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Novel approach to the deposition of CdS by chemical bath deposition: the deposition of crystalline thin films of CdS from acidic baths

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Thin films of cadmium sulfide have been deposited from acidic solutions. The films have been characterised by electronic, photoluminescence (PL) and X-ray photoelectron (XPS) spectroscopies, scanning and transmission electron microscopy (SEM and TEM) and powder X-ray diffraction (XRD). The as-deposited polycrystalline CdS films are hexagonal, the crystallinity of the films is improved by annealing in air at 400 °C. The procedure also leads to a concentration of chloride at the surface of the films. Deposition from acidic baths may open up new simple synthetic routes towards the ternary cadmium–zinc sulfide system.

Introduction

There is considerable interest in the deposition of compound semiconductors by methods which involve relatively low capital expense and are technically undemanding on the experimentalist. One process to meet these criteria is Chemical Bath Deposition (CBD). Such processing methods are particularly appropriate for the production of devices for which large areas and low cost are essential such as solar cells. We have recently reviewed some of the chemistry underlying such processes.[1] Typical CBD processes for sulfides employ an alkaline medium containing the chalcogenide source, the metal ion and added base. 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. The technique under these conditions relies on the slow release of S^{2-} ions into an alkaline solution in which the free metal ion is buffered at a low concentration.

The deposition of good quality, adherent, specular and crystalline CdS has usually been associated with baths supersaturated with respect to the precipitation of cadmium hydroxy species, irrespective of the substrate. The deposition of ZnS by CBD is a more difficult proposition than that of CdS. In particular, it is evident that there is a much wider range of conditions in which the concurrent deposition of zinc sulfide or oxide occurs. There is also some debate in the literature concerning the mechanisms by which these films grow.[2] Two end point mechanisms are usually considered: an ion-by-ion process (usually considered the dominant mechanism for CdS, although the exact species involved are poorly defined) or a process in which colloidal clusters of the material formed in solution define the film (normally termed cluster-by-cluster and often held to predominate for ZnS).

We have detailed this incompatibility between the conditions for the deposition of zinc and cadmium sulfide in a recent review and have outlined the two particular challenges with the potential for application in this area.[1] The first is to reliably deposit ZnS films, which appears to be remarkably difficult to achieve in alkaline solutions due to the stability of hydroxy species; the second is to develop a bath for the deposition of (Cd,Zn)S ternaries. The (Cd,Zn)S ternary material has the hexagonal wurzite structure and a wider band gap than CdS[3] which should make it a better window material for use in CdTe heterojunction solar cells. Although there are a few reports of the CBD of the ternary, the most recent studies demonstrate that the production of good quality thin films is very difficult.[4]

Lincot and co-workers[5] have described a novel approach to the deposition of ZnS and have successfully deposited films of ZnS from a chemical bath containing zinc ions, urea, with no added complexant, at modestly acid values of pH. The process is understood to rely upon the slow hydrolysis of urea in the bath to provide hydroxide, which facilitates the decomposition of thioacetamide. In a typical deposition experiment (90 °C, 1 h), a conformal film *ca.* 60 nm thick was deposited on glass substrates. The films were characterised and comprised of good quality ZnS. We are interested in both developing this approach further and also utilising it as a first step towards defining a route to the ternary system (Cd,Zn)S. To the authors' knowledge there is only one previous report of acidic CBD of CdS, from baths containing thiosulfate.[6] In this paper, we report the successful deposition of CdS from acidic baths containing a cadmium salt, thioacetamide and urea. The success of this approach is a little surprising in that CdS deposition has in general been associated with baths which are supersaturated with respect to hydroxy–cadmium species.[7]

Experimental

Chemical baths used to deposit films

The CdS thin films were grown on commercial tin oxide (TO) glass substrates (LOF Tec 10, Libby-Owens Ford) from solutions containing cadmium salt (chloride; 0.02 mol dm^{-3}), urea (0.5 mol dm^{-3}) and thioacetamide (0.2–0.02 mol dm^{-3}) to obtain a solution (100 cm^3) of final pH 5.5–4.9 (adjusted by dropwise addition of 5 M HCl or NaOH). An EIL 7000 pH meter with temperature compensation and Russell glass electrode (calibrated against standard pH 7.00 and 10.00 buffers) were used to record solution pH. Substrates were degreased and cleaned thoroughly by ultrasonication using a standard procedure, before immersion in the chemical bath. The reaction mixture was maintained at the appropriate temperature (343–353 K) for deposition, with occasional stirring. Substrates were removed from the bath after the desired period of time, washed with de-ionised water and any adherent particulate matter removed by ultrasonic agitation. The substrates were allowed to dry under ambient conditions (*ca.* 2 h) before film characterisation or a further annealing step in air.

Characterisation of thin films

Electronic absorption spectra were recorded with a Philips PU 8710 spectrophotometer. X-Ray diffraction studies were performed using secondary graphite monochromated Cu-Kα radiation (40 kV) on a Philips X'Pert Materials Research

Table 1 Comparison of diffraction data for CBD CdS with literature values

CdS[a]		CdS[b]		Greenockite			Hawleyite		
d-spacing/Å	rel. int.	*d*-spacing/Å	rel. int.	*d*-spacing/Å	rel. int.	*hkl*	*d*-spacing/Å	rel. int.	*hkl*
3.581	54.18	3.582	30.37	3.586	62	100	3.36	100	111
3.347	100	3.360	78.84	3.360	91	002	2.9	40	200
3.157	88.25	3.163	100	3.163	100	101	2.058	80	220
2.466	8.52	2.655	33.51	2.452	29	102	1.753	60	311
2.066	33.8	2.447	18.84	2.070	48	110	1.68	10	222
1.895	29.94	2.383	32.89	1.900	50	103	1.453	20	400
1.759	22.56	2.372	21.47	1.793	8	200	1.337	30	331
		2.320	2.9	1.763	31	112	1.298	10	420
		2.066	27.85	1.732	15	201	1.186	30	422
		1.895	33.9	1.680	5	004	1.12	30	333,511
		1.769	66.89	1.582	3	202	1.028	5	440
		1.730	10.43	1.521	3	104	0.985	20	531
		1.678	12.49	1.400	15	203	0.918	5	620
		1.581	2.31	1.355	5	210	0.887	5	533
				1.329	8	211			
				1.304	4	114			
				1.258	9	105			
				1.226	2	204			
				1.195	9	300			
				1.160	14	213			

[a]As-deposited. [b]Air-annealed CBD CdS.

Diffractometer (MRD). Measurements were taken using a glancing angle incidence detector at an angle of 3°, for 2θ values over 20–60° in steps of 0.04° with a count time of 1 s. Scanning electron microscopy and EDAX measurements were conducted using a JEOL Superprobe 733 microscope. Samples were carbon coated before analysis. A JEOL-JEM 2010 transmission electron microscope operating at 200 kV was used for HRTEM studies and to obtain electron diffraction patterns. The XPS measurements were performed in the ultra-high vacuum chamber (base pressure 10^{-8} Pa) of a VG ESCALAB-Mk II (VG Scientific) using Al-Kα excitation (analyser pass energy of 50 eV). The energy scale was calibrated using C_{1s} (at 284.8 eV) as a reference. The photoluminescence measurements were recorded for samples using the 458.4 nm line of an Ar^+ laser at different excitation densities (20, 1, 0.06 W cm^{-2}), with a cryostat cold finger at 6 K.

Results and discussion

Structural studies

Glancing angle XRD measurements were recorded and the diffractograms compared with standards in the JCPDS data files (Table 1 and Figure 1). The as-deposited material appears to be composed of the hexagonal phase of CdS,[8] with little evidence for the incorporation of the cubic modification. In particular the peaks at 28.4° and 53° are associated only with the hexagonal phase; the absence of the peak at 31.5° also provides good evidence for the relative unimportance of the cubic phase in our as-deposited CBD CdS. The most significant feature of spectra of the films after annealing in air was an increase in the crystallinity of the films.

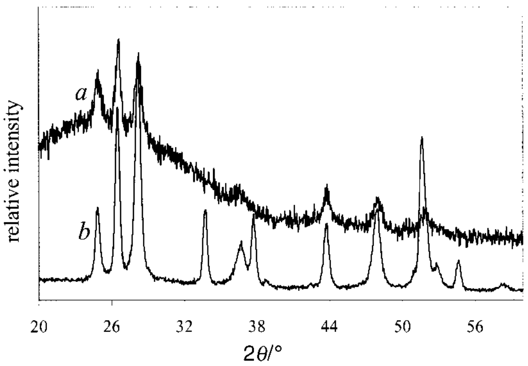

Fig. 1 Glancing angle XRD of CBD CdS. The crystallinity of (*a*) the as-deposited film is improved after (*b*) air annealing for 30 min.

Fig. 2 shows a SEM micrograph of an as-deposited CdS film. The films appear to be dense, conformal and composed of largely irregular shaped grains of diameter in the range 300–500 nm; EDAX results were consistent with thin CdS films deposited on tin oxide glass. These larger grains are comprised of smaller particles of 10–20 nm diameter. The TEM micrographs of thinner sections at the edges of grains appear to exhibit lattice fringes (Fig. 3). Thermal treatment of the samples provided films for which the diffraction pattern from thinner areas were bright, spotted and identified to be hexagonal CdS (Fig. 4).

It is widely known that CBD processes are associated with films which possess a relatively high concentration of impurities (*ca.* 0.1–1% wt/wt).[9] The use of XPS as an analytical technique for surfaces is common,[10] although the spatial resolution

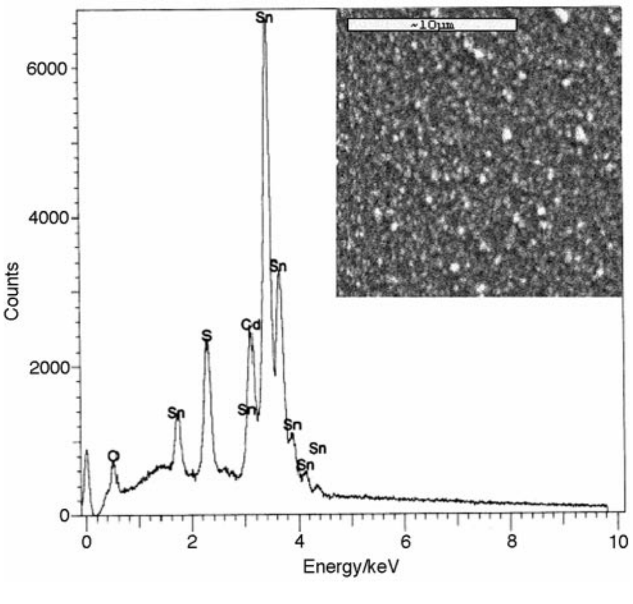

Fig. 2 SEM and EDAX of cadmium sulfide deposited on tin oxide glass from acid baths.

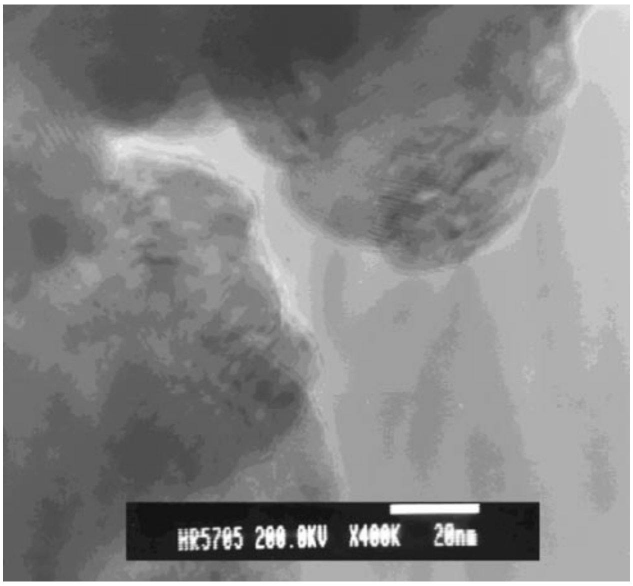

Fig. 3 Transmission electron micrograph of CdS film deposited from acidic chemical bath. Average particle diameter of the order 10 nm. Lattice fringes are observed from edge features of the film.

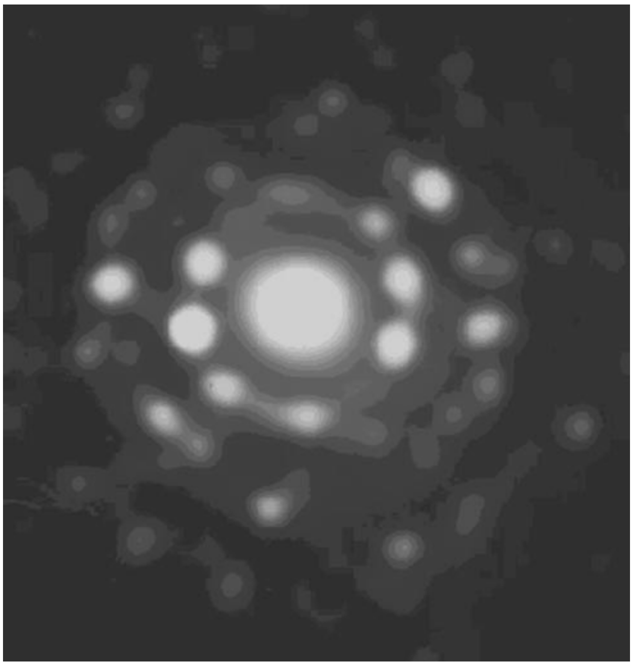

Fig. 4 Electron diffraction pattern obtained from air-annealed CdS film.

Table 2 XPS data obtained for acidic CBD CdS films. Photoelectron peak assignments made by comparison with literature values (see ref. 9). Annealing of the films reduces the nitrogen impurity to below the detection limits of the instrument, concentration of surface chloride is apparent after annealing

	Binding energy/eV	
Photoelectron peak	CdS as-deposited	CdS air-annealed
Cd $3d_{5/2}$	405.1	405.1
Cd $3d_{3/2}$	411.9	411.9
Cd (Auger)	1105.2/1111.2	1105.0/1111.5
S $2p^a$	162.0	162.0
N 1s	395.7	
O 1s	531.9	531.8
C 1s	284.8	282.8
Cl $2p_{3/2}$		199.5

^{a}S 2p components are observed as a broad peak.

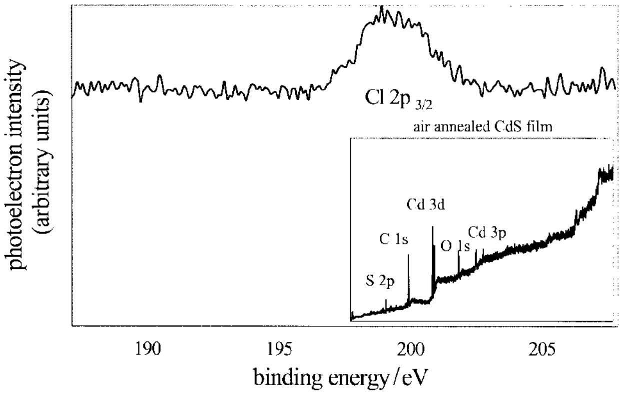

Fig. 5 X-Ray photoelectron spectra of air-annealed CBD CdS. The development of a weak chloride peak with binding energy at 199.5 eV is highlighted. The inset shows the major peaks in the spectrum.

($\approx$0.2 mm) is relatively poor. The basis of the chemical shift of a core photoelectron peak is the change in electrostatic potential on the core electron when the valence electron charge density is accepted or withdrawn from the atom, hence a relationship exists between the binding energy and the chemical state of the element. Or, in other words, non-equivalent atoms of the same element in a solid give rise to core-level peaks with measurably different binding energies. The XPS spectra for our CBD CdS were typical for CdS films reported by other workers.[11] An important observation was the presence of carbon, nitrogen and oxygen as impurities in the as-deposited films (Table 2). Upon annealing of films in air, the nitrogenous contaminant was reduced to a concentration below the detection limit of the instrument; concurrently a concentration of chloride species was observed in the XPS spectrum (Fig. 5). Similar observations have been made by ourselves and others employing the SIMS technique[12,13] and XPS.[14] The presence of a chloride-rich layer has been associated with efficient type-conversion of CdTe upon annealing of CdS/CdTe heterojunction devices.[15] The O 1s line ($\approx$532 eV) possesses a narrow bandwidth and symmetric shape and is a sensitive probe for the presence of oxidation products. The annealing process in air does not appear to degrade the CdS films; the absence of a photoelectron peak at 168.7 eV (S 2p for SO_4^{2-} of cadmium sulfate)[14] was an indication that formation of undesirable oxidation products was not a significant process. The broad nature of the O 1s peak was interpreted as a multiplicity of chemically and physically bound water in the surface region.

Optical and electronic characterisation

The spectra of the films were typical for those reported by many workers for polycrystalline CdS thin films.[16] All films were optically transparent, pale orange to red in colour. This colour changed to pale yellow upon annealing in air at 673 K. The change in colour with thermal treatment is a widely reported phenomenon and is the subject of some debate for CdS thin films.[17] The bandgaps of the films were determined before and after annealing. The linear dependence of α^2 with $h\nu$ was indicative of direct bandgap material. Extrapolation of the linear region of the absorption profile from plots of α^2 *vs.* eV provided data on the change in bandgap upon annealing in air (Fig. 6). Annealing produced a more defined band-edge and shift in the bandgap from 2.39 eV to 2.32 eV.

The photoluminescence (PL) spectra of semiconductors can yield important information on the quality and composition of the material. By studying the dependence of the intensity of the PL emission with incident laser power, we can make deductions about the physical and chemical nature of the PL

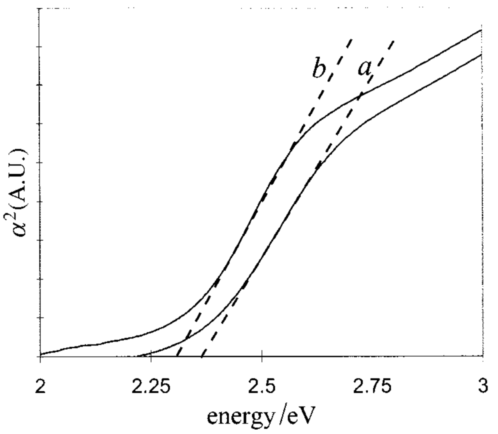

Fig. 6 Plot of the square of the absorption coefficient α *vs.* electronic absorption energy (eV). Extrapolation of the straight line edge of the electronic spectra to the *x*-axis yields bandgap energies of (*a*) 2.39 eV (as-deposited) to (*b*) 2.32 eV (air-annealed).

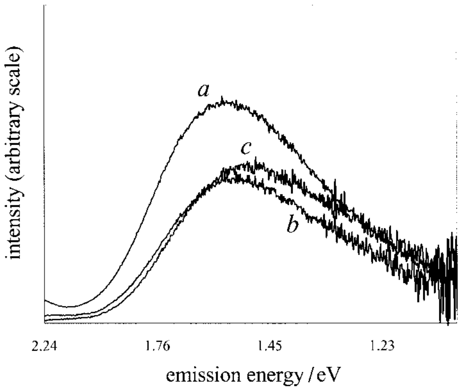

Fig. 7 Photoluminescence (PL) emission spectra for acid CBD CdS films produced from Bath A. The spectra were recorded for different excitation densities of (*a*) 20 W cm^{-3}, (*b*) 1 W cm^{-3} and (*c*) 0.06 W cm^{-3}. Units on intensity scale are arbitrary to allow presentation of the spectra on a single plot.

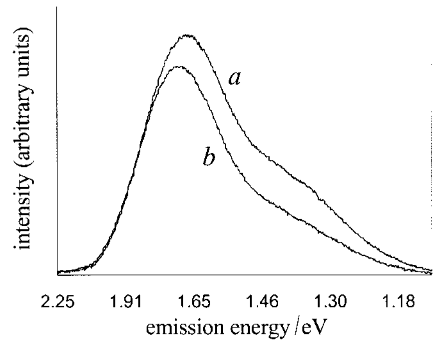

Fig. 8 Effect of annealing on the PL emission spectra of acid CBD CdS films. A red-shift of the low energy tail is observed; (*a*) air annealed, (*b*) as-deposited.

emission.[18] A variety of electron–hole radiative recombination processes can occur. The most useful PL emission for study is that which originates from near band-edge emission, because it gives us information on the electron–hole pair (excitons) energy states. We only observe these excitonic transitions at very low temperatures (usually below 10 K) because the electron–hole pairs have very small binding energies and are easily dissociated by thermal energy (thermal quenching).

We have established from TEM/SEM measurements of acid CBD CdS that our thin films are polycrystalline, consisting of large primary particles (*ca.* 300–500 nm in diameter) which are composed of smaller grains of around 10–20 nm in diameter. As the materials possess many grain boundaries, we would expect that our CBD CdS films would have poor PL efficiencies, as grain boundaries often provide an effective route for non-radiative processes.[19] Grain boundaries and other defects such as dislocations cause a high perturbation to the crystal potential, which in turn produces dissociation of the excitons. The annealing process would be expected to increase the CdS grain size and thereby reduce the number of grain boundaries.

It is reported that the concentration of chalcogenide reagent in the deposition bath has an effect on the optical and electronic properties of the resultant films.[1] In order to investigate further the phenomenon, two different chemical baths differing only in the concentration of thioacetamide (0.02 or 0.2 mol dm^{-3} for Bath A and B respectively) were used to deposit thin films of CdS on TO glass for PL characterisation. The reaction conditions and compositions of Bath A and Bath B ([Cd] = 0.02 mol dm^{-3}, [urea] = 0.5 mol dm^{-3}) were otherwise identical. In contrast to the observations made by other workers, for room temperature PL of CBD CdS films,[20] the PL emission for all samples consisted of a broad band with energy maxima in the range 1.59–1.45 eV (Fig. 7). In polycrystalline systems the PL emission lines are not sharp peaks but are broad bands because of the presence of many recombination sites; the grains will have different impurity concentrations, surface areas and defect types and concentrations (*e.g.* stacking faults). Hence the individual PL emission lines will have a range of energies and form a broad band. Films deposited from Bath A on the tin oxide side of the TO glass also produced an additional band centred at 1.36 eV.

Annealing of the films at 400 °C for 0.5 h produced a bathochromic shift of the low-energy component(s) of the PL emission and an increase in PL emission intensity (Fig. 8). Increasing the concentration of thioacetamide from 0.02 mol dm^{-3} to 0.2 mol dm^{-3} produced a decrease in the PL emission energy. It was observed that there was a hypsochromic shift of around 0.03 eV for the PL spectra of films deposited on the glass side of the TO glass substrate, in comparison with those films formed on the tin oxide layer.

The likely origin of the broad emission band is the reaction of photogenerated positive holes h^+ (*via* the exciting laser) in the valence band with sulfur vacancies V_S. We can also consider the radiative recombination of photogenerated conduction band electrons e^-_{CB} with deep electron traps $V_S^{\cdot}$. In bulk CdS the material is slightly sulfur deficient and hence contains S^{2-} vacancies (V_S). These vacancies are very deep level traps for electrons; also they can exothermically extract an electron from a full valence band.[21] This will produce a positive hole in the valence band and a V_S (called a F-centre). The ionised vacancy can then accept a photogenerated conduction band electron and so the process can continue.

The PL emission intensity is known to vary with the intensity of the exciting laser. The relationship is often given as

$$I_{\mathrm{PL}}\ \alpha\ I_{\mathrm{L}}^{k}$$

where k is a number between 0 and 2, I_{PL} is the luminescence intensity and I_{L} is the laser intensity. In general, for PL emissions which originate from excitonic process (*i.e.* electron–hole pairs) the value is between 1 and 2, for PL emissions which originate from electron donor–acceptor (D–A) pairs or free-to-bound excitons (an exciton which is reduced in energy because it is bound to an impurity atom) we have k-values of less than 1. The k-values for our CBD CdS were calculated and are given in Table 3.

As the power of the exciting laser is varied over more than two orders of magnitude, it is known that the value of k is not constant for D–A or free-to-bound PL emission bands, but is constant for excitonic processes. Increasing the laser power also causes a blue shift or widening in the PL emission

Table 3 Photoluminescence characteristics of CBD CdS films with variable intensity laser excitation

	Ph_{max}/eV (intensity)				
	Bath A			Bath B	
Laser intensity/ W cm^{-2}	Film 1[a]	Film 1;1 (glass side)[a]	Film 2[b]	Film 3[a]	Film 4[b]
20	1.562(15.52)	1.594(19.26)	1.557(34.5)	1.524(30.57)	1.476(44.87)
1	1.548(2.27)	1.582(1.985)	1.524(4.42)	1.512(3.4)	1.454(4.58)
0.06	1.525(0.205)	1.562(0.194)	1.486(0.502)	1.512(0.25)	1.44(0.39)
k-value/R^2 (best-line-fit value)	0.744/0.993	0.791/0.999	0.728/0.999	0.826/0.995	0.817/0.613

[a]As-deposited films. [b]Air-annealed films.

bands for D–A pair processes. The PL emission from our CBD CdS films is blue-shifted with increasing excitation laser power, which would be consistent with D–A or free-to-bound type emission. The k-values for the PL emission maxima were found to be in the range 0.72–0.83, the values were larger for films deposited from Bath B (*i.e.* higher concentration of thioacetamide). The k-values were found to decrease after annealing of the films. For films deposited from Bath A, the k-values decreased from 0.744 to 0.728, for films from Bath B the k-value decreased from 0.826 to 0.816. A reduction in the k-value is generally associated with an increase in competing recombination processes, which can be radiative or non-radiative. As the PL intensity actually increases after annealing, this would suggest that the competing process is radiative. For CBD CdS there are many impurities incorporated in the films which can be neutral, ionised donors or acceptors. For PL emissions which occur from D–A pairs, we can observe sharp line spectra for pairs which are close but broad bands for D–A pairs which are relatively distant from each other. To observe these phenomena we require high excitation laser densities to overcome the increased non-radiative recombination rates for close D–A pairs. These experiments will be the subject of a future study.

Conclusions

In this work we have demonstrated that conformal crystalline CdS thin films of good morphology can be deposited from moderately acidic baths. We believe this is the first time that cadmium sulfide thin films have been deposited by electroless methods from acidic baths containing thioacetamide. The adherence is in this case good and the films do not resemble in this property, or their morphology, those deposited for conditions undersaturated with respect to hydroxy–cadmium species at alkaline pH. The as-deposited films appear to be hexagonal phase; air-annealing increases the crystallinity of the films and induces a migration of chloride ions to the surface region, as detected by XPS. No definitive evidence for significant oxidation of the CdS upon air-annealing was found. Low temperature PL spectra exhibit complex intensity-dependent characteristics, which are consistent with donor–acceptor transitions and a change of radiative recombination pathway upon annealing of CdS films. These results open up the possibility of depositing ternary films of (Cd,Zn)S under acidic conditions. We are actively developing acidic baths for the deposition of ternary materials.

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