



# Ternary cadmium zinc sulphide films with high charge mobilities



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## ABSTRACT

Cadmium zinc sulphide thin films with high charge mobilities are obtained from acidic chemical baths employing the corresponding metal chlorides, urea and thioacetamide. The films are characterized by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, inductively coupled plasma mass spectrometry, absorption spectroscopy and charge transport measurements. The compositional control afforded by the technique and the resultant changes in the structural, optical and electronic properties of the films are critically examined. We find good correlation between structure and properties at extremes of the composition range.

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## 1. Introduction

The ternary semiconductor cadmium zinc sulphide ( $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ) has received much attention over the last two decades [1–4]. Much of the interest in these solids is due to their band gaps being between 2.53 and 3.70 eV, a spectral range crucial for applications such as solar energy generation. A combination of smaller lattice constant (compared to CdS) and wider band gap make cadmium zinc sulphides particularly attractive for use in  $\text{CuInGaSe}_2$  and related solar cell architectures. Performance gains underpinned by greater lattice compatibility and lower absorption losses are widely anticipated [5]. Renewed focus in the area of renewable energy generation has lent impetus to the search for routes capable of producing good quality thin films of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  [6].

A number of processes have been developed for the preparation of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  thin films including electrodeposition [7], chemical bath deposition (CBD) [5], successive ionic layer adsorption and reaction (SILAR) [8] and metal organic chemical vapour deposition [9]. Chemical bath deposition with the ability to inexpensively

produce high quality deposits over large areas is particularly attractive [10–12]. Previous studies suggest that deposition of ternary  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  solids by chemical bath deposition is challenging due to differing hydrolytic stabilities of the two metal ions and the gross insolubility of  $\text{Zn}(\text{OH})_2$  [13,14].

In a series of articles, we have previously shown how CdS and Cd rich Cd–ZnS alloys can be obtained by from acidic medium [4,14,15]. This method uses thioacetamide to generate the sulphide and urea hydrolysis to regulate the pH. The acidic CBD route provides films of a well defined ternary composition, in contrast to those reported from basic solution. This paper reports the deposition and characterization of cadmium zinc sulphide thin films  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  ( $0 \leq x \leq 1$ ) across the entire composition range by CBD under acidic conditions.

## 2. Experimental

Aqueous solutions of cadmium chloride (0.05 M), zinc chloride (0.15 M), urea (5 M) and thioacetamide (1 M) were prepared. Different volumes of these solutions were mixed together in a beaker to obtain a 70 mL solution with overall metal ion concentration of 0.01 mol. The concentrations of Zn and Cd ions in solution were independently ascertained by atomic absorption spectroscopy. In this mixture, 0.1 mol of urea and 0.08 mol of thioacetamide

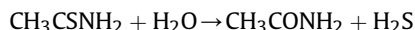
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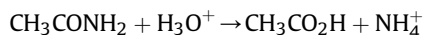
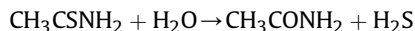
were also present. The pH of the solution was adjusted to 4 by drop-wise addition of 2 M HCl. A Mettler-Toledo pH meter with temperature compensation and glass electrodes (calibrated against standard pH 4.01, 7.00 and 9.21 buffers) was used to monitor the pH of the solution. The reaction mixture was stirred and maintained at a temperature of 353 K. The pre-treated silica glass substrates were immersed vertically into the prepared baths 5 min after visible turbidity was first apparent. The substrates were removed from the bath after 2 h, washed in de-ionised water and any adherent particulate matter removed by ultrasonic agitation. The substrates were allowed to dry under ambient conditions before film characterization.

Optical absorption spectra were recorded with a Cary 5000 spectrophotometer within the wavelength range of 800–200 nm, at room temperature. X-ray diffraction studies were performed using secondary graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) source over the diffraction angle  $2\theta$  between  $3^\circ$  and  $80^\circ$  on a Bruker D8 powder X-Ray Diffractometer. The scan time for each sample was three hours. Scanning electron microscopy (SEM) measurements were conducted using a Philips XL30 FEG SEM. The elemental composition of the samples was determined using an energy dispersive X-ray analysis (EDAX) attached to the scanning electron microscope. Films were carbon coated using a GATAN Model 682 precision etching coating system before carrying out the SEM and EDAX. The sheet resistance was measured using a Keithley 2400 source measure unit employing Os–Ir four point probes.

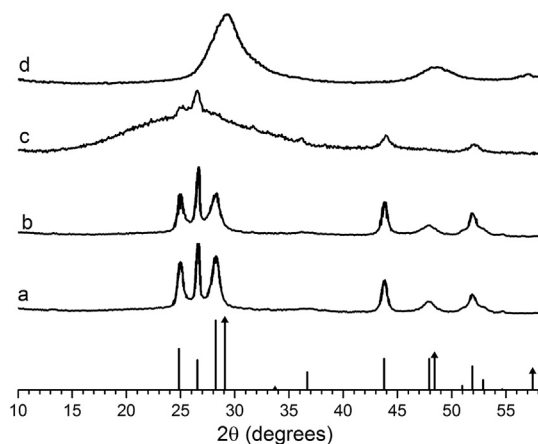
The deposition involves the generation of sulphide ions by the decomposition of thioacetamide under acidic pH at elevated temperature.



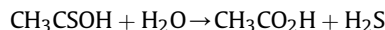
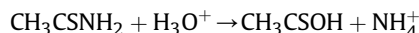
The decomposition could proceed by one of the two pathways [16,17], producing either acetamide ( $\text{CH}_3\text{CONH}_2$ )



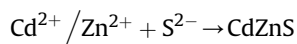
or thioacetic acid ( $\text{CH}_3\text{CSOH}$ ) as intermediates.



**Fig. 1.** X-ray diffraction patterns of (a) CdS; (b)  $\text{Cd}_{0.86}\text{Zn}_{0.14}\text{S}$ ; (c)  $\text{Cd}_{0.4}\text{Zn}_{0.6}\text{S}$ ; (d) ZnS deposits. The films obtained were annealed for 1 h at  $420^\circ\text{C}$  in an inert atmosphere (under  $\text{N}_2$  flow). The intensities and positions of the standard peaks are indicated. The line capped with triangles correspond to reflections from the cubic phase, while the others belong to hexagonal CdS.



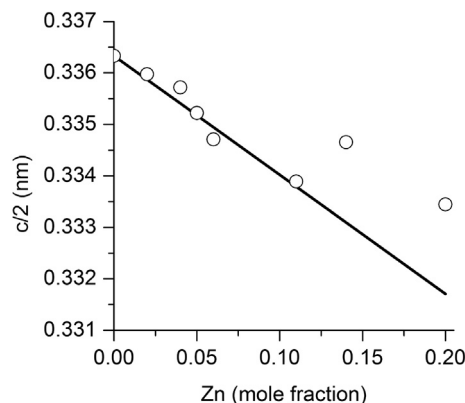
The liberated sulphide ions react with Cd and Zn ions to deposit CdZnS.



Urea in the medium moderates the pH by hydrolysis [4,14,15]. At the end of deposition, well-adhered, translucent yellow films were obtained.

X-ray diffraction revealed a number of structural variations accompanying composition change in  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  deposits. The pattern from pure CdS films consisted of reflections that are broader than what is expected from bulk CdS, but is clearly assignable to the hexagonal wurtzite phase (JCPDS, reference code: 00-001-0780, see Fig. 1a). Prominent peaks at  $24.8^\circ$ ,  $26.5^\circ$  and  $28.2^\circ$  can be attributed to reflection from the (100), (002) and (101) planes of CdS in wurtzite form. We note that the peaks at  $28.2^\circ$  and  $52.9^\circ$  are unique to the hexagonal structure and further, the reflection characteristic of the cubic phase at  $31.5^\circ$  is absent, implying that cubic CdS is not present [4]. The relative intensity of the (002) reflection is high, indicating the deposits are oriented with the c-axis perpendicular to the substrate. Such growth is particularly sought after as it is epitaxial with the (112) planes of  $\text{CuInGaSe}_2$  and  $\text{Cu}_2\text{ZnSnS}_4$  active layers used in thin film solar cells [5]. In contrast to CdS, pure ZnS deposits consisted of reflections due to the cubic form (see Fig. 1d), albeit with broader peaks. Hence, ZnS prefers the cubic phase and is less crystalline than CdS. We note that poorer diffraction by ZnS is not due to changes in film thickness as comparable diffraction patterns were obtained when precipitates at the bottom of the vessel were used.

It is expected that the introduction of smaller Zn ions in CdS, by altering the feed ratio in the mother liquor would bring about tangible structural changes including in the lattice constants. The introduction of small quantities of Zn ions (below 12%) yields diffraction patterns similar to the one in Fig. 1a albeit with reflections shifting to higher angles indicating a contraction of the lattice. A typical pattern is in Fig. 1b. A plot of the position of the  $d_{002}$  reflection (located by analysis of derivatives) versus the mole fraction of Zn is close to linear (see Fig. 2). The lattice parameters of mixed crystals often obey a simple regularity: in that they depend linearly on the composition. This is particularly valid for substituted solid solutions such as CdZnS [18]. Adherence to this relationship



**Fig. 2.** Plot showing the variation of  $d_{002}$  reflection as the mole fraction of Zn is increased in annealed CdZnS deposits.

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