://www.genplot.com/.
  - [19] M.G. Sandoval-Paz, M. Sotelo-Lerma, A. Mendoza-Galván, R. Ramírez-Bon, Thin Solid Films 515 (2007) 3356.
  - [20] JCPDS 41-1049.
  - [21] D.R. Lide, Handbook of Chemistry and Physics, 84th ed., CRC Press, 2004.
  - [22] S.W. Gaarenstroom, N.J. Winograd, Journal of Chemical Physics 67 (1977) 3500.
    [23] V.G. Bhide, S. Salkalachen, A.C. Rastog, C.N.R. Rao, M.S. Hegde, Journal of Physics
  - D: Applied Physics 14 (1981) 1647. [24] J.S. Hammond, S.W. Gaarenstroom, N. Winograd, Analytical Chemistry 47 (1975) 2194.
  - [25] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook
  - X-Ray Photoelectron Spectroscopy, Ed Perkin-Elmer, 1979.
  - [26] J.C.C. Fan, J.B. Goodenough, Journal of Applied Physics 48 (1977) 3524.
  - [27] H. Willemen, D.F. Van De Vondel, G.P. Van Der Kelen, Inorganic Chimica Acta 34 (1979) 175.
  - [28] A.S. Tselesh, Thin Solid Films 516 (2008) 6253.
  - [29] N. Mori, S. Ooki, N. Masubuchi, A. Tanaka, M. Kogoma, T. Ito, Thin Solid Films 411 (2002) 6.
- [30] M.S. Setty, A.P.B. Sinha, Thin Solid Films 144 (1986) 7.
- [31] H. El Maliki, J.C. Berne'de, S. Marsillac, J. Pinel, X. Castel, J. Pouzet, Applied Surface Science 205 (2003) 65.
- [32] P.C. Rieke, S.B. Bentjen, Chemistry of Materials 5 (1993) 43.
- [33] J. A. García Valenzuela, Tesis de Maestría en Ciencias de Materiales Synthesis and Characterization of CdS Films: by Chemical Bath Deposition, Thesis for the Master's Degree in Materials Sciences), Departamento de Investigación en Polímeros y Materiales de la Universidad de Sonora, January 6, 2009.
- [34] P. Roy, S. Kumar Srivastava, Materials Chemistry and Physics 95 (2006) 235.