Control of morphology and optical properties of PbS nanostructured thin films by deposition parameters: study of mechanism

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ABSTRACT
PbS thin films were grown on glass substrates by chemical bath deposition (CBD) using lead nitrate, thiourea and sodium hydroxide in aqueous solutions at three different temperatures (22, 36 and 50 °C). The microstructure and morphology evolution of the films were investigated using X-ray diffraction, scanning electron microscopy and atomic force microscopy. Optical properties were studied using UV–Vis–IR spectroscopy. The results indicate that temperature plays an important role in controlling the morphology and optical properties of nanostructured PbS thin films through changing deposition mechanism. The active deposition mechanism changed from cluster to ion-by-ion mechanism with an increase in deposition temperature from 22 to 50 °C, and consequently, film properties such as morphology, optical absorption and preferred orientation changed completely.

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Introduction
PbS is an important binary IV–VI semiconductor material with a rather small band gap (0.41 eV at 300 K) and relatively large exciton Bohr radius (18–20 nm) [1], which results in good quantum confinement of both holes and electrons in nano-sized structures [2]. These inherent properties make PbS one of the most important functional materials used as thin films for several applications such as IR detectors [3], photovoltaic cells [4], thin-film transistors [5], LEDs [6], gas and biosensors [7–12], and photonic crystals [13].

In recent years, various techniques have been used to deposit PbS thin films including microwave-assisted chemical bath deposition (CBD) [2], successive ionic layer adsorption and reaction (SILAR) technique [14–17], atomic layer epitaxial process [18], pulse electro-deposition [19], spray pyrolysis [20] and chemical bath deposition.

Chemical bath deposition method, also called chemical solution deposition technique, has become an attractive method due to many reasons, including low cost, no requirement of sophisticated instruments, freedom to deposit materials on a variety of...
substances, suitability for large-scale deposition areas and ability of tuning thin-film properties by adjusting and controlling the deposition experimental parameters [21].

It was realised that changing CBD parameters such as temperature and solution composition leads to nanoparticles with different sizes and shapes [22], which change the value of the band gap with respect to the effective mass model.

CBD process uses controlled chemical reactions to achieve thin-film deposition by precipitation. It is necessary to eliminate spontaneous precipitation in order to form a thin film [23]. Chemical deposition of films on solid substrates can take place via two major mechanisms.

The first mechanism is ion-by-ion mechanism, in which the film is formed by sequential ionic reactions. If the reaction progresses in alkaline medium, a complex agent is required to prevent the formation of hydroxide precipitates.

If the complex concentration is not adequate to completely prevent the formation of metal hydroxides, cluster mechanism occurs. In this case, a small amount of colloidal hydroxide will be formed, which then reacts with anions generated in the bath and produces the final product. On the other hand, research has shown that the dominant mechanism of deposition is dependent on the reaction conditions and changing the dominant mechanism during deposition is possible [24].

Although Shandalov et al. [25] showed the ability of laser light scattering in qualitative identification of dominant mechanism in chemical deposition of PbSe, this method has not yet been used in chemical deposition of PbS thin films. Furthermore, few research works on the impact of deposition mechanism on the properties have been carried out. Each mechanism leads to different particle size and morphology, which affect film properties. Therefore, for the synthesis of a film with specific properties, we should be able to predict reaction mechanism.

In this work, effect of deposition temperature on active deposition mechanism and film properties was investigated.

**Material and methods**

PbS thin films were deposited on clean, spectroscopic glass substrates at different temperatures (22, 36 and 50 °C). All the reagents were purchased from Merck Chemical Co. and were used without further purification.

According to previous studies, the aging of precursor solutions will affect the deposition rate [26]. Therefore, fresh precursor solutions were utilised to remove probable noise caused by aging. Prior to deposition, substrates were cleaned with the cleaning procedure of Obeid et al. In brief, substrates were washed with hot distilled water, immersed in 20% HCl for 24 hr, and washed with acetone. Then the substrates were cleaned ultrasonically with deionized water (DI) water for 20 min [2].

To prepare the reactive solution, 40 mL of 0.146 M NaOH and 100 mL of DI water were mixed. After dropwise addition of 8 mL of 0.175 M lead nitrate to the stirring mixture, pure N₂ was passed through the reaction solution for 1 hr in order to diminish levels of dissolved O₂ and CO₂. Then the reaction beaker was placed in a thermostatic bath to reach the desired temperature. Eight millilitres of 1 M thiourea solution was then added to the reaction mixture. Finally, the clean glass substrates were placed in the solution at 70 ° with respect to the horizon using the Plaxi holder to prevent large particles from
adhering to the growing film. The samples were taken out after 30 min, rinsed with DI water and then air dried. The greyish obtained films were well adherent to the substrate and homogenous. The reactions process for synthesis of lead sulphide films through ion-by-ion and cluster mechanisms have been previously reported [27,28].

Structural characterisations of the films were determined by X-ray diffraction (XRD) method using a Philips PW3710 at room temperature with Cu Kα radiation ($\lambda = 1.5405 \text{Å}$, time/step = 0.5 s, step size = 0.02). In order to determine crystallite size from XRD, the Scherrer formula was used. Field-emission gun scanning electron microscopy (FE-SEM) studies were carried out using a HITACHI S-4160 microscope, in order to determine the morphology of the films. Film thickness was measured from cross sections while surface topography was observed in plan view. The surface morphology of the thin films was characterised with an Auto probe CP (Park Scientific Instruments) atomic force microscope (AFM). AFM imaging was performed under ambient conditions using commercial Si3N4 cantilevers in contact mode at a scan rate of 1 Hz. The optical transmittance and reflectance spectrum were recorded on a Perkin Elmer Lambda950 spectrophotometer in the wavelength range of 200–3100 nm.

Results and discussions

Figure 1 shows the XRD patterns of the samples deposited at 22, 36 and 50 °C. By comparing the spectra with standard lead sulphide cards, it becomes clear that the single-phase lead sulphide with face centered cubic (FCC) structure has been synthesised and all diffraction peaks belong to rock salt phase of PbS (JCPDS file #592). The non-appearence of any other reflection lines indicates that other crystalline phases, such as carbonates

![Figure 1](image_url). X-ray diffraction pattern of samples grown on glass for 30 min at (a) 22 °C, (b) 36 °C and (c) 50 °C.
or oxides of Pb, are not present with measurable concentration within the films. Moreover, sharp peaks in the spectra show good crystallinity of the samples.

Structural parameters calculated from XRD of films including the lattice constants, the crystallite size, the peak positions and intensities are summarised in Table 1. An increase in deposition temperature leads to larger crystallites (from 7.8 to 35 nm). Although due to large exciton, Bohr radius of PbS (18 nm) particles with a diameter smaller than 40 nm can be considered quantum dots.

Diffraction patterns indicate that increasing deposition temperature from 22 to 36°C causes development of a (111) texture $(I_{111}/I_{200} = 1.94)$. However, more increase in deposition temperature leads to rehabilitation of (100) texture $(I_{111}/I_{200} = 0.89)$. This means that the preferred orientation changes from (200) plane to (111) with increasing temperature from 22 to 36°C. The intensity ratio $(I_{111}/I_{200})$ for film grown at 22°C is 0.56, while the bulk value is equal to 0.84. These changes in the intensity ratio indicate that preferred orientations of PbS thin film grown by CBD strongly depend on deposition temperature.

As mentioned above, film thicknesses were measured using cross-sectional FE-SEM images. For each sample, two different points were selected for imaging, and finally, the average values of measured thicknesses were reported as film thickness (Table 1). Figure 2 represents cross-sectional FE-SEM images at different deposition temperatures.

Figure 3 illustrates the thickness and surface roughness of PbS film versus deposition temperature. The plot feature indicates that the thickness and roughness index (root mean square (RMS)) of the film noticeably ascended with the increasing temperature.

| Deposition temperature (°C) | Intensity (cts) | $2\theta$ (°) | $d$ (Å) | $a$ (Å) | Crystallite size (Scherer’s equation) (nm) | Average particle size (by AFM) (nm) | Film thickness (nm) | $I(I_{200})$ |
|-----------------------------|----------------|-------------|--------|--------|------------------------------------------|-------------------------------|-------------------|-------------|
| 22                          | (111) 20.88    | 26.076      | 3.42   | 5.919  | 7.8                                      | 37                           | 118               | 0.557       |
| (200) 37.48                 | 30.154         | 2.96        | 5.925  |        |                                           |                              |                   | 0.319       |
| (220) 11.94                 | 43.191         | 2.09        | 5.924  |        |                                           |                              |                   | 0.193       |
| (111) 178.57                | 26.035         | 3.42        | 5.928  |        |                                           |                              |                   |             |
| 36                          | (200) 91.96    | 30.139      | 2.96   | 5.930  | 28.5                                     | 114                          | 346               | 1.942       |
| (220) 71.14                 | 43.119         | 2.10        | 5.935  |        |                                           |                              |                   | 0.773       |
| (111) 92.07                 | 26.002         | 3.43        | 5.938  |        |                                           |                              |                   | 0.257       |
| 50                          | (200) 103.16   | 30.101      | 2.97   | 5.938  | 35.0                                     | 137                          | 413               | 0.892       |
| (220) 48.66                 | 43.096         | 2.10        | 5.937  |        |                                           |                              |                   | 0.472       |

Figure 2. Cross-sectional FE-SEM images of PbS thin film deposited on glass substrates for 30 min at (a) 22°C, (b) 36°C and (c) 50°C.
from 22 to 36°C, but higher deposition temperatures lead to increased thickness and reduced roughness index (RMS).

The histogram distribution and three-dimensional (3D) surface images of a 5 × 5 μm² area of PbS thin film deposited at different temperatures, obtained by AFM, are shown in Figure 4. The histogram distribution indicates that increasing the deposition temperature leads to larger average particle size and broader particle size distribution, which may be due to the transition in active deposition mechanism. Progress of ion-by-ion mechanism is accompanied by increase in the particle size. However, in the cluster mechanism, film growth occurs via adsorption of hydroxide clusters and by converting them to sulphide. Therefore, the particle size does not vary significantly by increasing the thickness of the film [24].

FE-SEM images illustrated in Figure 5 exhibit the evolution of the film morphology with deposition temperature. As observed in Figure 5(a), the film deposited at room temperature for 30 min consists of round particles with typical size of 130 nm and does not completely cover the substrate. A well-adherent and extremely compact film, which covers the entire surface of the substrate, is obtained by increasing deposition temperature to 36°C (Figure 5(b)). Typical particle size has also increased to 250 nm. A significant change in particle shape from round particles to faceted occurs with increasing the deposition temperature to 36°C. Further increase of deposition temperature to 50°C (Figure 5(c) leads to a significant increase in the particle size (around 500 nm) and complete transformation in particle shape to rectangular pyramids. Despite the relatively high film thickness (around 400 nm), the film is less compact compared to that deposited at 36°C and even on the substrate some devoid points of nanoparticle are observed.

It was understood that deposition growth resulted in a reduction of anions and cations in solution. This decrease may change the deposition mechanism from cluster to ion-by-ion [29]. Since the surface characteristics of thin films significantly affect film properties, it is important to anticipate which mechanism will form the surface of the film at different temperatures. The observed drastic variation in particle size, morphology and preferred
orientation, which occur with the increasing deposition temperature, could be attributed to a shift of active deposition mechanism at different deposition temperatures.

The UV–Vis–IR absorption and reflection spectra of PbS thin films deposited at different temperatures are shown in Figure 6. For all samples, the absorbance is enhanced from IR region to UV region. The spectrum of film deposited at room temperature (22°C) illustrates a sharp slope absorption edge around 450 nm. With the increasing deposition temperature, the absorption edges are gradually red shifted. The film grown at 36°C demonstrates increased absorption intensity, which may be due to the more compactness of the film compared to the other film.

The film synthesised at 22°C has a high absorbance in UV–Vis region and a reflection of about 50% in the NIR region (wavelengths of over 1300 nm).

The two films synthesised at 36 and 50°C have a relatively good absorbance at wavelengths below 1300 nm and their reflection is in the 10%–30% range in 300–2400 nm wavelength range. The film deposited at 22°C demonstrates higher R values compared to those deposited at 36 and 50°C. Valenzuela et al. [30] showed that surface roughness greatly influences optical properties. Therefore, the observed difference in the R values of

**Figure 4.** AFM histogram distributions and 3D surface images of nanocrystalline PbS thin films deposited at (a) 22 °C, (b) 36 °C and (c) 50 °C. The area is 5 × 5 μm² in all images.
the film deposited at 22 °C with two other films can be attributed to the significant differences in surface roughness (Figures 3 and 4).

The film synthesized at 22 °C can be used for low-transmission-type solar control coating due to high reflection in the NIR region and low transmission in the UV–Vis region [31]. The other two films can be applied in solar cells considering their lower reflection and relatively good absorption in wavelengths below 1300 nm.

Previous studies showed that round particles are indicative of the cluster mechanism and ion-by-ion mechanism is slower than cluster mechanism and leads to larger...
particles [2,21,22,24]. Consequently, it can be concluded that thin films deposit at room temperature for 30-min growth by cluster mechanism.

However, in the sample deposited at 36 °C for 30 min, clear changes in particle shape were observed and the film deposited at 50 °C for 30 min was composed of large rectangular pyramids. This clear change in morphology can be attributed to the change in active growth mechanism from cluster mechanism to ion-by-ion.

It is obvious that the reactions take place more rapidly at upper deposition temperatures. Thus, the depletion of precursors occurs much faster compared to films deposited at 22 °C. The change in active mechanism is expected to occur in shorter time with increasing deposition temperature. This expectation is consistent with the findings of this study. The morphology of the film synthesised at 22 °C indicated that the surface of the film was created by cluster mechanism. However, the surface morphology of the films synthesised at 50 °C (large rectangular faceted particles) is a sign of the full transition to ion-by-ion mechanism.

**Conclusions**

PbS thin films were successfully prepared by chemical bath deposition on glass substrate at three different temperatures. Under the same conditions of reaction solution and reaction time, the surface of the film synthesised at 22 °C by cluster mechanism consists of round particles, whereas the surface of the film synthesised at 50 °C by ion-by-ion mechanism consists of large rectangular faceted particles.

The film synthesised at room temperature is less rough (softer) than the other two films, which causes the greater reflection of this film and makes it appropriate for solar control coating.

These results indicate that particle shape and preferred orientation of PbS films prepared by CBD are strongly dependent on deposition temperature. Finally, this study showed that deposition temperature is effective in determining dominant deposition mechanism and consequently optical properties of PbS thin films.

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**Disclosure statement**

The authors declare no competing financial interest.

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