

# Development of low temperature approaches to device quality CdS: A modified geometry for solution growth of thin films and their characterisation

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## Abstract

Cadmium sulphide thin films have been grown using a modified chemical bath deposition method with four innovative features: i) ethylenediamine was used as the complexing agent, enabling the use of low cadmium concentrations, ii) a rectangular bath geometry with heated glass plate walls was employed, iii) a low deposition temperature (30 °C) was used and iv) nitrogen gas was flowed over the substrate surface during growth. The latter two features eliminate the formation and adherence of gas bubbles on the substrate during growth, hence reducing pinhole formation. On inspection, films were found to be specularly reflective and homogeneous with no visible pinholes. Characterisation was performed by atomic force microscopy, grazing incidence X-ray diffraction, optical transmittance and photoluminescence spectroscopy. It was shown that films possessed a low surface roughness value of 5.2 nm, were highly crystalline, textured, had a grain size of 15 nm and a bandgap of 2.42 eV. Preliminary results from CdTe/CdS thin film photovoltaic devices demonstrate a notable efficiency of 9.8%.

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## 1. Introduction

Cadmium sulphide (CdS) deposited by chemical bath deposition (CBD) has found widespread use in the fabrication of research scale CdTe/CdS solar cells, the current world record efficiency of 16.5% having been achieved with a device containing CBD CdS [1]. Nevertheless, there are some issues with this method of deposition and the quality of the resulting films. The chemical mechanism of CdS CBD is typically the thermal decomposition of thiourea ( $\text{CS}(\text{NH}_2)_2$ ) in the presence of a cadmium salt in a basic aqueous solution containing ammonia ( $\text{NH}_3$ ) [2]. Although widely used, ammonia is difficult to handle on account of its volatility. Another issue is that film

quality is often degraded by the formation of pores at the CdS/transparent conductor interface, or pinholes present in the entire CdS layer. Two methods of improving film quality are reported in the literature: firstly the use of ultrasonic agitation during bath deposition [3] and secondly the use of plasma cleaning of the transparent conducting oxide surface prior to CdS deposition in order to improve its wetting [4], both methods yielded improved films.

In this work a modified CBD process was used to overcome the limitations of conventional CBD growth. Firstly, ethylenediamine was used as a low volatility alternative to ammonia [5], its use also allows a reduced aqueous cadmium concentration to be employed, hence decreasing the amount of cadmium waste generated. Secondly, to lessen the interference of gas bubbles, which form on the substrate surface and impede local CdS deposition and hence form pinholes,

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two features were incorporated: i) a low growth temperature (30 °C) was employed and ii) nitrogen gas was bubbled over the substrate. These reduced both the formation and residence of gas bubbles on the substrate during growth. Finally, a modified bath geometry with flat plate heated walls was used.

## 2. Experimental details

The substrates used for CBD CdS growth were 10×10 cm soda-lime glass coated with a 100 nm layer of indium tin oxide (ITO: 15 Ω/□ sheet resistance) obtained from Merck Display Technologies. These were thoroughly cleaned by ultrasonic agitation in deionised water and then acetone, followed by a refluxing process in isopropyl alcohol. The chemical bath had parallel walls comprising two 20×20 cm water heated glass plates separated by a 2 cm gap in which the substrates were immersed during CBD growth. During deposition the solution was magnetically stirred and nitrogen gas was bubbled over the substrates, gas was injected into the solution through a PTFE tube with around 50 0.5 mm diameter holes at a rate of approximately 1 L per minute. The chemical bath comprised of an aqueous solution of cadmium chloride ( $\text{CdCl}_2$ , 0.001 mol  $\text{dm}^{-3}$ ), ethylenediamine ( $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , 0.012 mol

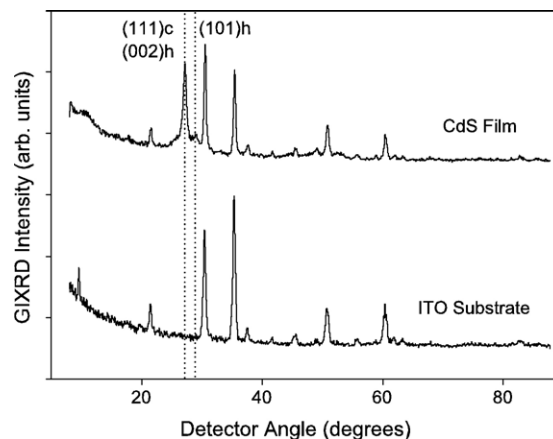


Fig. 2. GIXRD scans showing an as-grown CdS film (top) and an ITO substrate (bottom). Dotted lines indicate the two CdS peaks.

$\text{dm}^{-3}$ ), sodium hydroxide ( $\text{NaOH}$ , 0.01 mol  $\text{dm}^{-3}$ ) and thiourea ( $\text{CS}(\text{NH}_2)_2$ , 0.01 mol  $\text{dm}^{-3}$ ) [6]. A solution pH of 12 (at 20 °C) was employed and the bath temperature was held constant at 30 °C for a deposition time of 75 min.

Film thickness measurements were made using a Tencor Instruments Alpha-step 200 profilometer. Grazing incidence X-ray diffraction (GIXRD) scans were taken with a Bede D1 diffractometer using  $\text{Cu K}\alpha$  radiation at an angle of incidence of 0.5° with the detector scanned in the plane perpendicular to the film and containing the incident beam. Optical transmission measurements were made using a Perkin Elmer Lambda 19 UV–VIS spectrophotometer. Photoluminescence measurements were made at 4 K in a closed cycle helium cryostat using the 457.9 nm line of an argon ion laser. Atomic force microscope (AFM) images and measurements were taken in tapping mode on a Digital Instruments Nanoscope IV multi-mode microscope using commercially available Pelco Tap300 silicon tips with a radius of less than 10 nm; a scan size of 1  $\mu\text{m}$  was used.

Using this CBD CdS, preliminary CdTe/CdS solar cell devices were fabricated and evaluated at the University of Parma. The best performing device was produced from CdS initially annealed in a  $10^{-4}$  Pa 20%  $\text{H}_2$  80% Ar mixture at 400 °C for 20 min. A 9  $\mu\text{m}$  CdTe layer was deposited by close space sublimation at source and substrate temperatures of 680 °C and 500 °C respectively. This was followed by an *in-situ*  $\text{HCF}_2\text{Cl}$  treatment, subsequently followed by the application of a sputtered  $\text{Sb}_2\text{Te}_3$  and Mo back contact [7]. The cell efficiency was measured under 65  $\text{mW cm}^{-2}$  illumination from a xenon source Oriel solar simulator calibrated with a silicon solar cell standard.

## 3. Results and discussion

As-grown CdS films were 75 nm thick, specularly reflective, homogeneous with no visible pinholes, yellow in colour and optically transparent. An AFM image (Fig. 1a) shows that the surface is composed of regular features with an approximate lateral size of 200 nm and height of 10 nm, the root mean square (RMS) surface roughness as calculated by the microscope software was found to be 5.2 nm. An AFM image of the bare

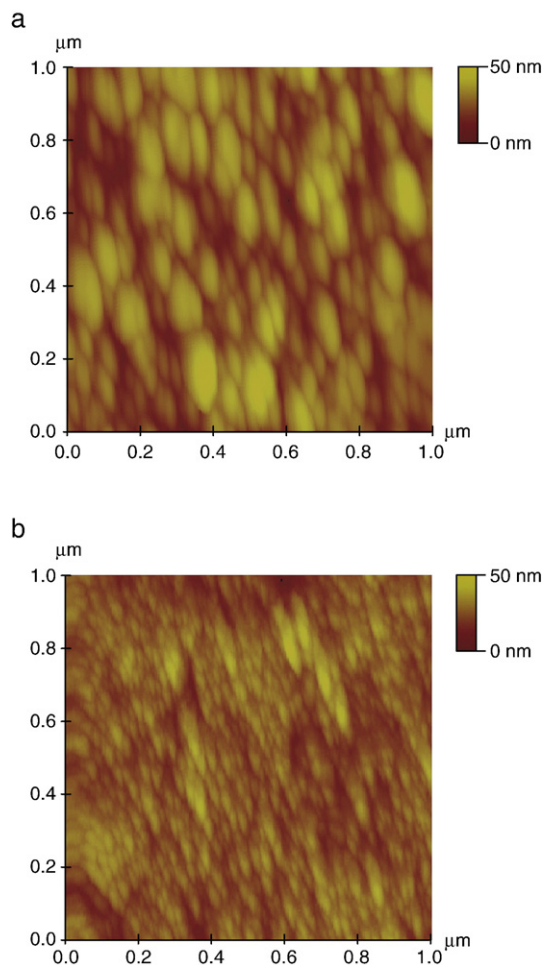


Fig. 1. AFM image of a) a CdS film on ITO and b) a bare ITO substrate. Sample area is 1×1  $\mu\text{m}$ , vertical resolution is 50 nm per division.

ITO substrate is shown for comparison in Fig. 1b (1.6 nm RMS surface roughness, lateral feature size approximately 50 nm).

GIXRD scans of an as-grown CdS film and an ITO substrate are shown in Fig. 2. Two CdS peaks can be distinguished, the first at  $27.14^\circ$  which could be assigned to either the hexagonal (002) or the cubic (111) reflection and a second, considerably smaller, shoulder at  $28.85^\circ$  assigned to the hexagonal (101) peak. From these data it is not possible to determine whether the film is present in the thermodynamically stable hexagonal phase, metastable cubic phase, a mixture of these phases or a polytype [8]. Nevertheless it is possible to conclude that the film is highly textured in either the [002] direction (if in the hexagonal modification) or the [111] direction (if in the cubic modification). With only two diffraction peaks, it is not possible to distinguish grain size and strain and within the film using a Williamson–Hall plot. The Scherrer formula was therefore applied to the main (002)/(111) peak with the assumption that all of the broadening is attributed to particle size alone. Using this assumption, the grain size was found to be 15 nm. It is also noted that the position of both these peaks is shifted to higher detector angles than expected for CdS (it was first verified that the ITO peaks were not shifted from their expected positions, in order to exclude the possibility that there was an offset in the

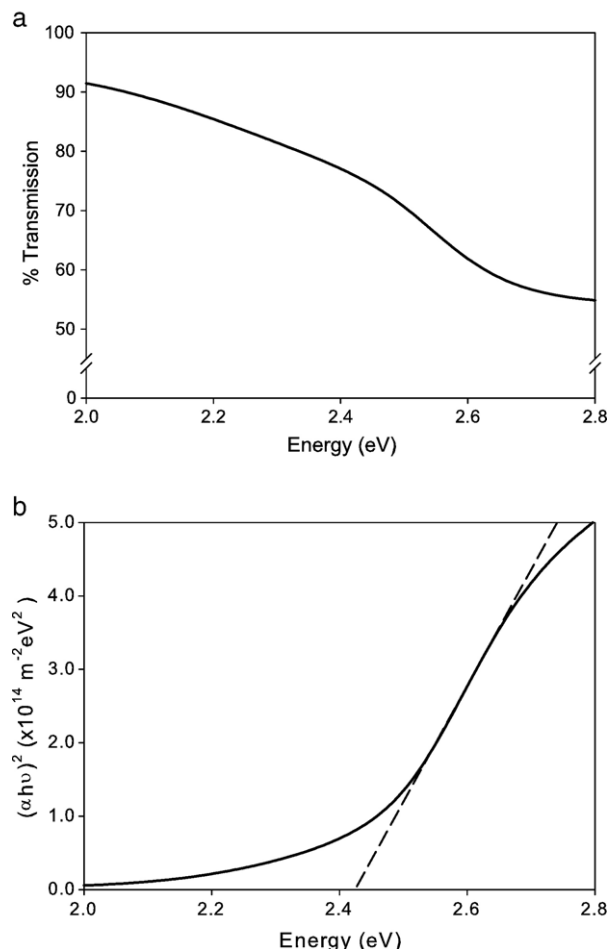


Fig. 3. a) Optical transmittance spectrum of a CdS film and b)  $(\alpha(h\nu))^2$  against  $h\nu$  for a CdS film.

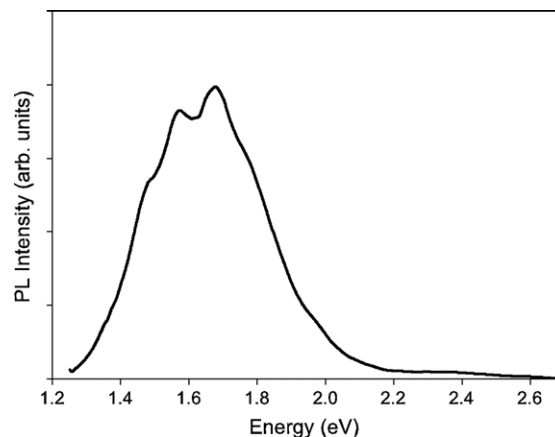


Fig. 4. A photoluminescence spectrum of a CdS film taken at 4 K.

detector angle), indicating qualitatively that there is a considerable amount of compressive strain contained within the CdS films.

A typical optical transmittance spectrum is shown in Fig. 3a. As expected, there is a reduction in the level of transmission at the fundamental bandgap value ( $E_g$ ) of CdS, this is a moderately weak feature as the film is relatively thin; this also accounts for the high transmission ( $\sim 60\%$ ) at energies above  $E_g$ . The bandgap was estimated by plotting  $(\alpha(h\nu))^2$  against  $h\nu$  (Fig. 3b) and taking the intersection of the tangent to the  $(\alpha(h\nu))^2$  axis, giving a value of 2.42 eV.

A typical photoluminescence spectrum is shown in Fig. 4. This exhibits a broad luminescence band located around 1.2–2.0 eV, which is typical for CBD grown CdS and is referred to as the red band. The red band is commonly ascribed to either sulphur vacancy states [9] or surface states [10].

In order to evaluate the potential solar cell performance of the CdS in this study, CdTe/CdS test devices were fabricated, and the current–voltage parameters for the best performing device are shown in Table 1. The cell performance is encouraging, in particular the efficiency figure of 9.8%, especially as that besides an annealing treatment, no further optimisation of either the substrate or CdS layer has yet been attempted.

#### 4. Conclusions

A modified CBD growth method with four innovative features has been developed to produce crystalline, homogeneous, pinhole-free CdS thin films on large area ( $10 \times 10$  cm) substrates. The approach embodies a flat plate reactor configuration and uses ethylenediamine as the cadmium complexing

Table 1  
Current–voltage parameters for a CdTe/CdS cell under  $65 \text{ mW cm}^{-2}$  illumination intensity

Area ( $\text{cm}^2$ )	$V_{oc}$ (mV)	$J_{sc}$ ( $\text{mA/cm}^2$ )	FF (%)	$\eta$ (%)
0.53	770	16.52	50.0	9.8

Parameters shown are the cell area, open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF) and efficiency ( $\eta$ ).

agent. Reaction occurs at near ambient temperature (30 °C) and dry nitrogen gas was passed over the substrate surface during growth, in order to remove any adherent gas bubbles and thereby prevent the formation of pinholes. These enhancements resulted in deposition of high quality CdS suitable for use in photovoltaic devices, as demonstrated in a preliminary study of CdTe/CdS test cells that exhibit a promising efficiency of 9.8%.

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