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Optimization of Chemical Bath Deposited Cadmium Sulfide Thin Films

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ABSTRACT

We report the optimization of CdS thin film grown by chemical bath deposition where homogenous reactions are minimized. The optimum parameters have enabled us to maximize the thickness of the deposited film in a single dip and to grow thicker films by periodically replenishing the concentration of reactants while the substrate remains continuously dipped in the reaction bath. Characterization results reveal the deposited CdS films exhibit improved optical and electrical properties.

Introduction

Cadmium sulfide (CdS) is known¹ to be an excellent heterojunction partner of p-type cadmium telluride (CdTe) or p-type copper indium diselenide (CuInSe₂) due essentially to its high electron affinity. It is widely used as a window material in high-efficiency thin-film solar cells based on CdTe or CuInSe₂ owing to its transparency and photoconductivity among other properties. The thickness of CdS film required for the fabrication of these cells is in the range¹ of 0.05 to 0.1 μm. However, in other applications²⁻⁴ of CdS, which include photochemical cells, light meters, image intensifiers, etc., the working thickness is well above 1 μm.

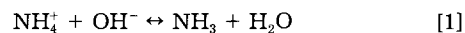
The commonly used methods for depositing CdS thin films^{1,5} are vacuum evaporation, sputtering, spray pyrolysis, and chemical bath deposition (CBD). The latter method^{1,6} is a low-cost and a scaleable technique for the deposition of high quality CdS films.

Although CBD is ideally suited for the fabrication of window material in thin-film solar cells, it cannot be readily used for other applications requiring thicker high-quality films. This is because, (i) the thickness of CdS films formed by CBD tends to saturate^{1,6,7} between 0.05 and 0.2 μm, and (ii) at longer reaction time the resulting films, though thicker, have a duplex structure.⁷ This structure consists of an inner layer which is very adherent and an outer layer which is less adherent despite its visual appearance. These limitations exist because CBD is a limited source growth process. In addition, the heterogeneous reaction (or atom-by-atom⁷ growth of the film on the substrate) competes with the homogenous reaction, which further depletes the reactants to form CdS colloids in the

bulk of the solution. A predominantly homogenous reaction often terminates the heterogeneous reaction, and the film then grows by adsorption^{6,7} of colloids, leading to a porous overlayer.

Here, we report the optimization of chemical bath-deposited CdS thin films where homogenous reaction is minimized and the thickness of film deposited in a single dip maximized. For a concentration of cadmium salt that is as low as 0.005 M, a good quality 0.5 μm thick film was obtained. It is also shown, using these optimization results, that thicker CdS film can be deposited by periodically replenishing the reactants while keeping the substrate continuously dipped in the reaction bath, or by the traditional multiple dips method.

Review of the CdS growth mechanism.—In a heated aqueous alkaline solution, CdS is grown^{1,6,8} by the reaction between cadmium salt (*e.g.*, cadmium acetate or Cd(CH₃COO)₂), thiourea (SC(NH₂)₂), and ammonia water (NH₄OH), with ammonium salt (*e.g.*, ammonium acetate or NH₄CH₃COO) as a buffer. From the cadmium side, the main chemical equilibria involved in the formation of either CdS films or colloids are as follows



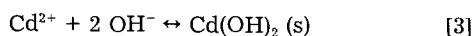
The presence of ammonium salt, however, promotes the forward reaction in Eq. 1. This then reduces the pH, or OH⁻ concentration, in the reaction bath according to the relation⁶

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{NH}_3]_0}{[\text{NH}_4^+]_0} \right)$$

Here, [NH₃]₀ and [NH₄⁺]₀ are the initial ammonia water and ammonium salt concentrations, respectively, and pK_a is

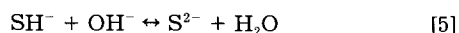
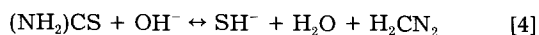
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reported⁶ to be 9.2 at 25°C. As a result, Cd²⁺ is predominantly used up in Eq. 2 to form cadmium tetraammine complex ions (Cd(NH₃)₄²⁺), especially if NH₃ concentration is sufficiently high. These ensure that the product of [Cd²⁺] and [OH⁻] is less than the solubility product⁹ of Cd(OH)₂ (1.2 × 10⁻¹⁴) and prevent the equilibrium reaction

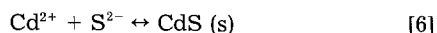


from taking place in the bulk of the solution.

For CdS colloid formation we have, in addition to Eq. 1 and 2



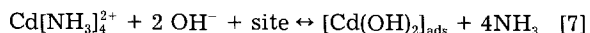
and



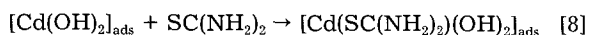
Equation 6 takes place if the cadmium and sulfide ions ionic product is greater than the solubility product⁹ of CdS (7.1 × 10⁻²⁸).

Mechanisms of CdS film growth on substrates have been proposed by many authors.^{6,7,10,11} The most explicit, however, is that of Ortega-Borges and Lincot,⁶ which in addition to Eq. 1 and 2 is as follows

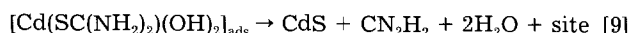
(A) Reversible adsorption of cadmium hydroxide species



(B) Formation of surface complex with thiourea



(C) Formation of CdS with site regeneration



It is inferred from these equations that CdS film grows at a lower rate. To ensure this, NH₃ must be present in sufficient amount to bind Cd²⁺ in cadmium tetraammine complex ions, but OH⁻ and NH₃ are both introduced in the solution in the form of NH₄OH. Therefore, to allow the slow process at the surface of the substrates described by Eq. 7 through 9 to take place predominantly over the direct hydrolysis of thiourea (reactions 4 and 5) in the bulk of the reaction bath, ammonium salt must be present to control OH⁻ concentration and stabilize the tetraammine complex ions. Consequently, CdS colloid formation is minimized, which is the subject of our study.

Experimental

The choice of deposition parameters has been guided by kinetic studies carried out by other authors.^{6,7,10,11} Each experimental solution contained 300 ml of deionized water. This was prepared by adding into the beaker containing the stirred deionized water at 85°C, Cd(CH₃COO)₂, NH₄CH₃COO, NH₄OH, and SC(NH₂)₂ from 0.5, 2, 14.8, and 0.5 M stock solutions, respectively, in that order. The cleaned glass or SnO₂/glass substrates, held by a substrate holder, were immersed in the solution prior to adding thiourea. The substrate size was 3.9 × 3.9 cm. The substrate cleaning steps were: (i) washing with Liquinox soap, (ii) ultrasonic cleaning in Liquinox soap solution, (iii) washing in distilled water, (iv) soaking in chromic acid, (v) washing in acetone, (vi) washing in methanol, (vii) ultrasonic cleaning in distilled water, (viii) ultrasonic cleaning in isopropanol, (ix) washing in deionized water, (x) ultrasonic cleaning in deionized water, (xi) boiling in deionized water until used. The last six steps were also used for cleaning the substrate holder, the stirrer, and the thermometer after rinsing with 10% HCl solution. The experiments were carried out in a hood. The deposition time ranged between 30 and 240 min. During the deposition the approximate starting times of the homogeneous and heterogeneous reactions were observed. Homogeneous reaction was marked by a turbid and opaque reaction bath. A predominant heterogeneous reaction was characterized by a clear reaction bath,

while yellowish CdS film formed on the substrate. After each deposition, the coated substrate was ultrasonically cleaned in boiling deionized water and dried.

Before the multiple dip or continuous dip deposition, the growth of CdS films using optimal parameters was studied to find the saturation point of the film thickness. For multiple dip deposition, the substrate was taken off the reaction bath at about the saturation point and the process was repeated using the same substrate. In the case of continuous dip deposition, reactants were replenished periodically at about the saturation point of the initial deposition cycle. Reactant concentrations in the replenishing solution were the same as those in the initial cycle, except that of ammonium acetate which was changed.

Thickness, optical transmission, composition, and dark conductivity of the deposited films were determined. The film thickness was measured using an α-step profilometer. X-ray fluorescence spectroscopy was used to determine the compositions of CdS films. Optical transmission of the films was measured using a Perkin-Elmer UV-visible spectrophotometer. For dark conductivity measurement, ohmic contacts were made by evaporating two coplanar In/Ag electrodes onto the surface of a CdS film deposited on glass. The contact separation was 13 mm, the bias voltage was 9.9 V, and the current was measured using a Keithley 614 electrometer.

Results and Discussion

Optimization.—Figure 1 shows the dependence of grown CdS film thickness on [NH₃] introduced as NH₄OH in the reaction bath with [Cd(CH₃COO)₂] = 0.002 M, [NH₄CH₃COO] = 0.04 M, and [SC(NH₂)₂] = 0.012 M. We note that [Cd(CH₃COO)₂]:[SC(NH₂)₂] = 1:6. The thickness peaks at about 0.6 M of ammonia. It is relatively thin at low ammonia concentration and decreases rapidly at higher ammonia concentrations.

For the same growth conditions, Fig. 2 shows the observed approximate homogeneous and heterogeneous reaction starting times. At low [NH₃], the homogeneous reaction starts shortly after thiourea is introduced to the reaction bath. This is because there is insufficient NH₃ to bind Cd²⁺ into Cd(NH₃)₄²⁺. And excess Cd²⁺ together with available S²⁻ satisfy the conditions described by Eq. 6. Therefore, the homogenous nucleation of CdS colloids in the solution dominates and the film growth takes place mainly by adsorption of colloids.

The increase in [NH₃], however, increases the approximate homogeneous reaction starting time and allows the heterogeneous reaction to be observed first. At [NH₃] ≥ 0.6 M, though, there is a time delay in the starting of both reactions, the time difference is about 6 min and appears to be constant. This time difference corresponds to the period during which heterogeneous reaction is predomi-

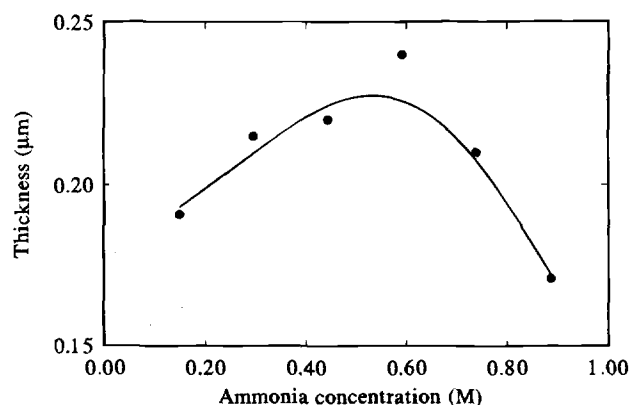


Fig. 1. Influence of ammonia concentration on CdS film thickness. Growth conditions: $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.002 \text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]:[\text{SC}(\text{NH}_2)_2] = 1:6$, $[\text{NH}_4\text{CH}_3\text{COO}] = 0.04 \text{ M}$, time of deposition 30 min.

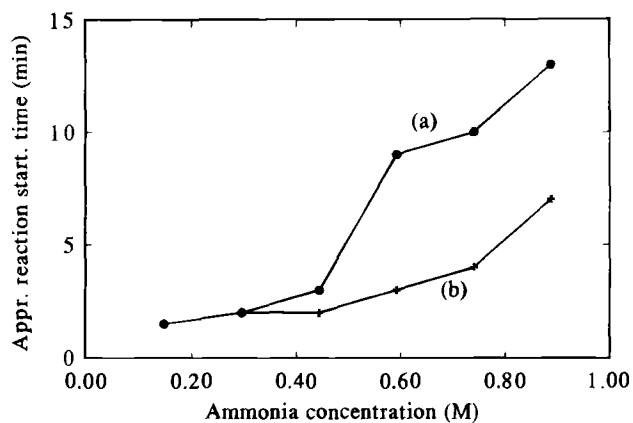


Fig. 2. Effect of ammonia concentration on the approximate reaction starting time: (a) homogenous reaction and (b) heterogeneous reaction. Growth conditions same as in Fig. 1.

nantly taking place. This means that $[\text{NH}_3] \geq 0.6 \text{ M}$ is sufficient to bind Cd^{2+} into complex ions needed for slow growth described by Eq. 7 to 9. However, excess NH_3 overstabilizes the complex ions and reduces the growth rate. This explains why the film thickness decreases rapidly beyond $[\text{NH}_3] = 0.6 \text{ M}$. Therefore, under this growth condition, 0.6 M ammonia has been chosen as the concentration that stops or minimizes the early homogeneous reaction.

On the other hand, the homogenous reaction eventually observed when there is sufficient NH_3 , and thus more hydroxide ions, may be due to excess sulfide ions. The excess S^{2-} are produced by rapid hydrolysis of thiourea, as shown in Eq. 1, 4, and 5. This rapid hydrolysis may also be aided by high concentration of thiourea in the reaction bath, since the ratio of concentrations of Cd^{2+} to S^{2-} precursors is 1:6. It is therefore important to find $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2]$ that minimizes the homogeneous reaction.

Figure 3 shows the influence of $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2]$ on (a) homogeneous, (b) heterogeneous reactions starting times, and (c) film thickness. Here, concentrations of cadmium acetate, ammonium acetate, and ammonia (NH_4OH) are fixed at 0.002, 0.04, and 0.6 M, respectively. The ratio of cadmium acetate to thiourea is varied by varying the thiourea concentration. This figure can be divided into regions I and II. The first corresponds to a region where the film is thick and where homogeneous reaction is present. The thick film obtained here might have been partly deposited by atom-by-atom growth and

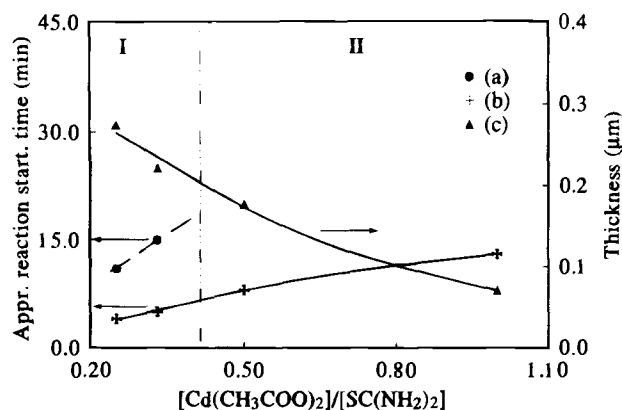


Fig. 3. Influence of $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2]$ on the approximate reaction starting time: (a) homogenous reaction, (b) heterogeneous reaction, and (c) the effect of the same reactants ratio on CdS film thickness. Growth conditions: $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.002 \text{ M}$, $[\text{NH}_4\text{CH}_3\text{COO}] = 0.04 \text{ M}$, $[\text{NH}_3] = 0.6 \text{ M}$, time of deposition 45 min.

partly by adsorption of colloids. In region II, however, the growth rate is low, but very minimum homogeneous reaction takes place. This may imply that CdS films grow predominantly in this region by heterogeneous reaction. In addition, this lower growth rate is due to reduced thiourea concentration. These results corroborate the fact that atom-by-atom growth is favored by slow growth rate and colloid formation by fast growth rate.

The second region is of interest in this work. For our study, the selected ratio of cadmium acetate to thiourea that minimizes the homogeneous reaction throughout the deposition period is 0.5.

We mentioned in the CdS growth mechanism review section and confirmed in our investigations that growth rate decreases with increase in ammonium acetate concentration. Generally, for our optimal ratios of $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$, with the bath temperature at 85°C , the growth rate is reduced and the homogeneous reaction remains minimum if the cadmium-to-ammonium salts ratio lies in the interval $0 < x < 0.12$.

To buttress this point, we consider the growth curve in Fig. 4. The growth conditions are: (a) $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.005 \text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.07$ which lies in the stated interval; (b) $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.005 \text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.13$ which does not lie in the interval. The concentrations of remaining deposition reactants are obtained from the quoted ratios. These growth curves are similar to those reported by other workers.⁶ They are characterized by an incubation or nucleation region, a linear growth region, and a saturation region. The shorter incubation period and the slightly steeper linear growth region indicate that (b) has a higher growth rate than (a). It is also observed that (a) and (b) saturate at about 0.5 and 0.4 μm , respectively. Since the cadmium and sulfide source concentrations are the same, one would expect the saturation thickness of the latter to also be about 0.5 μm . This did not occur, because some reactants were lost to colloid formation as expected. Other authors^{6,12} reported concentrations of cadmium salt and thiourea much higher than those used here to obtain film thickness that saturates at about 0.2 μm or less. This shows that minimization of the homogeneous reaction with the deposition conditions stated previously encourages atom-by-atom growth and maximizes film thickness.

Growth of thicker films.—Maximum concentrations of primary cadmium and sulfur precursors reported by Ortega-Borges and Lincot⁶ to produce high-quality CdS films are about six to ten times those used in this study to deposit 0.5 μm film. This means that there is room to grow micron-range good film in a single dip using our opti-

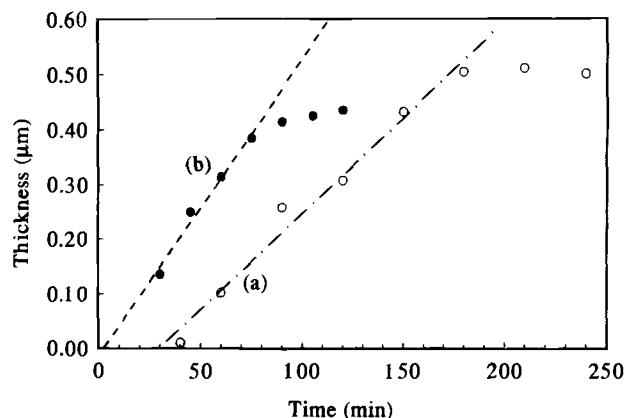


Fig. 4. Growth curve of CdS films grown by CBD: (a) $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.005 \text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.07$; (b) $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.005 \text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.13$. Other growth conditions: $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$.

Table I. Effect of $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}]$ in the replenishing reactants on the percentage thickness yield per cycle.

$[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}]$	Yield/Cycle
0.08	42%
0.11	47%

mization parameters. In this study, the growth of thicker film is carried out by multiple dip and by continuous dip.

For a given reaction bath, the thickness yield per subsequent dip in multiple dip deposition is found to range from 100 to 120% of the initial thickness. This agrees with the results obtained by other authors.⁸ The difference here, nevertheless, is that 1 μm thick film can be achieved in two dips.

Though ammonium salt acts as a buffer in the chemical bath deposition process, it holds the key to the successful deposition of thicker film by continuous dip. Table I shows the effect of $[\text{Cd}(\text{CH}_3\text{COO})_2]$ to $[\text{NH}_4\text{CH}_3\text{COO}]$ ratio in the replenishing reactants on the percentage thickness yield per cycle. The reference thickness here is that of the initial cycle. The yields shown are those where $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}]$ lies in the interval $0 < x < 0.12$. As seen in the table, when the ratio is high there is a high growth rate and hence high yield per cycle. However, when the ratio is outside this interval, homogeneous reaction takes place, leading to the growth of a porous overlayer. Despite the fact that this new method is limited by low yield owing to the constraint placed on the ammonium salt concentration, it is the least laborious method of growing thicker film.

Characterization.—Figure 5 shows a typical optical transmission spectrum of our films. Generally, the optical transmission of CdS film depends on the thickness¹³ because of the increase in diffuse scattering from the adsorbed colloids, especially when the film is deposited in the presence of heavy homogeneous reaction. Film thickness investigated ranged from 0.05 to 1 μm . The optical transmission of these films below the bandedge of CdS film ranged from 60 to 100%. Nair *et al.*¹⁴ reported 20 to 50% optical transmission for a 0.5 μm chemically deposited CdS film at 85°C, whereas for the same or higher film thickness deposited at the same temperature, we have recorded a transmission that is well above 60%. This suggests that minimization of the homogeneous reaction improves the optical transmission below the bandedge.

The plot of the square of the absorption coefficient *vs.* photon energy is shown in Fig. 6. Curves a, b, and c are those of films deposited by continuous dip, single dip, and

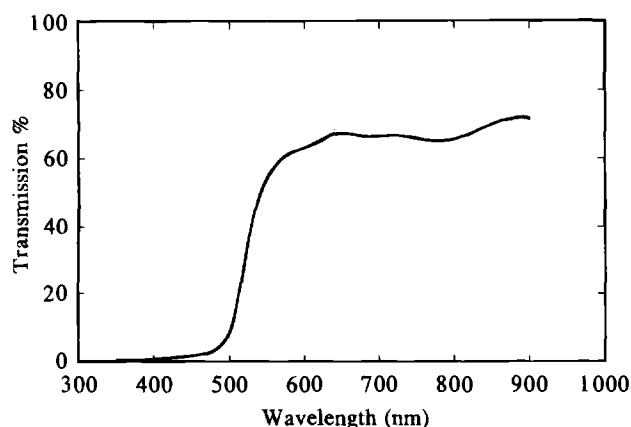


Fig. 5. Typical optical transmission spectrum of a CBD-grown CdS thin film. Growth conditions: $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.007\text{ M}$, $[\text{NH}_4\text{CH}_3\text{COO}] = 0.1\text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$. Film thickness 0.6 μm .

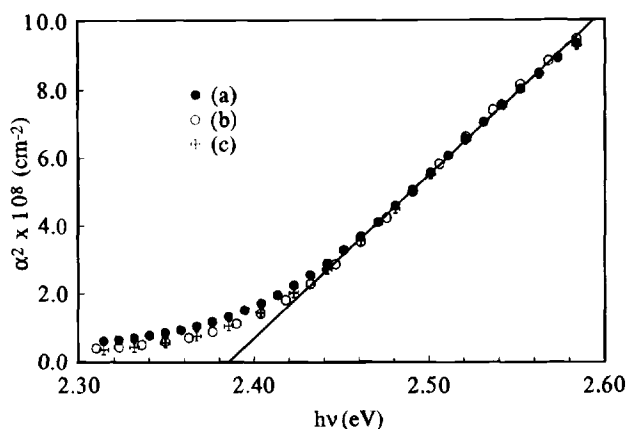


Fig. 6. Plot of absorption coefficient squared vs. photon energy: (a) continuous dip, (b) single dip, (c) multiple dips. Growth conditions: (a) and (c) $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.005\text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}] = 0.07$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$; film thicknesses 0.7 and 1 μm , respectively; (b) $T = 85^\circ\text{C}$, $[\text{Cd}(\text{CH}_3\text{COO})_2] = 0.002\text{ M}$, $[\text{NH}_4\text{CH}_3\text{COO}] = 0.04\text{ M}$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$; film thickness 0.2 μm .

multiple dips, respectively. About the characteristic energy of CdS, they all exhibit similar optical properties. As can be seen, deposited films have 2.39 eV as bandgap, a value that agrees with the 2.42 eV value^{15,16} generally accepted for bulk CdS.

From x-ray fluorescence spectrum, an approximate ratio of cadmium to sulfur of 1:1 was obtained. This result is in line with that reported in the literature.¹²

The dark resistivities of our as-deposited films are between 10^3 and $10^4\ \Omega\text{-cm}$. Values reported in the literature^{1,8,13} for CBD-grown CdS film are in the range of 10^5 to $10^{12}\ \Omega\text{-cm}$ before any thermal annealing. After annealing, the dark resistivities typically drop to about 10^{-1} to $10^3\ \Omega\text{-cm}$. This high resistivity^{12,13} of the as-deposited films has been attributed to the chemisorbed O_2 at the grain boundaries. Our results show that by minimizing the homogeneous reaction, as-deposited CdS film with low resistivity is obtainable. This could mean that under very minimum homogeneous reaction, little O_2 chemisorption takes place.

Conclusion

In chemical bath deposition of CdS films, if ratios of various reactants in the reaction bath at 85°C satisfy the conditions $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{SC}(\text{NH}_2)_2] = 0.5$, $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_3] = 0.0033$, and $[\text{Cd}(\text{CH}_3\text{COO})_2]/[\text{NH}_4\text{CH}_3\text{COO}]$ lies in the interval $0 < x < 0.12$, the homogeneous reaction is minimized, the quality of deposited film is improved, and its thickness maximized. Using these growth conditions we have demonstrated for the first time that thicker CdS films could be deposited by continuous dip.

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The Effect of pH Changes on the Giant Magnetoresistance of Electrodeposited Superlattices

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ABSTRACT

We have studied the effect of electrolyte pH on the "giant magnetoresistance" in Co-Ni-Cu/Cu superlattices prepared by electrodeposition. Films grown at low pH (1.8 ± 0.1) exhibited giant magnetoresistance (GMR) of over 15% while, depending on layer thicknesses, films grown at high pH (3.3 ± 0.1) exhibited either predominantly anisotropic magnetoresistance (AMR) or much smaller GMR than possible at low pH. Also, the films grown at low pH were found to have a higher magnetization than those grown at high pH. The different magnetic and magnetotransport properties observed for different values of the electrolyte pH are accompanied by changes in the shapes of the current transients recorded during film growth and by changes in the composition of the superlattices. A possible explanation of these results is that reducing the electrolyte pH leads to a more abrupt interface between the ferromagnetic and nonmagnetic layers by suppressing Co dissolution.

Introduction

Since the discovery of the giant magnetoresistance (GMR) in Fe/Cr¹ superlattices the properties of magnetic superlattices have been extensively studied, both because of their importance for technological applications such as magnetoresistive sensors and because of their fundamental scientific interest. Magnetic superlattices such as Fe/Cr,² Co/Cu,³ Co-Fe/Cu,⁴ and Ni-Co/Cu⁵ exhibit particularly large GMR at room temperature.

At present, GMR superlattice films are generally produced by vacuum deposition methods; sputtering and molecular beam epitaxy (MBE). Although electrodeposition has some obvious advantages (in particular the apparatus required is extremely cheap) relatively little work has been done using this technique.⁶⁻¹¹ Recently, we have shown that it is possible to grow well-ordered superlattices with repeat distances as short as $\sim 15 \text{ \AA}^{12}$ and we have also demonstrated that superlattices electrodeposited both on polycrystalline Cu substrates and on n-type GaAs (100) exhibit significant GMR.⁶⁻⁹ Of course, as is the case with superlattices grown by other techniques, the properties of electrodeposited superlattices generally depend on parameters such as the thicknesses of the magnetic and nonmagnetic layers and the choice of substrate, but in addition to these, factors such as the cathode potential, the concentration and the pH of the electrolyte used to grow the superlattices are important. Recently, Lenczowski *et al.*¹¹ studied the properties of Co-Cu/Cu superlattices elec-

trodeposited at pH 4 to 4.5 in detail by varying parameters such as the substrate texture, layer thicknesses, the Cu concentration in the electrolyte and the use of additives. They observed that superlattices with relatively thin Cu layers (*e.g.*, 16 Å) exhibited anisotropic magnetoresistance (AMR) while those with thicker Cu layers (*e.g.*, 40 Å) exhibited GMR.

In this paper, we concentrate on the effect of the electrolyte pH on the GMR in electrodeposited Co-Ni-Cu/Cu superlattices. We compare the structural, magnetic, and magnetotransport properties of superlattices prepared at low pH (1.8 ± 0.1) and high pH (3.3 ± 0.1) and discuss the significant differences observed. At the higher pH, like Lenczowski *et al.*,¹¹ we observe AMR for some films, but show that if they are grown at low pH, superlattices with thin Cu layers exhibit larger GMR than those with thicker Cu layers.

Experimental

Polycrystalline copper sheets having a strong (100) texture and a thickness of 0.5 mm were used as substrates. These were polished first mechanically and then electrochemically using 50% H₃PO₄. Our superlattices were deposited in a three-electrode cell from an electrolyte containing nickel sulfamate Ni(SO₃NH₂)₂ = 2.3 mol/liter; cobalt sulfate CoSO₄ = 0.4 mol/liter; copper sulfate CuSO₄ = 0.05 mol/liter; and boric acid H₃BO₃ = 0.5 mol/liter using a potentiostat controlled by a computer.^{6,13,14} The computer also integrates the net current (*i.e.*, the deposition current minus any dissolution current) to give the net charge passed between the anode and the cathode. When this charge reaches the value corresponding to the desired

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