Control of the crystalline phase and morphology of CdS deposited on microstructured surfaces by chemical bath deposition

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ABSTRACT
Chemical bath deposition (CBD) has been used extensively to deposit thin films of CdS for window layers in solar cells. The microtopography or roughness of the surface, however, can affect the quality of the film by influencing the morphology, uniformity, or crystal phase of the CdS film. Here, we have demonstrated that thin films of CdS can be successfully patterned on surfaces bearing micropillars as a model surface for roughness. The phase purity of CdS deposited on the micropillar surfaces is uniform and conformal with the formation of packed clusters on the micropillars at pH 10 that form flower-like structures at long deposition times. Smaller crystallites were observed on micropillar arrays at pH 8 with “network” like structures observed at long deposition times. Additionally, by controlling the pH of the chemical bath, the hexagonal and cubic crystal phases of CdS were both accessible in high purity at temperatures as low as 85 °C.

1. Introduction

Semiconductor materials prepared as nanostructured particles and thin films are extremely important in technology with potential applications in optoelectronic devices, photo-sensors, transducers and as optical waveguides [1]. Among these, thin films of cadmium sulfide (CdS) have been widely studied because of their use as a window coating in solar cells [2]. CdS thin films also have applications in optoelectronic devices such as photo-conducting cells, photo-sensors, transducers, laser materials, optical wave guides and non-linear integrated optical devices [2,3]. Several synthetic methods have been developed to produce nano-scale, micro-scale, and thin films of CdS including hydrothermal [4], electrochemical [5], and chemical bath deposition (CBD) [6]. Among these synthetic methods, CBD is one of the simplest and inexpensive large-area deposition techniques [7,8]. Deposition of CdS using CBD is based on the slow release of Cd²⁺ and S²⁻ ions in an aqueous alkaline bath and subsequent condensation of these ions onto a substrate [9].

Several literature reports have demonstrated that both the cubic and hexagonal crystal structures of CdS films are accessible through CBD; however, generating phase pure samples remains a challenge with variables such as temperature, pH, and identify of the substrate affecting the crystalline phase of the resulting film. For example, Lejmi and Savadogo [10] found that CdS films deposited on glass substrates resulted in the cubic phase predominantly (20% hexagonal and 80% cubic) when the deposition was carried out for more than 1 h in the presence of hetero-polyacids. It has also been reported that crystal structure and optical properties of CdS films can vary depending on the type of substrate used (i.e. glass, polycarbonate, polyethylene terephthalate, and octadecytrichloro-silane functionalized silicon) [8,11].

Given the importance of the substrate on the crystal structure and the fact that textured, corrugated or
non-uniform substrates can be potential targets for CdS deposition, the current study was developed to test the effect of substrate topography on the uniformity and crystal structure of the CdS films deposited using CBD. To our knowledge there are no current reports on the deposition of CdS using CBD on microstructured surfaces although there is one report on the growth of polygonal rings and wires of CuS on microstructured surfaces via CBD [12]. In addition, while the pH has been linked with phase purity, no direct or systematic studies have been performed on the effect of pH on the purity of the crystal phase. Herein, we demonstrate both that the CBD method can be used for conformal and uniform deposition of CdS films onto patterned microstructures, and that the phase purity of CdS varies with deposition time and pH but not necessarily with the identity of the substrate. Both the metastable cubic CdS and the high temperature bulk hexagonal type CdS are accessible at low temperatures (85 °C) with varying pH on textured surfaces bearing micropillar arrays.

2. Experimental details

A silicon wafer bearing a hexagonal array of micropillars was used as a master mold from which the micro-structures were then used to make poly(dimethylsiloxane) (PDMS) molds using soft lithography techniques as described elsewhere [12,13]. The micropillars with dimensions, \( d = 1 \, \mu m \), \( l = 4 \, \mu m \), and interpillar spacing \( d_{int} = 3 \, \mu m \), were then replicated in epoxy from the PDMS mold and used for CBD experiments [14]. The epoxy micropillar arrays and flat epoxy (control) samples were immersed in a solution containing thiourea, cadmium acetate, and ammonia as the sulfur source, cadmium source, and complexing agent, respectively. Cadmium acetate (Cd(CH₃COO)₂)(Sigma-Aldrich) and ammonium hydroxide (NH₄OH)(Sigma-Aldrich) were used without further purification. Epoxy substrates (25.4 mm \( \times \) 76.2 mm glass slides, or epoxy substrates) were immersed in a solution containing thiourea, cadmium acetate, and ammonia as the sulfur source, cadmium source, and complexing agent, respectively to produce micropillar arrays with a thin CdS film. The CdS-coated samples were analyzed by XRD and SEM.

Cadmium acetate (Cd(CH₃COO)₂)(Sigma-Aldrich), ammonium acetate (NH₄CH₂CO₂)(Sigma), thiourea (SC(NH₂)₂)(Sigma-Aldrich) and ammonium hydroxide (NH₄OH)(Sigma-Aldrich) were used without further purification. Epoxy OG-142 (EPO-Technology) was used to make the epoxy substrates. Epoxy samples bearing an array of hexagonal micropillars (\( d = 1 \, \mu m \), \( l = 4 \, \mu m \), and interpillar spacing \( d_{int} = 3 \, \mu m \)) were fabricated using a double replication technique [13]. Briefly, a Si wafer bearing an etched hexagonal array of micropillars was used as a master mold from which the microstructures were then replicated into poly(dimethylsiloxane) (PDMS) using soft lithography techniques, then the microstructures were replicated in epoxy from the PDMS mold and used for CBD experiments. Flat epoxy samples were also generated from PDMS molds as control samples.

The CdS deposition method was adopted from Oladeji and Chow [14]. Briefly, distilled water (250 mL) was heated to 85 °C while stirring. When the temperature reached 85 °C, two substrates (25.4 mm \( \times \) 76.2 mm glass slides, or epoxy substrates) were immersed into the solution and allowed to equilibrate. Cadmium acetate (0.5 M, 1.20 mL), ammonium acetate (2.0 M, 6.00 mL) and ammonium hydroxide (14.4 M, 12.16 mL) were added to the beaker. When the solution temperature reached 85 °C, thiourea (0.5 M, 7.00 mL) was added. Finally, the volume was adjusted to 300 mL by adding pre-heated, neutral distilled water at 85 °C. CdS deposition was carried out for 30 min, 100 min, 180 min and 240 min. The volume was kept constant by adding pre-heated water (2–10 mL, 85 °C). After deposition, one substrate was sonicated in warm water for 5 min and air-dried and the other was simply air-dried. To study the effect of pH on CdS deposition, the initial pH of the solution was adjusted to 10 or 8 by varying the NH₃ concentration. The pH of the solution was measured through the course of the reaction. The pH dependent experiments were performed with a Cd:S ratio of 1:6. Flat epoxy samples and glass cover slips were used as control samples. CdS thin films deposited at pH 10 and pH 8 had an average thickness of 0.228 \( \mu m \) and 0.204 \( \mu m \) respectively.

SEM was used to characterize all samples. CdS particles in solution were separated by centrifugation (4500 rpm, 30 min) and vacuum dried. Characterization of the deposited glass slides, epoxy substrates and CdS powder were performed using SEM (FEI Quanta 600) and XRD (Bruker D8 Advance). UV–vis absorption spectra were taken on a Cary 4E spectrophotometer. Photoluminescence spectra were carried out on a Fluorolog-3 Spectrofluorimeter at an excitation wavelength of 420 nm. The thickness of the CdS thin films was measured using a Dektak XT profilometer.

3. Results and discussion

CdS can exist either in the hexagonal wurtzite (WZ, P6₃mc) or cubic zinc blende (ZB, F₄₃m) structures [15,16]. Under laboratory conditions, the WZ structure is the most thermodynamically stable phase of CdS although the energy difference between the WZ and metastable zinc-blende (ZB) structure is only a few milli-electron volts per atom [15]. It has been reported that colloidal CdS generally crystallizes in the same WZ structure as with the bulk [17] whereas, nanocrystalline CdS crystallizes both the WZ structure and the less stable ZB structure [18]. Here, we observe that the WZ structure and ZB co-exist under similar CBD reaction conditions and that the observed crystalline phase is highly dependent on the pH of the solution.

Time dependent-XRD data were obtained for CdS deposition experiments carried out at pH 8 and pH 10 from 30 to 240 min on the micropillar arrays, flat epoxy samples (control), glass slides (control), and solid precipitates. The observed crystal structure did not vary based on the type of substrate used (microstructured, flat epoxy, or glass slides) and the same crystal structure was observed on the epoxy substrates as the precipitated solid particles isolated from the reaction. Experiments on the deposition of CdS were carried out at pH 8 by adjusting the concentration of ammonia added to the initial reaction mixture (see Section 2 for details). Fig. 1 shows the XRD data obtained at pH 8 with varying deposition time from 30 min to 240 min. It is clear that at pH 8, the hexagonal (WZ) phase is dominant and phase pure irrespective of the deposition time. The relative intensity of the CdS (002) peak formed at pH 8 was higher than the bulk hexagonal crystal phase, suggesting preferential growth along the c-axis rather than random orientation [16,19,20]. No impurities were observed that could be attributed to the CdS cubic phase at pH 8 (e.g. absence of (200) cubic (ZB) peak). Notably, the phase is
accessible at temperatures as low as 85 °C and phase pure even though the WZ phase of CdS is reported to be a high temperature phase that is generally achieved at temperatures above 800 °C, with many groups reporting a minimum cubic to hexagonal phase transition temperature of 300 °C. This suggests that pH plays a major role in the decomposition kinetics of thiourea and aids in the formation of this high temperature phase at temperatures as low as 85 °C.

Fig. 2 demonstrates XRD patterns of CdS deposition at pH 10 with varying reaction time (30–240 min). Significantly, at pH 10, the ZB crystal structure was observed on the micropillar arrays, flat epoxy samples (control), glass slides (control), and solid precipitates. The ZB structure is dominant at all time intervals with three distinct features at 2θ = 26.5°, 43.9°, and 52° together with a small broad peak at 32° that are characteristic of the (111), (220), (311) and (200) reflections of the ZB phase. Some impurity peaks are visible throughout the reaction process due to the presence of the WZ structure. Importantly, the metastable ZB structure is dominant and nearly phase pure under these CBD conditions. This is consistent with observations that the cubic CdS phase is accessible via precipitation techniques.

The pH was monitored for the reaction in which the initial reaction conditions were adjusted to pH 10. A drop of two pH units (from pH 10 to pH 8) was observed during the course of this reaction (3 h), which suggests that the ammonium hydroxide equilibrium greatly influences the crystal phase and is a likely reason that the reaction results in a mixture of hexagonal and cubic crystal structures.

Others have also reported that varying the ammonia and ammonium acetate concentration can alter the structure of CdS thin film [19] by affecting the pH of the reaction. At pH 10, the high ammonium concentration shifts the equilibrium towards the formation of ammonia that is subsequently complexed as Cd(NH₃)⁴⁺ and results in a significant drop in pH (Eqs. (1) and (2)) [20]. The hydrolysis of thiourea (Eqs. (3a) and (3b)) is highly sensitive to the pH, temperature, and the catalytic effect of certain solids species and surfaces [21]. Thiourea decomposition takes place at a fast rate in an alkaline solution with a high concentration of OH⁻ present for the hydrolysis of thiourea. Available Cd²⁺ reacts with the free S²⁻ and precipitates as CdS (Eq. (4)). This process drives the hydrolysis of the thiourea equilibrium continuously to right [20]. Cd(NH₃)⁴⁺ complex formation (Eq. (2)) also affects the Cd(OH)₂ formation during the course of the reaction (Eq. (5)).

\[
\begin{align*}
\text{NH}_4^+ + \text{OH}^- & \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \\
\text{Cd}^{2+} + 4\text{NH}_3 & \leftrightarrow [\text{Cd(NH}_3)_4]^2^+ \\
(\text{NH}_2)_2\text{CS} + \text{OH}^- & \leftrightarrow \text{SH}^- + \text{H}_2\text{O} + \text{CN}_2\text{H}_2 \\
\text{SH}^- + \text{OH}^- & \leftrightarrow \text{S}^2^- + \text{H}_2\text{O} \\
\text{Cd}^{2+} + \text{S}^2^- & \leftrightarrow \text{CdS} \\
\text{Cd}^{2+} + 2\text{OH}^- & \leftrightarrow \text{Cd(OH)}_2
\end{align*}
\]
In the literature, two mechanisms have been reported for the formation of CdS by CBD: the ion-by-ion mechanism and cluster (hydroxide) mechanism. Depending on the reaction precursors, the mechanism can transition from one to the other through the course of the deposition [20]. In the cluster (hydroxide) mechanism, small amounts of Cd(OH)$_2$ initially form on the substrate and CdS forms when the OH$^{-}$/C0$^2$ groups in Cd(OH)$_2$ are replaced by S$^{2-}$/C0$^2$ ions. This cluster mechanism can be simple (Eq. (6)) or can lead to the formation of a complex (Eq. (7)) that subsequently decomposes.

\[
\text{Cd (OH)}_2 + S^{2-} \rightarrow \text{CdS} + 2OH^{-} \tag{6}
\]

\[
\text{Cd (OH)}_2 \cdot \text{SC (NH}_2)_2 \rightarrow \text{CdS} + \text{CN}_2\text{H}_2 + 2\text{H}_2\text{O} \tag{7}
\]

In the ion-by-ion mechanism, the presence of a surface (substrate) facilitates the heterogeneous nucleation. This mechanism is likely to occur when Cd(OH)$_2$ formation is less favorable and can be categorized as a simple ion-by-ion mechanism (Eq. (8a)) or a complex-decomposition ion-by-ion mechanism (Eq. (8b))

\[
\text{Cd}^{2+} + (\text{NH}_2)_2\text{CS} \leftrightarrow [(\text{NH}_2)_2\text{CS} \cdot \text{Cd}]^{2+} \tag{8a}
\]

\[
[(\text{NH}_2)_2\text{CS} \cdot \text{Cd}]^{2+} + 2\text{OH}^{-} \rightarrow \text{CdS} + \text{CN}_2\text{H}_2 + 2\text{H}_2\text{O} \tag{8b}
\]

At pH 10, the cubic (ZB) crystal structure is prominent, highlighting the fast hydrolysis of thiourea and controlled release of Cd$^{2+}$. Under these conditions, both the cluster mechanism and the ion-by-ion mechanism can occur simultaneously leading to a mixture of crystal structures; however, the cluster (hydroxide) mechanism is favored since Cd(OH)$_2$ can form on the surface of the substrate, which leads to a prominent cubic phase.

At pH 8, S$^{2-}$ ions are not released in appreciable amounts due to the slow thiourea decomposition at a low concentration of OH$^{-}$ which decreases the likelihood of Cd(OH)$_2$ formation [20,22]. Under these conditions the ion-by-ion mechanism is favored over the cluster mechanism that leads to the prominent hexagonal phase. When the reaction is carried out at pH 8, the hexagonal phase is dominant. In addition, impurities of the hexagonal phase are observed when the experiment is carried out at pH=10 as the pH decreases over time to approximately pH 8, which again provides evidence that pH affects the formation of the crystal structure.

Fig. 3 shows SEM images of CdS thin films deposited on the epoxy surfaces at pH 10 with varying deposition times from 30 min to 240 min. Compact and conformal CdS thin films were observed on the micropillars with granular-like morphology (Fig. 3A). These granules consist of smaller CdS particles with a crystallite size of 32.4 nm based on the Scherrer equation. The dense aggregates are consistent with the fast hydrolysis of thiourea at pH 10 which leads to a high deposition rate. The micropillar array substrates coated with the CdS film were immersed in water and sonicated for 5 min. The integrity of the films on the micropillar arrays was not affected (Fig. 3B). Flat, flower-like structures were also observed on the tips of the micropillars in some samples at longer deposition times (Fig. 3B, 180 min), which were unaffected by sonication. In all samples, small colloidal particles are observed at the bottom surface of the epoxy micropillar substrate.

Fig. 4 demonstrates representative SEM images of CdS films deposited on the micropillar arrays at pH 8 from 30 to 240 min. Aggregates and precipitates were observed for some samples at 30 min that may be due to either more fragile adhesion of the CdS film to the micropillars at short deposition times, which makes the films vulnerable to sonication (Fig. 4A) or through loose CdS aggregates formed in solution that deposit on the surface. At longer deposition times, a uniform and conformal layer of CdS is observed for all samples. Fig. 4B shows a side view of the micropillar structures where it is evident that even the tiny ridges, that result from the etching of the micropillars and present in the original Si master, are uniformly coated.
with CdS. Capillary forces formed as the aqueous solution dries from between the microstructures can result in the clustering of the microstructures. Clustering can be avoided with careful sample handling and slow drying. Beyond 180 min, “web-like” and “network-like” structures start to grow from the tips of the pillars (Fig. 4C and D). This suggests that the tips of the pillars act as a nucleating surface that catalyzes the formation of the “network-like” CdS particles, which is consistent with the ion-by-ion mechanism. These nanogrowths were formed by the fusion of spherical CdS clusters that grow and connect neighboring pillars (Fig. 4D).

UV–vis absorption spectra of the CdS thin films deposited at pH 8 and pH 10 are shown in Fig. 5A. The absorption onset value obtained for thin films deposited at pH 8 was approximately 499 nm with a band gap of 2.49 eV. The relationship between the particle size, \(d\), and band gap \(E_g\) can be calculated based on the effective mass approximation (EMA) for particles larger than 4 nm [23]

\[
E_g = E_g(0) + \frac{\alpha}{d^\beta} 
\]

where \(E_g(0)\) is the band gap of bulk CdS (2.42 eV), and \(\alpha\) and \(\beta\) are constants that were determined to be 13 eV/nm\(^2\) and 2 respectively from data taken from Lippens and Lannoo [24]. The band gap calculated for a particle of approximately 42.2 nm based on XRD and Scherrer’s equation analysis is 2.41 eV (see Supporting information). The absorption onset value for pH 10 samples was approximately 507 nm with a band gap of approximately 2.45 eV as calculated from the optical absorption. This is in good agreement with the average particle size of approximately 32.4 nm based on the XRD and Scherrer’s equation analysis. A slight blue-shift in the absorption spectra as compared to the bulk value is attributed to smaller and polydisperse crystallite size.

Photoluminescence (PL) spectroscopy of the CdS films on the glass substrates was performed at room temperature (Fig. 5B) with an excitation of 420 nm. The samples were yellow but transitioned over time to a darker yellow-orange color for both pH 8 and pH 10 experiments (for both glass and epoxy substrates). WZ and ZB types CdS thin films had emission spectra dominated by a broad peak between 2.10 eV and 2.13 eV known as the “yellow band” that arises from interstitial Cd or S vacancies [7,25]. A less intense peak at 1.87 eV, commonly referred to as the “red band,” was also observed which has been attributed to S vacancies in radiative recombination. The broad emission spectra are likely to contain bands in the “orange” (2.07–2.18 eV) due to
donor–acceptor recombination and “green” (2.18–2.54 eV) associated with deep donor-states to the valence band (WZ to ZB phase transformation) [26–28]. The PL spectra are consistent with other CdS films grown via CBD with little difference between WZ and ZB phases [25,29,30]. A more intense “red band” observed in our samples is likely due to higher levels of interstitial Cd or S vacancies as a result of excess thiourea used in our reaction conditions; however, a more detailed temperature dependent study is necessary to de-convolute the spectra.

4. Conclusions

CBD can be used for the conformal deposition of CdS films on corrugated or non-uniform surfaces such as epoxy micropillar arrays with dimensions as small as \( d = 1 \text{um} \) and \( h = 4 \) that can withstand mild sonication. We have demonstrated that both the ZB and WZ crystal structures of CdS are accessible by varying the pH of the CBD reaction. Under reaction conditions in which a large excess of thiourea is present, both the cluster mechanism and the ion-by-ion mechanism can occur, which results in the possibility of obtaining either the ZB or WZ crystal structure. pH plays two major roles including affecting the decomposition kinetics of thiourea as well affecting the \( \text{Cd}^{2+} \)-complex formation. The cluster (hydroxide) mechanism is likely favored at \( \text{pH}=10 \) since \( \text{Cd(OH)}_2 \) can form on the surface of the substrate that leads to a prominent cubic phase, while the ion-by-ion mechanism is likely favored at \( \text{pH}=8 \) and results in the hexagonal phase. The deposition of CdS on the micropillar surfaces is uniform and conformal with the formation of packed clusters on the micropillars at \( \text{pH} = 10 \) that form flower-like structures at long deposition times. Smaller crystallites are observed on micropillar arrays at pH 8 with “network” like structures observed at long deposition times. This work suggests that the crystal structure of CdS and phase purity can be controlled by maintaining the pH of the CBD reaction constant at \( \text{pH}=10 \) for cubic and \( \text{pH}=8 \) for hexagonal crystal structure.

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Appendix A. Supporting information

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References