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Characteristics of nanocrystalline thin films of cadmium sulphide deposited at the water-oil interface

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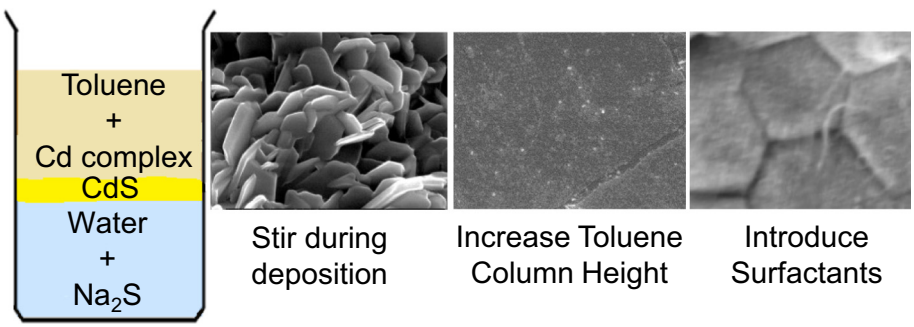
GRAPHICAL ABSTRACT



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ABSTRACT

Thin films of nanocrystalline CdS were obtained at the water-toluene interface by reacting cadmium diethyldithiocarbamate in toluene with aq. Na_2S. Three parameters unique to the topical deposition scheme: the effect of column heights, stirring and the action of molecular surfactants are systematically investigated. The obtained nanocrystalline aggregates are characterized by scanning- and transmission electron microscopy, X-ray diffraction and profilometric measurements. Conditions for obtaining smooth device quality thin films have been identified during these experiments.

1. Introduction

The area surrounding the interface between water and oil is emerging as a exciting medium for the growth and deposition of nanocrystalline thin films [1–5]. Starting with molecular precursors, nanostructured forms of topical materials such as: Au, Ag, CdS, PbS, ZnS, Fe_2O_3 and CeO_2 as well as graphene composites [6,7] have been obtained using this technique. Detailed studies have been carried out in an attempt to uncover the growth mechanism, particularly in the case of Au using X-ray scattering, photoelectron spectroscopy and electron microscopy [3,5,8,9]. The interfacial deposition scheme is low cost, soft, scalable and is potentially capable of depositing films over large areas. In a typical reaction, a metal precursor dissolved in toluene is layered atop an aqueous column containing a precipitation agent such as Na_2S. If suitable precursors are chosen, the reaction proceeds at the region of contact between the two liquids and yields a film adhered to the water-oil interface. The deposit can then be transferred to a substrate of choice.

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Despite the apparent simplicity of the scheme, processes underpinning interfacial precipitation are complex. Current understanding of surface potentials, diffusion and heat transport mechanisms across water-oil interface are insufficient to advance the area. Even the very nature of the interface between liquids such as water and toluene is subject to much debate [1]. Modelling or predicting the course or the outcome of an interfacial reaction is therefore fraught with difficulty. At present progress in this area is largely driven by experiments. It has be shown empirically that nature of deposits can be altered by conditions such as time, temperature and reagent concentrations [1,3]. However, parameters unique to the technique such as the role of column heights and effect of molecular surfactants are virtually unexplored [3,10]. The former can significantly alter interfacial pressure leading to deposits with new and interesting forms [1]. We considered it important to systematically explore the influence of such factors in dictating the macroscopic structure and properties of the interfacial deposits. We have chosen to study nanocrystalline thin films of CdS, a II-VI semiconductor with a band gap of 2.42 eV, an established photo-conductor with several current and many potential uses [11–14].

2. Methods and materials

The cadmium diethyldithiocarbamate precursor for the deposition of interfacial films was prepared following previous reports. Briefly, 15 mmol diethylamine and 15 mmol of carbon disulphide were added to a stirred 40 ml methanol containing 20 mmol sodium hydroxide. The addition was marked by the solution turning pale yellow. The mixture was then cooled to 4 °C using an ice bath and a 40 ml methanol solution containing 7 mmol cadmium chloride was added dropwise resulting in formation of a pale yellow precipitate. The solid was isolated and purified by re-crystallizing from toluene. Elemental analysis: found (%) (calculated): C 29.56 (30.00); H 4.57 (4.80); N 6.82 (6.80); S 30.67 (31.00); Cd 27.32 (27.40).

2.1. Deposition of CdS thin film at the water-toluene interface

CdS thin film was prepared by layering 30 ml of toluene containing 0.12 mmol cadmium diethyldithiocarbamate over a 30 ml aqueous column containing 0.25 mmol Na_2S in a beaker. The reaction vessel was introduced into an oven preheated to the desired temperature for different times. Following heating, the entire area of contact between the two liquids tuned to yellow signalling the formation of CdS thin film. The liquid phases stayed colourless. The thin film at the interface was transferred to different supports by dipping the substrates at an incline across the interface and moving them gradually upward.

2.2. Characterization

X-ray diffraction was carried out with a Philips Xpert diffractometer utilizing monochromatic CuKα radiation. Samples for diffraction consisted of precipitates deposited on glass substrates. Scanning electron microscopy (SEM) was carried out with Philips Excel microscope equipped with a 30 kV field emission gun or Delong Instruments LVEM5, low-voltage electron microscope. Film thickness were measured with Dektak 8 surface profile measuring system.

3. Results and discussion

Standard conditions for CdS deposition consisted of reactions carried out at 40 °C for two hours with 30 ml aqueous layer and a 30 ml toluene layer measuring 2 cm in height. Following this scheme, continuous thin film CdS deposits strongly adhered to the interface are obtained and were subsequently transferred to glass substrates. The following reactions take place in the vessel:

$$Cd(S_2CNEt_2)_{(oil)} + Na_2S_{(aq.)} \rightarrow CdS_{(interface)} + Na(S_2CNEt_2)_{(aq.)}$$

Scanning electron microscopy revealed growths that were dominated by microscopic platelets with rounded edges. High resolution imaging revealed coarse grained surfaces on the deposits hinting at a possible nanostructure (see Fig. 1a). Transmission electron microscopy carried out on interfacial growths treated with ultrasound to separate flocculates revealed that the films consists of hexagonal particles with rounded edges with overall dimension of around 7.0 nm (Fig. 1b). The X-ray diffraction pattern consists of broader than usual peaks characteristic of fine particulates of hexagonal CdS (see Fig. 2a). Profilometric measurements on flat glass substrates yielded average thickness of 90 nm. The optical bandgap was estimated to be 2.52 eV. The measured grain sizes, thickness and band gap are inline with a previous report of interfacial CdS obtained under similar conditions [15]. The effect of different variables on the standard scheme are presented below.

3.1. Effect of surfactants

Three surfactants with proven ability to bind to CdS: octylamine, tri-*n*-octylphosphine oxide(TOPO) and tetra-octylammmonium bromide(TOAB) were introduced in different quantities at the start of the reaction to evaluate their effects on the growth and deposition of thin films. The affinity of octylamine and TOPO to CdS is well established and routes to alkylamine or TOPO/TOP capped CdS nanocrystals abound [16,17]. TOAB is less well-known, but has been shown to quench luminescence by binding to the surface of CdS quantum dots [18]. We find that the intro-

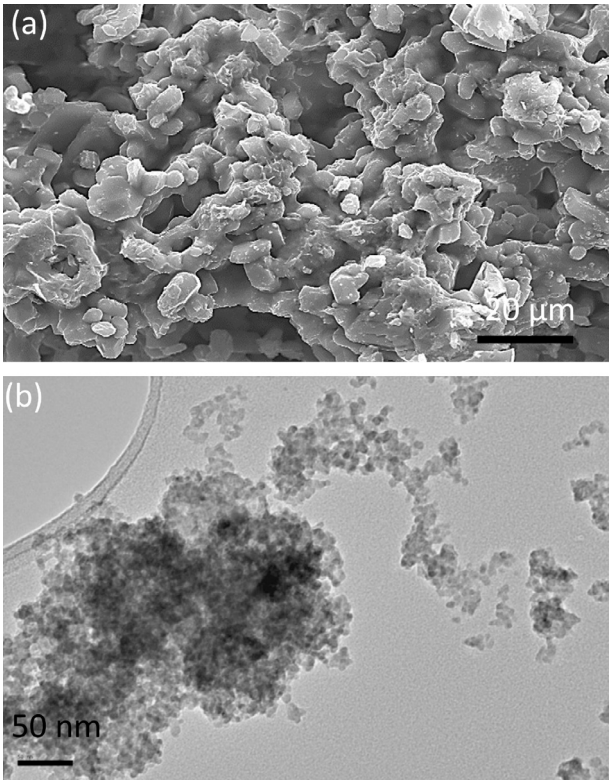

Fig. 1. Electron microscopic images of CdS nanocrystalline films. The films were obtained by reacting 30 ml of 33.3 mM aqueous Na_2S and 30 ml of 0.5 M toluene solution of $Cd(S_2CNEt_2)_2$ at 40 °C after 2 h.