# *In situ* kinetic studies of the chemical bath deposition of zinc sulfide from acidic solutions

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Adherent and uniform films of zinc sulfide have been deposited reproducibly by chemical bath deposition (CBD), onto low iron content microscope slides, under acidic conditions from solutions containing zinc(II) chloride, urea and thioacetamide. *In situ* measurements using a quartz crystal microbalance suggest that film growth occurs after a short induction period, *via* an initial rapid phase (deposition rate of 91 nm h$^{-1}$), followed by a slower process (growth rate of 52 nm h$^{-1}$). The ZnS films are predominantly of the hexagonal modification (wurtzite structure), as determined by X-ray powder diffraction. Scanning electron micrographs of the deposited layers, obtained on samples removed at regular intervals from the bath, suggest that as the reaction proceeds, uniform film growth is associated with increasing particle size, rather than continuous nucleation and deposition of new primary particles. EDAX spectra of the films are typical of thin CBD-deposited layers of ZnS; signals attributable to elements within the glass substrate are also detected. Grain size distributions have been investigated using computational image analysis, and an average grain growth rate of 33.7 nm h$^{-1}$ has been calculated.

## Introduction

Zinc sulfide (ZnS) is a wide, direct band gap semiconductor which crystallises in both cubic and hexagonal forms. A diverse range of applications exists for thin films of ZnS, primarily within photovoltaic or optoelectronic devices.[1–4] Various techniques have been employed to prepare thin films of ZnS, including r.f. sputtering, metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE).[5,6] Such vapour-phase deposition methods demand the use of either vacuum conditions and/or complex equipment. In contrast, chemical bath deposition (CBD), also known as chemical solution deposition, is a method that is simple, convenient and inexpensive. Films may be deposited at low temperatures on a variety of substrates. The thickness of the deposited layers may be readily controlled by variation of the deposition time. The process should be easily adaptable to large area processing with low fabrication cost. Thin films deposited by this method can be of high quality and studies of the deposition of ZnS by CBD form the subject of the present work. The CBD method has been successfully employed to deposit a broad range of semiconductor materials as thin films, including binary materials, such as cadmium sulfide (CdS),[7–11] indium trisulfide (In$_2$S$_3$)[12] and bismuth trisulfide (Bi$_2$S$_3$),[13] together with ternary phases, such as copper indium diselenide (CuInSe$_2$)[14–17] and cadmium zinc sulfide (Cd$_{1-x}$Zn$_x$S).[18,19]

The CBD process typically, although not exclusively, involves the decomposition of suitable precursors in alkaline solutions, such as a chalcogenide source in the presence of a metal salt. The reaction takes place between the dissolved reactants, generally in aqueous solution, at low temperatures (typically within the range *ca.* 303–353 K). In principle, the process utilizes a controlled chemical reaction to effect deposition by precipitation. Substrates, a large number of which may be coated during the course of a single cycle, are immersed in a solution containing the chalcogenide source, the metal ion, added acid or base (to modify the solution pH) and a chelating agent. The latter is used to control the speciation (especially the extent of hydrolysis) of the metal ion. The rate of deposition may be controlled by adjusting: the temperature of the bath, pH, stirring rate and the relative concentration of the reactants within the solution (chalcogenide source, chelating agent and/or metal ion). Film deposition occurs from solution, the solubility product of the compound in question (at least in part) maintains the stoichiometry of the deposited material. In general, the controlling physicochemical factors for successful CBD are the supersaturation of the solution and the kinetics of the growth process, the latter especially in relation to the catalytic activity of the deposition surface. Equilibria are usually rapidly established within stirred solutions (most of the metal ions are labile), and hence thermodynamic models are useful in assessing the initial stages of deposition from such chemically reactive baths. Studies of the speciation of metals in chemical baths also permit determination of the initial degree of supersaturation within the system.

The deposition of ZnS by CBD represents a more difficult proposition than that of CdS. In particular, it is evident that there is a much wider range of conditions within which the concurrent deposition of ZnS and/or zinc oxide (ZnO) may occur. Many workers have used a second ligand (hydrazine is a popular choice) in chemical baths for the deposition of thin films of ZnS. Ortega-Borges and Lincot.[20] reported that ammonia–thiourea baths yield films that are neither homogeneous nor adherent, but there was a marked improvement upon addition of hydrazine. In a related observation, Dona and Herrero[7] postulated that the addition of hydrazine, although not essential for the growth of ZnS, led to improvements in the films with respect to homogeneity, specularity and growth rate. The same authors suggested that the rate-determining step for the heterogeneous process may involve the dissociation of a bond between the metal ion and the ligand,

DOI: 10.1039/b205158n

although such an explanation is unlikely since zinc is a labile metal ion. Another suggestion was that the hydrazine complexes have a lower coordination number and, therefore, provide less steric impediment to the approach of the sulfide ion. It is also possible that hydrazine might behave as a bridging ligand and perhaps facilitate surface binding.

It is important to appreciate that, at a constant pH, the addition of a second ligand can only lead to a reduction in the free metal ion concentration. In the case of zinc, this will reduce supersaturation with respect to either the oxide/hydroxide phases or the sulfide.

A more detailed investigation into the addition of amines has been undertaken by Mokili et al.[21] It was observed that the addition of: hydrazine, triethanolamine or ethanolamine to ammonia-containing baths resulted in increased growth rates. Notably, the use of hydrazine gave a four-fold increase in the maximum rate of film growth. Other amines tended to increase the rate, but were not held to significantly alter the speciation within the bath. Hence, for hydrazine and triethanolamine, it was suggested that such molecules exert some effect upon the rate at which sulfide ions are delivered to the system. Dona and Herrero[7] have speculated that the relationship between complexing agents and growth rates are typical of a system within which two competing processes are occurring, namely heterogeneous and homogeneous precipitation. They consider the heterogeneous process to be limited both by the "adsorbability" of the complex ion and by the availability of "adsorption points" upon the surface of the substrate.

More recently, Chow and Oladeji[22] reported the deposition of ZnS from a system composed of hydrazine, ammonia, thiourea and added ammonium sulfate. Deposition was investigated both at room temperature (close to 294 K) and at higher temperatures. In the case of deposition at lower temperatures, bath composition might be considered to remain constant. A recent modelling study[23] has sought to provide an insight into the nature of the species that are present within such chemical baths. The formation of ternary complexes, comprising one metal and two different ligands, has been overlooked by all workers who have attempted to discuss speciation within the deposition bath. Values for the stability constants for all possible ternary species were determined and used to model the speciation of zinc in the chemical baths developed by Chow and Oladeji.[22] The incorporation of constants for such species exerts two effects upon the system, notably (i) the formation of ternary complexes becomes important as the total hydrazine concentration tends towards that of ammonia and (ii) the incorporation of constants for the ternary species reduced the calculated free metal ion concentration in the system (pM), thus improving the stability of the solution with respect to hydrolysis.

The calculations supported a number of earlier remarks relating to the conditions most suited to the deposition of ZnS,[24] significantly (i) equivalent levels of supersaturation for the sulfide are typically found at pH values ca. 2.5 lower for ZnS than for CdS, (ii) if reactions are carried out in a high pH regime, more sulfiding agent (by approximately four orders of magnitude) will be required for the zinc system, whilst the degree of supersaturation for zinc, with respect to the hydroxide, will always be greater than for cadmium with respect to its hydroxide (values of pM and pH being equal) and (iii) at lower pH, the rate of hydrolysis of the sulfide source is likely to be reduced, thus, even if a lower pH is used, more sulfide source might be required. Bath conditions similar to those described herein have previously been reported,[25] the solution used containing zinc ions, urea and thioacetamide at modestly acidic pH values. The urea slowly hydrolysed in the bath to provide hydroxide ions, and thioacetamide hydrolysed as the hydroxide was released. The films deposited using such a method were found to exhibit band gaps close to that expected for ZnS.

# Experimental

## Preparation of substrates

In order to prepare adherent and uniform films in a reproducible manner, it was necessary to carefully clean the surfaces of the substrates used within the deposition experiments. Low iron content microscope slides (BDH, Rochester, UK) were degreased with trichloroethylene and acetone, immersed sequentially in deionised water and concentrated nitric acid, and rinsed with deionised water. The procedure was repeated prior to deposition using a freshly prepared solution of sodium hydroxide (5 N), followed by a final rinse with deionised water.

## Solution deposition of thin films of ZnS

Films of ZnS were deposited from stirred aqueous solutions containing zinc(II) chloride (0.02 mol dm$^{-3}$), urea (0.5 mol dm$^{-3}$) and thioacetamide (0.2 mol dm$^{-3}$), the total volume of the deposition solution being increased to 100 cm$^3$ by the addition of deionised water. The pH of the deposition solution was adjusted to a desired value, within the range 2.0 to 5.0 (determined using a EIL 7000 pH meter and calibrated Russel glass electrodes), by the dropwise addition of hydrochloric acid (5 M). In each experiment, the temperature of the deposition solution was maintained at 353 K. Substrates were removed from the deposition bath after the desired period of time, rinsed with deionised water under conditions of ultrasonic irradiation and finally allowed to dry in air.

## Quartz crystal microbalance measurements

Deposition rates for the CBD of ZnS were determined using a microbalance (Maxtek PM-700 Series Plating Monitor) equipped with quartz crystal oscillators (5 MHz; AT-cut; unpolished gold). Mass changes at the nanogram scale can be measured and, hence, the quartz crystal microbalance (QCM) technique is ideally suited to CBD investigations. The QCM apparatus was controlled and experimental data recorded digitally. Upon completion of each deposition experiment, the quartz crystal was rinsed sequentially with nitric acid (5 M) and deionised water in order to remove the deposited material. The process was repeated until a reproducible frequency response was observed for the crystal.

The theoretical basis of the QCM measurements is outlined below. The resonant frequency of a piezoelectric quartz crystal is modified as foreign matter is deposited upon the surface of the crystal. The reduced frequency is proportional both to the mass of the matter on the surface and, since the area of the crystal is constant, to the thickness of the deposited film. In practice, it is necessary to employ piezoelectric quartz single crystals of a defined nature (AT-cut), since such crystals retain a zero frequency temperature coefficient and known frequency constant ($N_q = 1.670 \times 10^5$ cm Hz) in the thickness shear mode. As a consequence, the relation of the thickness of a thin film ($TK_f$) is given by eqn. 1,

$$TK_f = N_q \rho_q / \rho_f f^2 (f_q - f)$$

where $\rho_q$ is the density of the quartz (2.65 g cm$^{-3}$), $\rho_f$ the density of the material (in the case of ZnS, a value of 4.09 g cm$^{-3}$ is assumed), $f_q$ the resonant frequency of the uncoated crystal and $f$ the resonant frequency of the loaded crystal.

## Film characterisation

Electronic absorption spectra were acquired using a Philips PU 8710 UV-vis spectrophotometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG ESCALAB-Mark II instrument equipped with an ultra-high vacuum chamber (base pressure 10$^{-8}$ Pa), using Al-K$\alpha$

excitation and an analyser pass energy of 50 eV. Scanning electron microscopy (SEM) and elemental detection by analyzed X-rays (EDAX) measurements were conducted using a JEOL Superprobe 733 microscope. Samples were carbon coated in order to prevent charging during analysis. X-Ray powder diffraction (XRPD) measurements were performed using a Siemens D5000 diffractometer (Cu-Kα radiation/graphite-diffracted beam monochromator). Data were recorded across a $2\theta$ range of 10 to 90°, using a step size of 0.02° and a scan rate of 2 s per step. Phase identification was carried out using the Joint Committee of Powder Diffraction Standards (JCPDS) database.

## Results and discussion

### Quartz crystal microbalance measurements

The deposition of material onto the surface of the QCM was investigated and data were collected at intervals of 3 s over the desired deposition period. Typical results are illustrated in Fig. 1. Empirically, films deposited in the pH range 3.8 to 4.0 were found to be adherent and the process reproducible. Consequently, all films described hereafter were prepared under such bath conditions. Under these acidic CBD process conditions, growth of thin films of ZnS may be viewed as occurring in three stages: an initial induction period, then a rapid initial period of growth, followed by a slower process. The rate of growth (measured in terms of mass increase) in each phase is approximately zero order for each stage of the growth process, an initial rate (0 to 600 s) of 91 nm h$^{-1}$ (accurate to within 99%) being followed by a phase of slower deposition, at a rate of 52 nm h$^{-1}$.

### UV-vis spectroscopy

Electronic spectra of the deposited layers were recorded and plots of the square of absorbance ($\alpha^2$) versus energy (eV) were obtained, the data being found to be consistent with a direct band gap material (Fig. 2). Typically, band gaps of the ZnS films deposited under the conditions outlined were determined to be 3.52 eV, which compares favourably with the literature value for hexagonal ZnS, measured at room temperature, of 3.54 eV.[26]
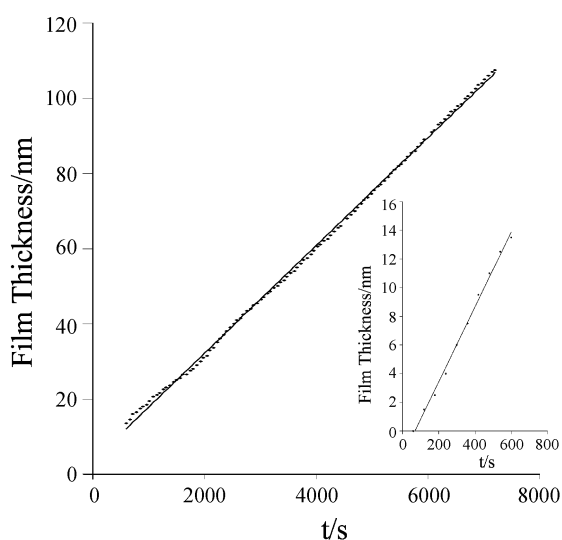


**Fig. 2** Determination of band gap of CBD-deposited ZnS films (deposition time = 10800 s) from UV-vis measurements. The band gap of the material is calculated to be 3.50 eV, a value which is comparable to the literature value of 3.54 eV.

### X-Ray photoelectron spectroscopy

X-Ray photoelectron spectra (Fig. 3) obtained for as-deposited materials were observed to be consistent with thin films of ZnS, photoelectron lines with binding energies associated with zinc (140 eV, 3s; 1022 eV, 2p$_{3/2}$) and sulfur (165 eV, 2p) being recorded. The signals at binding energies of 531 (1s) and 976 eV (Auger) are ascribed to the presence of oxygen within the structure of the glass substrate rather than evidence for the deposition of oxide material. The observation of signals attributable to silicon (102 eV, 2p) and sodium (1072 eV, 1s) confirms the porous nature of the deposited layer. Further evidence in support of this interpretation was derived from EDAX spectra, acquired in concurrence with SEM studies of the deposited layers.



**Fig. 1** QCM measurements obtained during the CBD of ZnS thin films. Films were deposited on low iron content microscope slides ([Zn$^{2+}$] = 0.02 mol dm$^{-3}$, [urea] = 0.05 mol dm$^{-3}$, [thioacetamide] = 0.2 mol dm$^{-3}$, pH 3.8). Under such conditions, film deposition occurs in two stages: a rapid initial period of growth, followed by a phase of slower deposition.
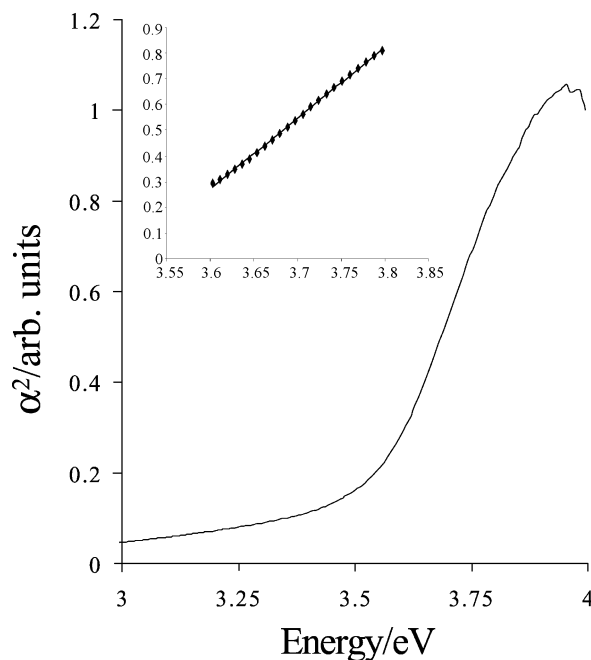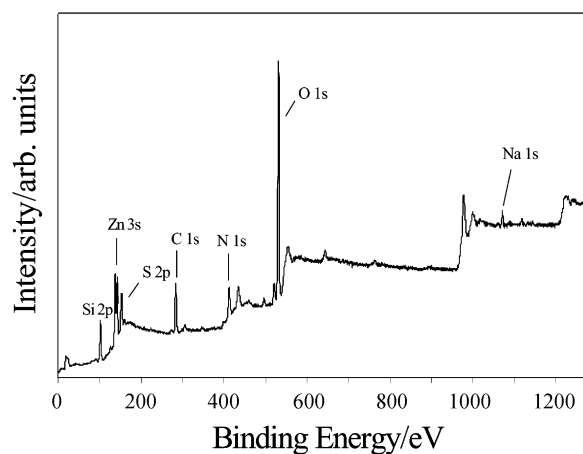


**Fig. 3** Wide scan XPS spectrum of ZnS CBD film on low iron content microscope glass, deposited from an optimised chemical bath solution ([Zn$^{2+}$] = 0.02 mol dm$^{-3}$, [urea] = 0.05 mol dm$^{-3}$, [thioacetamide] = 0.2 mol dm$^{-3}$, pH 3.8, deposition time = 10800 s). The observation of signals corresponding to both the C 1s and N 1s photoelectron states provides evidence in support of the incorporation of impurities (derived from the organic precursors) within the deposited film.
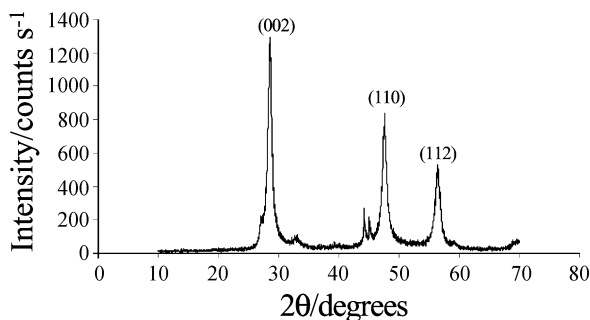
**Fig. 4** XRPD pattern of CBD-deposited ZnS film, deposited upon low iron-content glass ($[Zn^{2+}]$ = 0.02 mol $dm^{-3}$, [urea] = 0.05 mol $dm^{-3}$, [thioacetamide] = 0.2 mol $dm^{-3}$, pH 3.8, deposition time = 10800 s).

## X-Ray powder diffraction

The crystalline nature of the prepared films is evident from the X-ray powder diffraction pattern (Fig. 4). The most significant feature within the observed pattern, at $2\theta$ = 28.54°, is assigned to the (002) reflection of the wurtzite structure.[27] Two other prominent features are observed at $2\theta$ = 48.4 and 57.5°, which may be assigned to either (112) and (110) reflections from wurtzite or (220) and (311) of the cubic modification of ZnS (sphalerite). However, the strength of the (002) signal and absence of additional reflections for the cubic form suggest that the wurtzite phase is predominant. Due to the attenuated nature of the films deposited for less than 180 min, it was not possible to determine the particle size within films by using the Scherrer relationship (*i.e.* it was not possible to collect satisfactory diffraction data over the entire deposition experiment and determine particle sizes).

## Scanning electron microscopy and EDAX

Scanning electron micrographs were obtained from ZnS films deposited using the CBD technique for various regular intervals of time; the resulting images are displayed in Fig. 5. In the initial stages of film deposition, it is evident that a thin film is formed rapidly and that a relatively conformal layer is established within a period of 15 min. Moreover, it is apparent that under the experimental conditions employed, as film deposition proceeds, the uniform growth of layers of ZnS is associated with an increase in average particle size, rather than the continuous nucleation and deposition of new primary particles during the process. The EDAX spectra are typical of CBD-deposited films of ZnS, whilst the detection of elements present within the glass substrate [notably silicon (Si), sodium
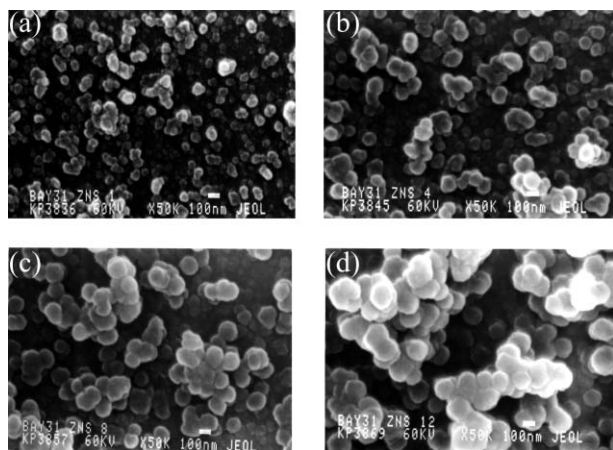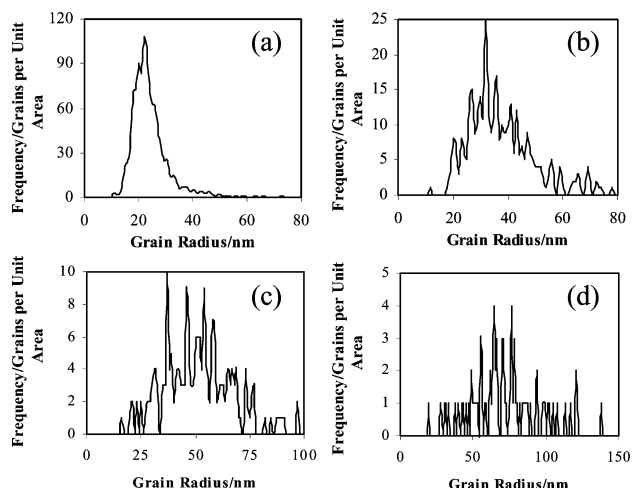


**Fig. 6** Grain size distributions within ZnS CBD films prepared over (a) 900, (b) 3600, (c) 7200 and (d) 10800 s. Under the bath conditions employed ($[Zn^{2+}]$ = 0.02 mol $dm^{-3}$, [urea] = 0.05 mol $dm^{-3}$, [thioacetamide] = 0.2 mol $dm^{-3}$, pH 3.8), uniform film deposition is associated with an increase in average particle size, rather than the continuous nucleation of new primary materials.

(Na), calcium (Ca), magnesium (Mg), potassium (K) and aluminium (Al)] is consistent with the thin nature of the films.

Grain size distributions (Fig. 6) were investigated using an image analysis routine, described in detail elsewhere.[28] The general approach may be summarized as follows. Micrographs were scanned in the form of bitmap images, such data being sharpened by the application of a matrix technique, and the grain boundaries were identified by thresholding. Subsequently, the modified images were skeletonised by carrying out an iterative reduction of the boundary width on a grain-by-grain basis. Such a process enabled a variety of data to be obtained from the skeletonised images, such as grain area, centroid position and mean particle radius, the latter being calculated for a circle of equivalent area to that of a particular grain. In the present study, numerical values for the mean radii of ZnS particles of 23.70 ($\sigma$ = 6.95), 37.42 ($\sigma$ = 12.76), 51.01 ($\sigma$ = 15.85) and 71.13 nm ($\sigma$ = 24.73 nm) were obtained, for deposition over 900, 3600, 7200 and 10800 s, respectively. These data were used to construct a plot of mean grain radius as a function of deposition time (Fig. 7), which was found to be linear. An average grain growth rate of 16.85 nm $h^{-1}$ has been calculated. Since the micrograph images indicate the ZnS particles to be generally spherical in nature, it is possible to obtain an approximate value of 33.7 nm $h^{-1}$ for the average rate of increase of the diameter of the grains.



**Fig. 5** Scanning electron micrographs of CBD-deposited ZnS films grown over (a) 900, (b) 3600, (c) 7200 and (d) 10800 s. In each case, the size of the scale marker is 0.1 μm.
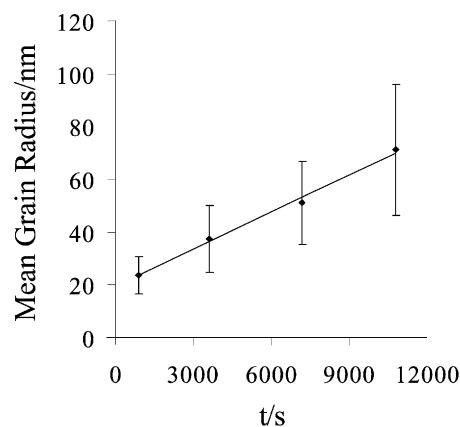


**Fig. 7** Plot of mean grain radius as a function of deposition time observed during the CBD of ZnS films under acidic process conditions.

The apparent discrepancy, with respect to the QCM measurements, is rationally interpreted as evidence for the removal of non-adherent material during post-deposition rinsing of the as-deposited films.

## Conclusions

This investigation provides evidence that during the latter stages of deposition of thin films of ZnS by the CBD technique, uniform film growth is principally associated with an increase in particle size, rather than with repeated nucleation and deposition of new particles on the surface of the substrate.

The above observations are interesting from the perspective that continuous film growth, rather than supplementary particle nucleation, appears to be promoted by the chemistry inherent within the CBD process. As a consequence, it appears reasonable to speculate that the CBD-ZnS process may represent an attractive candidate for extension of the closed-loop recycling system demonstrated for the CBD of CdS.[29]

## Acknowledgements

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