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A novel method for the synthesis of the ternary thin film semiconductor cadmium zinc sulfide from acidic chemical baths†

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The deposition of ternary materials such as $Cd_{1-x}Zx_nS$ by chemical bath methods is a problem due to differing hydrolytic stabilities of the two metals. A novel approach to the deposition of this material has been developed in which moderately acidic baths are used.

There is considerable interest in the deposition of ternary derivatives of CdS such as $Cd_{1-x}Zn_xS$ for photovoltaic applications. The ternary material has the hexagonal wurzite structure and a wider band gap than CdS, which should make it a better window material for use in heterojunction solar cells.[1] There is the potential to tailor both the lattice parameter and band gap by compositional control to provide improvements in device efficiencies (*e.g.* by matching of electron affinities to minimize band discontinuities in p–n heterojunction assemblies). There are many fabrication techniques for such films including: CVD,[2] successive ionic layer and reaction (SILAR) processing[3] and sol–gel methods.[4] One driver for such research is to develop cheap reproducible and relatively simple route/s for applications where low capital cost is important for successful commercialisation, *e.g.* thin film photovoltaic technologies.

A method, which may meet the above criteria, is Chemical Bath Deposition (CBD).[5] We have recently reviewed some of the chemistry underlying such processes with some emphasis on the incompatibility between the conditions for the deposition of zinc and cadmium sulfide.[6] 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. There are a few reports of the CBD of the ternary $Cd_{1-x}Zn_xS$;[7] the most convincing studies demonstrate that the production of good quality thin films is very difficult by conventional chemical bath systems.[8]

Lincot[9] developed the deposition of ZnS from acidic solutions in which urea hydrolysis is used to control the pH and produced among the best ZnS films reported to date (for a detailed survey see ref. 6). We have reasoned that if CdS could be successfully deposited from similar baths, the possibility of depositing the true ternary as a solid solution could be improved as the problem of the gross insolubility of zinc hydroxy species would be reduced at lower pH.[10] At high solution pH the differences in the solubility products of the sulfide and oxide/hydroxide of zinc are much smaller than in the analogous cadmium system. Metathesis of surface bound $Cd_x(OH)_y$ to CdS may facilitate the deposition; the reaction is less favourable for the zinc species at high solution pH.

We have now demonstrated the deposition of crystalline thin films of CdS from acidic baths.[11] In this communication we report our initial, successful, attempts in developing this approach for ternary films, experiments which have at present been focussed on high cadmium compositions. In this context we believe that the overall CBD process has been driven towards an ion-by-ion mechanism of the type thought to predominate for CdS.

In a typical experiment, thin films (*ca.* 30–50 nm) of the ternary $Cd_{0.9}Zn_{0.1}S$ were grown on tin oxide glass substrates from acidic baths (pH 5.5–4.9) containing cadmium chloride (0.005 mol dm^{-3}), zinc chloride (0.015 mol dm^{-3}), urea (0.5 mol dm^{-3}) and thioacetamide (0.2 mol dm^{-3}). The stirred reaction mixture was maintained at 343–353 K for deposition, substrates were removed from the bath after 1–2 h, 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 characterization or a further annealing step in air.§ Some typical experiments are summarized in the supplementary material.†

This acidic CBD route provides films of a well-defined ternary composition, in contrast to those reported from basic solution.[8] As-deposited films were yellow-orange in colour and adherent, annealing in air (500 °C for 30 min) produced adherent and specular pale yellow films. Glancing angle X-ray diffraction (XRD) measurements were recorded and the diffractograms compared with data in the JCPDS data files. Air annealed films were optically transparent and highly crystalline, the pattern of prominent peak positions was consistent with a hexagonal "wurzite-type" structure[12] and is

Table 1 Glancing angle XRD (GAXRD) data obtained for ternary $Cd_{0.9}Zn_{0.1}S$ films on TO glass. Diffraction lines were indexed to the hexagonal structure. Lattice parameters were calculated ($a_o = 4.11$ Å and $c_o = 6.68$ Å; $c/a = 1.62$) from least squares fit to diffraction data

d-Spacing/Å	Intensity (%)	*hkl*
3.569	28.24	100
3.344	100	002
3.150	41.67	101
2.058	14.09	110
1.888	24.68	103
1.753	14.52	200
1.658	24.09	004

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†Electronic supplementary information (ESI) available: details of CBD experiments. See http://www.rsc.org/suppdata/jm/b0/b005544l/

‡Present address *b*.

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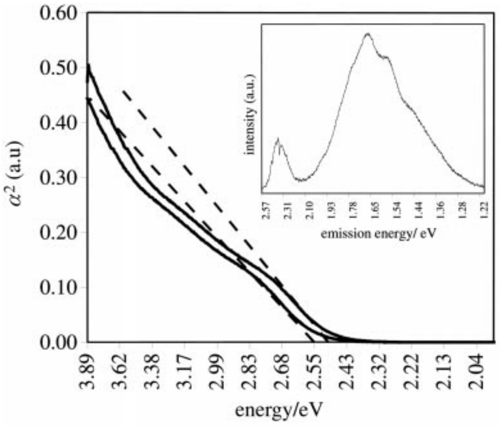

Fig. 1 Electronic absorption and low temperature (9.4 K) photoluminescence (PL) spectra (inset) of ternary $Cd_{0.9}Zn_{0.1}S$ thin films. PL intensities are reported in arbitrary units.

reported in Table 1. Lattice parameters were calculated ($a_o = 4.11$ Å and $c_o = 6.68$ Å) and the composition of the ternary was determined (assuming Vegard's Law) to be $Cd_{0.9}Zn_{0.1}S$ ($x = 0.086(9)$).

The bandgaps of the films were determined from electronic absorption spectra before and after annealing by the direct bandgap method (from plots of α^2 *vs.* energy) (Fig. 1). Annealing produced a shift in the bandgap from 2.55 eV to 2.50 eV (this work will be described in more detail in a future publication). The composition of the ternary $Cd_{1-x}Zn_xS$ was estimated from the relationship

$$E_g(x) = 2.42 + 0.69x + 0.61x^2$$

where $E_g(x)$ is the bandgap for the composition defined at x.[13] The calculated value for x was 0.11 for the annealed films which is in reasonable agreement with the value ~0.09 obtained *via* diffraction methods. Low temperature photoluminescence (PL) spectra of annealed films were complex and comprised of two broad emission bands, centred at ~2.4 eV (near bandgap emission) and ~1.65 eV (assigned to deep trap levels).

The surface morphology of films was assessed by scanning electron microscopy (SEM). Films were dense, homogeneous and composed of large grains (~500 nm diameter) with preferential growth on the tin oxide coated side of the TO glass substrate. Energy dispersive analytical X-ray analysis (EDAX) profiles were consistent with formation of the ternary compound, the approximate elemental ratios were estimated (from peak area analysis) as 8 : 2 : 10 Cd : Zn : S. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements presented further evidence of increasing crystallinity with thermal treatment (Fig. 2). Air-annealed films gave SAED patterns from their thinner areas which were bright, spotted and hexagonal. The large grains were found to be comprised of smaller primary particles (*ca.* 20–30 nm in diameter); no significant growth of these units with annealing was evident. X-Ray photoelectron spectroscopy (XPS) was utilized to gain information on the elemental composition and electronic state of the surface of the films (Fig. 3). The binding energies of the major peaks were consistent with the formation of ternary material. Minor features were assigned to carbon (C 1s 284.8 eV) and oxygen (O 1s 531.8 eV) which were tentatively attributed to incorporation into film during CBD; similar observations have been made by other groups.[14]

In conclusion, we report the first definitive evidence for the successful preparation of polycrystalline thin films of cadmium zinc sulfide by Chemical Bath Deposition (CBD) from acidic solutions. We have identified a novel approach based on the use of low solution pH. The films have been characterized 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 ternary composition has been defined to be $Cd_{0.9}Zn_{0.1}S$. The success of the approach is rationalized in terms of overcoming the fundamental differences between CdS and ZnS CBD systems and driving the process towards a surface controlled ion-by-ion deposition.

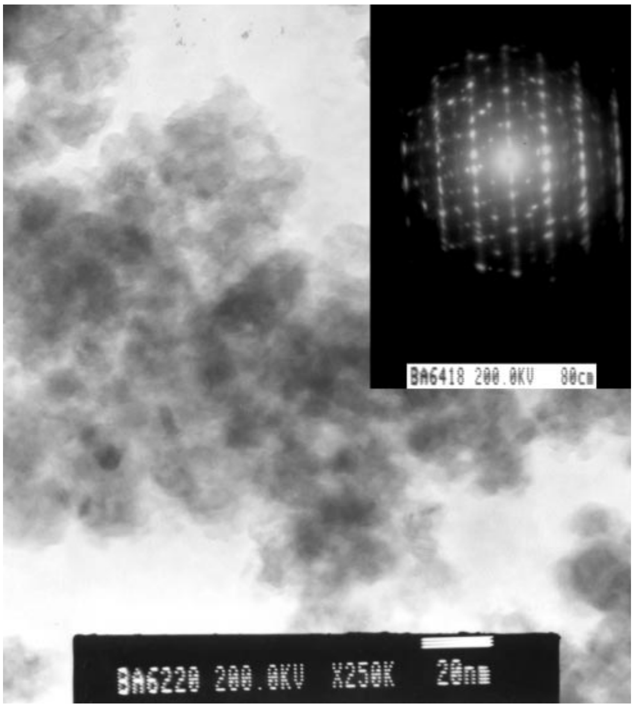

Fig. 2 TEM and SAED (inset) measurements of air-annealed $Cd_{0.9}Zn_{0.1}S$ films.

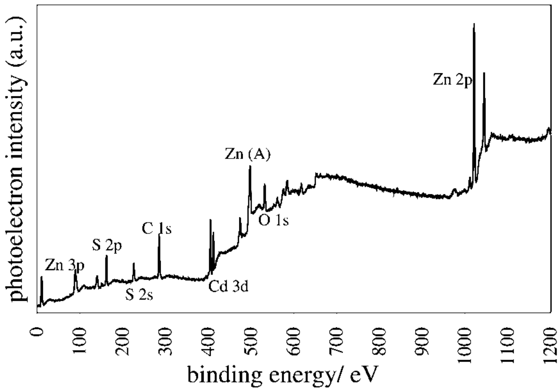

Fig. 3 X-Ray photoelectron spectrum of air-annealed $Cd_{0.9}Zn_{0.1}S$ films on TO glass.

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Notes and references

§Experimental: In a typical experiment good quality films (*ca.* 30–50 nm as determined by Quartz Crystal Microbalance (QCM) measurements) of the ternary $Cd_{0.9}Zn_{0.1}S$ were produced on commercial tin oxide (TO) glass substrates (Libby-Owens Ford) from acidic bath solutions (pH 5.5–4.9 adjusted by dropwise addition of 5 M HCl or NaOH) containing the desired concentrations of cadmium chloride (0.005 mol dm^{-3}), zinc chloride (0.015 mol dm^{-3}), urea (0.5 mol dm^{-3}) and thioacetamide (0.2 mol dm^{-3}). The stirred reaction mixture was maintained at the appropriate temperature (343–353 K) for deposition. Substrates were removed from the bath after the desired period of time (*ca.* 1–2 h), 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 characterization or a further annealing step in air.

Electronic absorption spectra were recorded with a Philips PU 8710 spectrophotometer. The PL measurements were obtained at 10 K using the 457.9 nm line of an Ar laser and excitation density of 3.0 mW mm^{-2} (spectral resolution of 2 nm), with a 495 nm long wavelength pass filter in front of the monochromator. X-Ray diffraction studies were performed using secondary graphite monochromated CuK_{α} radiation (40 kV) on a Philips X'Pert Materials Research 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 (SEM) (EDAX) studies were carried out on a JEOL J535CM instrument with a LINK QX2000 unit. Samples were carbon coated before analysis. A JEOL-JEM 2010 transmission electron microscope operating at 200 kV was used for TEM 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.

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