New Growth Processes for Nanometric layers of Cadmium sulphide by CBD and a Potential Application

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Abstract

In this work were explored two complex agents for growth CdS thin films by using chemical bath deposition. The first one – acetylacetone – lead us a homogeneous thin films, with hexagonal structure, 2.37 eV of energy bandgap and grain size of 3 nm. Whereas, for the second compound – glycine – the films also show hexagonal structure with high purity, high hexagonal crystallographic orientation, 2.53 eV of energy bandgap, grain size of 30 nm and 2.3 nm of surface roughness. Some morphology images are presented as well as the current behavior versus the voltage for a thin film transistor device (TFT), built in its gate structure, by CdS grown with glycine.

Keywords: Semiconductor Thin Films, Cadmium Sulfide Thin Films, Acetylacetone and Glycine.

Introduction

The recent advance in soft solution processing of inorganic materials offers an exciting opportunity to develop large-area manufacturing technologies for inorganic thin-film transistors (TFTs) [1]. The chemical bath deposition (CBD) is used for deposition techniques that produce a solid film in a single immersion through control of the kinetics of formation of the solid. Film thickness and composition can be easily controlled by changing simple reaction parameters such as reactant concentration, reaction temperature and deposition time. The deposition medium for CBD consists of one or more salts of metal M^{n+}, a source for a chalcogenide (if the film to be deposited contains S, Se, etc), a source of oxygen for oxide films and a complexing agent (e.g. ammonia, NH_3, EDTA) all mixed in aqueous solution. For oxides, water normally provides the oxygen. The processes that occur in the CBD solution consist in general of the following steps: (1) Time zero to equilibrium between the complexing agent and water; (2) Hydrolysis of the chalcogenide source (if the film is not an oxide); (3) Formation and/or dissociation of ionic metal–ligand complexes $[M(L)_i]^{n-ik}$, where L^k denotes one of more ligands, and (4), (5) Formation of the solids.

CBD for oxide or sulfide films from a metal cation M^{n+} complexed by *i* ligands L^{k-}, these steps can be depicted as follows [2]:

1) Dissociation of water and Complexant-water equilibrium:

$$nH_2 \leftrightarrow nH^+ nOH^-$$

$$2(L)_i^{k-} + 2H_2O \leftrightarrow 2(L)_iH^{-k+1} + 2OH^-$$

2) Thiourea hydrolyzes to form sulfides

$$nSC(NH_2)_2 + 2nOH^- \rightarrow$$

$$nS^{2-} + nCH_2N_2 + 2nH_2O$$

3) Displacement of ligands:

$$nOH^- + M(L)_i^{(n-ik)+} \rightarrow M(OH)_n\,(s) + (L)_i^{k-}$$

4) Deprotonation to form oxides

$$M(OH)_n(S) \rightarrow MO_{n/2}\,(s) + \frac{n}{2}H_2O$$

5) Total Reactions:

$$M(L)_i^{(n-ik)+} + \frac{n}{2} H_2O \rightarrow MO_{n/2}(s) + nH^+ + (L)i^{k-}$$

$$M(L)_i^{(n-ik)+} + nS^{2-} \rightarrow MS_{n/2}(s) + (L)_i^{k-}$$

The complexant is optional and is usually chosen based on the affinity of its ligands toward the metal. This makes step 3 the rate-determining step, adding a degree of control for thin film thickness. The hydrolytic process of reactions 4 and 5 can be accelerated by heating the solution, which induces deprotonation of the hydrated metal species (reaction (4)). This eliminates the need to use a base in reactions 4 and 5. For the oxide systems to be evaluated in this proposal, hydrolysis can occur even in acidic solutions when the metal cation is easily hydrolysable, as in the case of some of the metals to be evaluated here (Al^{3+},Zn^{2+}mIn^{3+}). In contrast, CBD of non-oxides requires the addition of basic solutions. In all CBD processes, whether oxide or non-oxide, a solvated metal complex reacts with a chalcogenide source to form a desired solid product. The main difference is that for oxides, the ‘‘chalcogenide source’’ is water, so that tighter control must be exerted over just two parameters (pH, T) to achieve a similar degree of control over the rate of hydrolysis and, therefore, control over the film’s microstructure and properties. For non-oxide films, the supply of chalcogenide anions can be controlled, in addition to pH and temperature, with the concentration of the chalcogenide source.

Since the early developments of TFT´s, metal chalcogenides such as Cu2S, CdS and CdSe have been applied as the semiconductor layer in MOS devices [3]. In fact, the first MOS patent included Cu_2S as the semiconductor active layer [4]. Since CBD is allow temperature process it makes it appealing for application in flexible electronics because the use of flexible plastic substrates adds a processing constraint: processing temperature. Maximum processing temperature must be less than 150ºC, well below the temperature used for traditional inorganic materials deposition. While traditional solutions to the above constraint exist, most cannot meet all of the criteria, not to mention realistic processing cost. CBD is among the most inexpensive, simple and convenient deposition technique to obtain inorganic thin films on large area substrates. An additional advantage of CBD is that the highest processing temperature is 100ºC, corresponding to the water boiling temperature, which is normally the main component of the reactive solution. Originally used for sulfide and selenide thin films, this technique has also been mostly used for materials for photovoltaic applications [5-11].

Problem Formulation

We considered the idea to synthesize CdS thin films by CBD method using other compounds as complexing agents, this in order to get a better control in its growth and high purity for applications to the nanoscaled optoelectronic devices. As a global result, we present two techniques to growing thin films using two different complexing agents: acetylacetone and glycine.

Experimental Method to produce CdS thin films using Acetylacetone

The acetylacetone was used as a ligand in the CBD in order to obtain CdS thin films, the nature of this agent is bidentate ligand and is convenient for the coupling with Cd ions [12]. The reaction conditions were determined experimentally.

The CdS thin films were deposited on glass slides substrates by means of the chemical bath technique. The reactive substances in the solution were: 2 ml of Cadmium Nitrate Tetrahydrated (0.1 M), 2 drops of 99% acetylacetonate, 6 drops of buffer pH 11 (NH_4OH/NH_4Cl), 2 ml of Thiourea (1M) and two amounts of 10 ml of waters, after the acetylacetone and before the thiourea.

The films were deposited in the substrate into the solution between 65 to 75°C, they were kept in the solution for 1 h. The obtained CdS films were flat homogeneous, green-yellowish, transparent and with very good adherence to the substrate. The gap energy of the films was 2.37 eV, for 10 minutes of reaction. Their thickness was approximately 100 nm, and they had a hexagonal crystalline structure.

The X-ray diffraction measurements were performed using a Rigaku Ultima III-XRD. Optical absorption spectra of the bilayers were recorded by an Ocean Optics USB4000-UV-VIS spectrometer. Atomic Force Microscopy AFM measurements were done in a DM09 Veeco Atomic Force Microscope.

Experimental Method to produce CdS thin films using Glycine

Glycine is the smallest of the 20 amino acids commonly found in proteins. It has been used as complexing agent for the electrochemical deposition of Fe, Ni and Cr thin films on stainless steel and copper substrates [13].

The CdS films were deposited on glass slide substrates in a 100 ml beaker containing the reaction solution prepared by the subsequent addition of 31 ml of deionized water, 4 ml of 0.1M cadmium nitrate tetrahydrated ($Cd(NO_3)_2$ V $4H_20$), 5 ml of 0.5 M glycine (NH_2CH_2COOH), 2 ml of pH 11 buffer, 5 ml of 1M thiourea ($(NH_2)_2CS$)

and deionized water to complete 60 ml. The mixture was initially stirred to homogenize and then its temperature was set at 80°C in a thermal water bath. The substrates were immersed in the solution at this temperature and removed after 18 min when the reaction finished, according to its appearance. There was not stirring during the deposition process. The deposited CdS films were yellowish, homogeneous, specularly reflecting with very good adhesion to the substrate. The thickness of the films was about 60 nm as determined from depth profiles performed with Veeco Dektak 8 profilometer. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) measurements with a Rigaku Ultima III diffractometer. The absorption spectra of the films were measured in a Perkin Elmer Lambda 19 spectrophotometer in the 350–800 nm wavelength range. The morphology and roughness of the surface films were investigated by atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd).

Problem Solution

After to have determined two sets of conditions to grow CdS thin films, we present the Results and Discussion of these two processes in a comparative way. We base our search for the reaction conditions in the general mechanism reaction presented in the introduction of this work.

In Fig. 1 it is shown the optical absorption spectra of these CdS thin films were grown using two different complexing agents, the gray line present the behavior for acetylacetone and the black line for glycine, respectively. As can be observed a low level absorption was presented between 550 and 750 nm for acetylacetone and for glycine its low absorbance range is from 505 to 750 nm, this is important for instance for the thin films solar cells purposes, where the CdS is normally used as a window material and it is required to have high transmission in the visible range, so that much more visible light penetrate into the active region.

For the glycine process, after 18 minutes of deposition the films has reached enough thickness and the reaction finished, also from the Figure 1 it is possible to conclude that this kind of films have an average transmittance of slightly major than 80 % within the optical region. While for the acetylacetone process, after 10 minutes of deposition the films have reached enough thickness with an average transmittance of the order of 60 % within the optical region, in this case the reaction continue until around 40 minutes.

The Fig. 2 shows the $(\alpha\ h\nu)^2$ vs hX plots like is typical for CdS thin films deposited by the CBD method or any other method. Since the absorption coefficient, α, for the allowed direct interband transition in a crystal is proportional to $(h\nu)^{-1}(h\nu\text{-}Eg)^{½}$, where hv is the photon energy and Eg is the value of the energy bandgap, we can estimate Eg by plotting $(\alpha\ h\nu)^2$ as a function of (hv-Eg). The energy bandgaps in these cases were Eg = 2.53 eV using glycine as complexig agent, and Eg= 2.37eV using acetylacetone as complexing agent. The CdS thin films can be considered good for use as a visible transmitting thin film, since the range of energies for a visible transmitting film is from 1.5eV to 3.0eV [14].

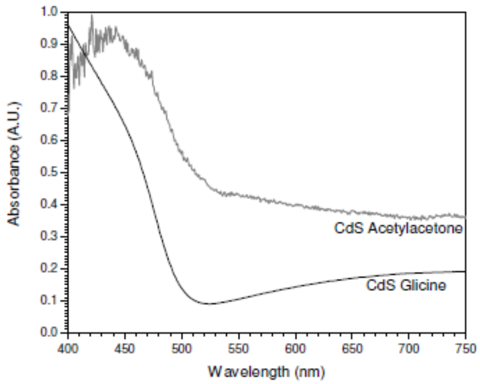

Fig.1. Optical absorption spectra of the CdS thin films using acetylacetone and glycine as complexing agent respectively. The gray line corresponds to acetylacetone process, and the black line for glycine.

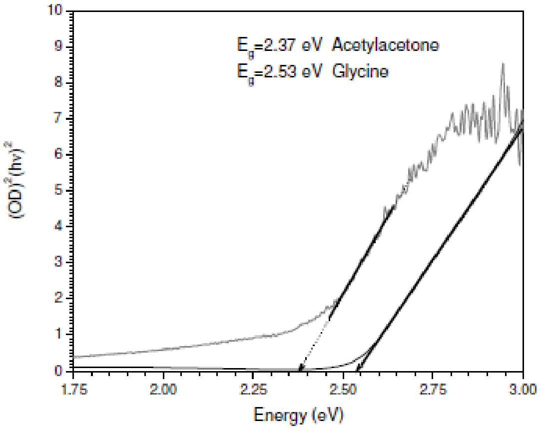

Fig. 2. $(OD)^2(h\nu)^2$ versus Energy, like utility to calculate Energy bandgap of the CdS thin films using acetylacetone and glycine as complexing agents, respectively. The gray line shows the behavior for acetylacetone and the dots for glycine.

The Fig. 3 shows the XRD patterns for the CdS thin films obtained by using acetylacetone and glycine as complexing agent in the CBD process. A hexagonal polycrystalline structure concerning to the X-ray analysis results for both processes [15]. From those diffractograms were calculated their grain sizes by the model of Debye-

Scherrer [16], resulting 3 nm for the acetylacetone process and 30 nm for the glycine process.

The pattern corresponding to the glycine process displays an intense peak at about 26.7° and weaker diffraction signals at about 28.6, 48.3 and 52.3°, which can be assigned to the reflections by (002), (101), (103) and (112) planes of the CdS hexagonal crystalline phase. The relative large intensity of the (002) diffraction peak clearly evidences the preferred crystalline orientation of the CdS crystallites along the [002] direction. The lattice constant, c, calculated from this pattern is 6.677 Å, which is shorter than 6.713 Å, the lattice constant of bulk CdS. The percentage of variation of the value of c for the CdS films, related to that of the bulk, is -0.54 %. Because the (002) crystalline orientation of the CdS film, the [002] direction is perpendicular to the substrate. Since c is measured along the c-axis in the [002] direction, the shrinkage of this lattice constant can be related with tensile stress along the film-substrate interface, as has been observed in other chemically deposited CdS films [17].

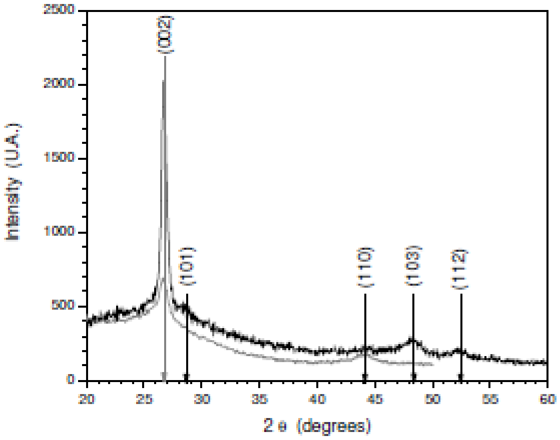

Fig. 3. X-Ray diffraction patterns of the CdS thin films using acetylacetone and glycine as complexing agent respectively. The gray line corresponds to acetylacetone and the black line for glycine.

By another hand, the surface morphology that conforms the thin film growth using acetylacetone as complexing agent was analyzed by the Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), it is illustrated in Fig. 4 and Fig. 5. The image obtained by SEM can be interpreted at a change in the flatness of the surfaces due to the global growing and to the clusters formation of nanocrystals, While the image obtained by AFM shows some regular surface morphology which is representative across the overall sample extension.

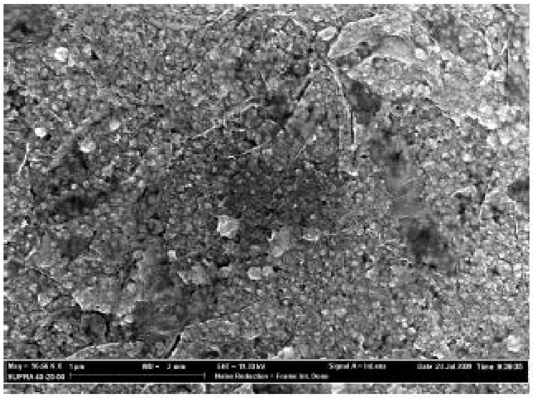

Fig. 4. SEM image of CdS thin film growth with acetylacetone as complexing agent.

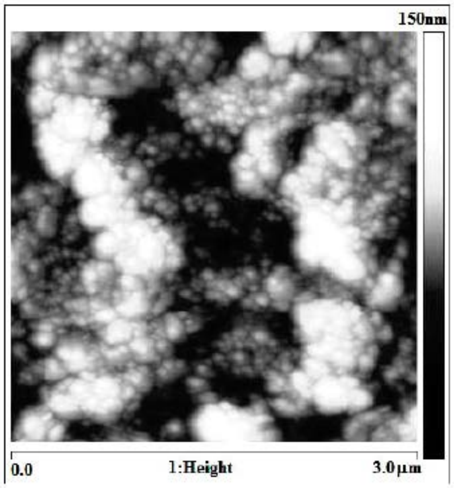

Fig. 5. AFM image of CdS thin film growth with acetylacetone as complexing agent

In Fig. 6 are shown AFM images of the CdS film surface growth using glycine as complexig agent, (a) A two-dimensional top view and (b) A threedimensional in perspective view. The smooth surface of the films exhibits a well-defined granular structure with nanometric-sized grains. The rms average roughness of the film measured in the displayed area is 2.3 nm [18]. Due the low roughness of this thin films the optical transmission increase in the visible region.

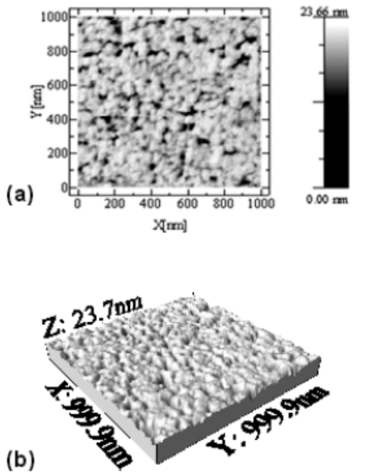

Fig. 6. AFM images of CdS thin films growth with glycine as complexing agent. (a) Top view AFM image of a representative area of the CdS thin film, showing its nanometric grain sizes, and (b) Perspective view of AFM image of the same representative area of the CdS thin film, showing its nanometric grains sizes.

Finally an appliance was suggested where it was used the process of CdS thin film with glycine, but growth on SiO_2/ Si p-type. This was the base to create a Thin Film Transistor as the shown one in schematic form in Fig. 7 (a). The plot in the Fig. 7 (b) shows the typical transistor behavior, here we can see the correlation between the current source-drain (Isd=Id) and the voltage source-drain (V_{sd}=V_d).

Conclusion

From this research we developed two new processes to synthesize CdS thin films of very good quality, comparable to the obtained with other techniques. So, we can conclude that the Chemical Bath Deposition technique has a high potential to contribute into built appliances in the actual nanometric scale order, such as the TFT. Here we purpose the use of Acetylacetone and Glycine by separate, both as complexing agents for the cadmium ion. We can recall that the respective grain sizes were 3 and 30 nm, their respective energy bandgaps were 2.37 and 2.53 eV, and their almost constant transmittance levels were 80% and 60%. For both processes the polycrystalline structure corresponds to a hexagonal phase.

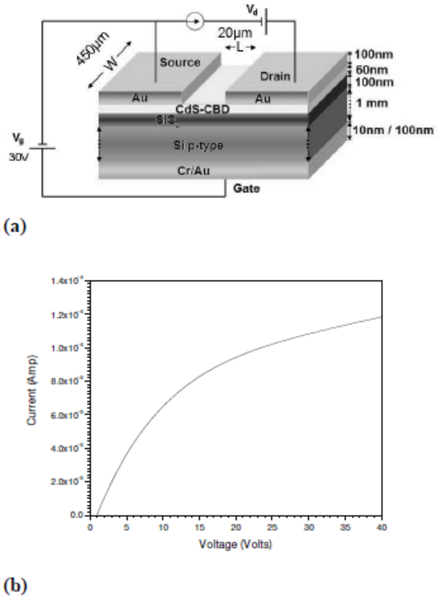

Fig. 7 Application of CdS thin film growth with glycine. (a) Schematic Thin Film Transistor, and (b) Current vs. voltage of CdS thin film growth with glycine as complexing agent.

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