



# Chemically deposited nanocrystalline lead sulfide thin films with tunable properties for use in photovoltaics



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## ABSTRACT

A refurbished chemical bath deposition technique was developed for growing thin film semiconducting nanocrystalline lead sulphide (PbS) for use in photovoltaics. The goal of this work was to produce good quality crystals, with the high mobility of holes and electrons required for effective carrier separation in photovoltaic applications, and to control other electro-physical properties. Tightly attached, densely compacted, nanocrystalline PbS films with tunable electrical, physical, and optical properties were deposited. Adherence to the substrate was attained by establishing firmly attached kernels on the substrate from which crystallization occurred. Nanocrystalline structures were precipitated onto the substrate by controlling the deposition temperatures, time, concentration of the chemical constituents and ionic products. Using this approach nanocrystalline thin film PbS layers with controllable thicknesses were proliferated. SEM images show rigid crystalline structure, and low impurity concentrations in the film. Hall Effect and spectroscopy measurements illustrate tunable electrical, physical, and optical properties. Carrier concentrations were achieved between  $6 \times 10^{16}/\text{cm}^3$ – $8 \times 10^{18}/\text{cm}^3$  and mobility ranged between  $3.4 \text{ cm}^2/\text{Vs}$ – $33 \text{ cm}^2/\text{Vs}$ . Photoconductivity was measured using 980 nm laser and blackbody at temperature of 450 °C and 800 °C. Results indicate low recombination rates on the surface. Prolonged exposure to air confirms resistance to oxidation, and stability of the optical and electro-physical parameters.

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## 1. Introduction

Lead sulphide (PbS) is an important direct narrow bandgap semiconductor material with an energy band gap of  $\sim 0.4 \text{ eV}$  at room temperature, 26 °C [1]. Applications for the PbS materials are extremely broad. Such materials have been used, integrated, or proposed for use in: solar radiation selective absorber coating for photo-thermal solar energy conversion - primarily developed for use in cold climates [2], solar radiation selective filter coatings for solar control - developed primarily for use in warm climates [3], imaging techniques [4], heavy metal concentration monitoring [5], laser applications [6], photodetectors, efficient heterojunction photovoltaic cells [7], and numerous other applications [8]. For these reasons, many research groups have shown a great interest in the development and study of this material prepared by various deposition processes such as electrodeposition [9], spray pyrolysis

[10], photoaccelerated chemical deposition [11], microwave heating [12], and chemical bath deposition (CBD).

The CBD method is presently attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films [13]. The characteristics of chemically deposited PbS thin films by CBD strongly depend on the growth conditions [14]. Although chemical bath PbS deposition has been shown to produce thin film nanocrystalline structures, there were many shortcomings in the resulting films. The films often were detached from the substrate and had low compactness of the crystals [15]. Manufactured crystals are often not continuous and not monocrystalline but rather consist of a set of separated spherical shaped nano-particles on the substrate [16]. Films are observed to have low mobility and high resistivity due to low packing density and impurity contamination in the film [17]. And finally, films were found to react with air to give lead carbonate and/or lead hydroxycarbonate on the surface [18].

In this paper, a technique is presented for deposition of firmly attached, tightly packed nanocrystalline PbS films with tunable

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electrical, optical, and physical properties for use in photovoltaic cells. The influence of the chemical deposition parameters on the carrier concentration, mobility, and film thickness is also demonstrated.

## 2. Experimental

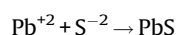
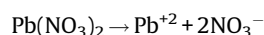
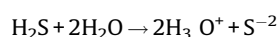
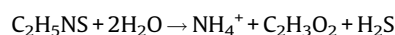
### 2.1. Synthesis of lead sulfide

#### 2.1.1. Seeding

Seeding was done on glass slide (22 mm × 22 mm × 1 mm) substrates. Prior to seeding, the substrates were cleaned to remove organic containments from their surfaces, using RCA-1 clean solution [19]. Glass slides were placed in boiling solution of 1:1:5 27% NH<sub>4</sub>:30%H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O for 15 min, rinsed with deionized water, and dried before use.

Seeding solutions contained 5 mL of polyvinyl alcohol [(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>] with concentration of 340 μM, mixed with 5 mL of lead (II) nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] with the concentration of 30 μM and 40 mL of thioacetamide (TAA) [C<sub>2</sub>H<sub>5</sub>NS] with the concentration of 3.3 μM [20]. All three constituents were mixed and 4 μL of nitric acid [HNO<sub>3</sub>], molarity of 1 M, were added to the solution. After addition of the nitric acid, the pH of the solution receded from 5 to 3. Acidity of the seeding bath had a profound effect on the seeding procedure. Substrates were then placed into the seeding solution with stir set at 50 RPM (required for uniform seeding). A 50 mL beaker containing seeding solution was maintained at 70 °C for 90 minutes and a tight seal was placed over the seeding beaker in order to prevent escape of the H<sub>2</sub>S gases. The optimal time, temperature, and constituent concentrations were determined using experimental data obtained from a series of experiments. Slight variations within the seeding procedures have produced unpredictable and uncontrollable results. Thus seeding was set to a standard and only deposition bath was used to alter the opto-electrical, and physical properties of the film.

Seeding experiments have shown that in an acidic medium TAA decomposes and releases hydrogen sulfide [H<sub>2</sub>S]. It is believed that hydrogen sulfide breaks apart further to release sulfide [S<sup>2-</sup>] ions. Lead (II) nitrate is also broken apart in the acidic medium to release Pb<sup>2+</sup>. The chemical reaction for seeding has not been explicitly elucidated; however, based on the deposition reaction described below, authors suspect that S<sup>2-</sup> precipitates Pb<sup>2+</sup> ions from the solution by following chemical process:

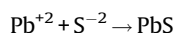
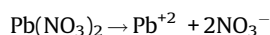
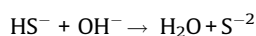
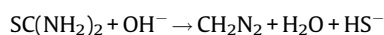


#### 2.2.2. Deposition

In the procedure as described by G. Hodes the chemical deposition process involves decomposition of a thiosulphate solution [21]. In this research thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] was used. From the onset it must be noted that the mechanism of this deposition has not been unambiguously elucidated up to the present time [22]. Authors accept this chemical reaction as reasonable. This method is further supported by the fact that concentrations of the OH<sup>-</sup> ions have a profound effect on the rate of crystal growth of PbS. Initial deposition parameters were taken from Cooperstein to be 18 mL of NaOH 2.75 M, 10 mL of Pb(NO<sub>3</sub>)<sub>2</sub> 340 mM, 10 mL of SC(NH<sub>2</sub>)<sub>2</sub> 990 mM, 240 mg Na<sub>2</sub>SO<sub>3</sub>, and 10 mL of C<sub>2</sub>H<sub>6</sub>O [20]. These

reagents were mixed in a 50 mL beaker in this order. Chemical reaction among the constituents caused darkening of the fluid. At 25 °C and concentrations stated above, constituent reaction takes place within several minutes, although the rapidity of the reaction was a function of temperature and constituent concentrations. Acidity of the chemical deposition bath was pH ~12. The seeded substrates were placed into the beaker with the chemical components, and the beaker was placed in a warm bath controlled at 25 °C for 30 min, and stirred at 50 RPM for uniform deposition.

Literature offers several elucidations for the reaction [22]. The prevailing explanation for the reaction is decomposition of thiourea and release of S<sup>2-</sup> ions, which precipitate Pb<sup>2+</sup> ions from the solution [23]. The initial step in the chemical process consists of breaking apart thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] with OH<sup>-</sup> ions to saturate the solution with HS<sup>-</sup> ions. Once the solution is saturated with hydrogen sulfide, the high concentration of hydroxide ions further breaks apart HS<sup>-</sup> and releases S<sup>2-</sup> ions. The highly alkaline solution also dissolved apart Pb(NO<sub>3</sub>)<sub>2</sub> to release the Pb<sup>2+</sup>



The solubility products equation, Eq. (1), [24]

$$K_s = P b^{+2} S^{-2} \quad (1)$$

where the constant  $K_s$  is solubility product Pb<sup>2+</sup>, S<sup>2-</sup> are ionic products, states that once the ionic products exceed the solubility product of PbS, precipitation occurs. Solubility product for PbS is found experimentally to be 10<sup>-28</sup> mol/L and is well studied and cited in literature [25]. In our work, breaking apart of the constituents was done by controlling the OH concentration in the deposition bath. The alkalinity of the deposition solution was measured to be pH~12. Excessive addition of NaOH did not have a profound effect on the basicity of the solution raising pH by 0.4 points at most. However, concentration of sodium hydroxide had a profound effect on the rate at which ionic products saturated the solution. The rate of precipitation is thus managed by controlling the concentration of NaOH in the emulsion. This gives a finely tunable method to control the growth of nanocrystalline PbS films. Once deposition was complete, samples were removed from the chemical bath, loose precipitation was washed with deionized water, and samples were stored for further analysis.

If successive PbS layers were to be deposited on the same glass, then following a rinse with deionized water and through drying, the sample was introduced into a new bath. No new seeding was required due to the already present crystalline structure of the samples.

### 2.3. Material characterization

#### 2.3.1. Interference spectroscopy

Film thickness was determined by interference spectroscopy. Fig. 1 shows the transmission and reflection spectra of a 547 nm sample measured as obtained using a Cary 5 E spectrophotometer. Eq. (2) governs optical measurement of the thickness,

$$d = \frac{m\lambda_m}{4n} \quad (2)$$

where  $m$  is an integer number starting from one and corresponding to the order of extremum, including maxima and minima, and  $n$  is

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