Optical and Structural Characterization of Cd-Free Buffer Layers Fabricated by Chemical Bath Deposition

William Vallejo 1,*, Carlos Diaz-Uribe 1 and Cesar Quiñones 2

1 Grupo de Investigación en Fotoquímica y Fotobiología, Facultad de Ciencias Básicas, Universidad del Atlántico, Puerto Colombia 081007, Colombia; carlosdiaz@mail.uniatlantico.edu.co
2 Institución Universitaria Politécnico Gran Colombiano, Bogotá 110231, Colombia; caquinones@poligran.edu.co
* Correspondence: williamvallejo@mail.uniatlantico.edu.co; Tel.: +57-5359-9484

Abstract: Chemical bath deposition (CBD) is a suitable, inexpensive, and versatile synthesis technique to fabricate different semiconductors under soft conditions. In this study, we deposited Zn(O;OH)S thin films by the CBD method to analyze the effect of the number of thin film layers on structural and optical properties of buffer layers. Thin films were characterized by X-ray diffraction (XRD) and UV-Vis transmittance measurements. Furthermore, we simulated a species distribution diagram for Zn(O;OH)S film generation during the deposition process. The optical results showed that the number of layers determined the optical transmittance of buffer layers, and that the transmittance reduced from 90% (with one layer) to 50% (with four layers) at the visible range of the electromagnetic spectrum. The structural characterization indicated that the coatings were polycrystalline (α-ZnS and β-Zn(OH)2 to four layers). Our results suggest that Zn(O;OH)S thin films could be used as buffer layers to replace CdS thin films as an optical window in thin-film solar cells.

Keywords: solar cells; buffer layers; thin films; chemical bath deposition

1. Introduction

Nowadays, the main primary energy source for electricity generation remains fossil fuels (oil, coal, natural gas), which are a non-renewable resource presenting a negative environmental impact due to emissions of greenhouse gases and other polluting by-products [1–3]. This traditional energy source does not warrant a long-term supply of the growing demand for energy created by population and industry growth [4–6]. This trend and the anthropogenic effect of human activities on the atmosphere, aquatic quality, and biodiversity are challenges for the near future [7,8]. This situation has generated great global interest in the search for new energy sources, preferably renewable ones. The Renewable Energy Police Network for the 21st Century (REN21) reported that 79.9% of the world’s total energy consumption was supplied by fossil fuels, 2.2% by nuclear energy, 6.9% by traditional biomass, and 11% by modern renewables (e.g., biomass/solar/geothermal heat (4.3%), hydropower (3.6%), wind/solar/biomass/ocean/geothermal power (2.1%), and biofuels for transport (1.0%). Among modern renewables, the global solar installed photovoltaic (PV) capacity grew more than 200 gigawatts (GW) in 2019 [9]. In the last 6 years, the increasing adoption rate of photovoltaic systems has also led to a price drop in excess of 80% [10]. Currently, crystalline silicon PV cells represent more than 85% of world PV cell market; however, the thin-film chalcogenide PV technology has shown a rapid growth compared to that of silicon due to its low cost of production [11]. The Cu(In,Ga)(Se,S)2 (CIGS) is one of the most researched materials as absorbent layers within thin-film PV technologies. In general, most of the CIGS-based solar cells include a very thin CdS (<100 nm) as a buffer layer to reduce crystalline mismatch between the chalcopryte absorber layer and the transparent ZnO front electrode [12,13]. In the last two decades, serious efforts have been made to replace the CdS buffer layer by other nontoxic...
material [14–16]. Actually, in their last report, Green et al. reported an efficiency value of 23.3% for CIGS cells free of Cd [17]. Different compounds have been reported as alternatives to fabricate Cd-free buffer layers (e.g., ZnS [18], Zn(O,S) [15], ZnSe [19], InS$_2$ [20], CdS [21]). Among the semiconductor options, Zn(O,OH)S coatings are widely used as thin films in the fabrication of luminescent materials, light-emitting diodes, electroluminescent devices, optical covers, reflectors, and dielectric filters [22–27]. Since Zn(O;OH)S films have n-type conductivity and a large direct Eg bandgap (3.6–3.9 eV), they are suitable for use as buffer layers for thin-film solar cells [28].

Various deposition methods have been reported for the fabrication of semiconductor thin films: (i) thermal evaporation [29,30], (ii) sputtering [31], (iii) atomic layer deposition [32], (iv) electrochemical [33], (v) chemical vapor deposition [34], and (vi) chemical bath deposition (CBD) [35–37]. Among the physical and chemical methods of thin film deposition, the CBD process is the most economic and technically suitable one (e.g., regarding lab equipment and temperature and pressure requirements) [38]. In the typical procedure, with a temperature below that of the boiling point of water and under atmospheric pressure, a source of metal and chalcogenide are mixed in a vessel. First, temperature and pH are adjusted. Then, the solid substrate is immersed inside the reaction vessel, and the thin deposition starts. CBD is a convenient method for buffer layer deposition. However, thin film semiconductors grown using the CBD process produce large amounts of waste solvent and chemicals that then require costly waste processing [39]. The possibility of increasing optical transmission and deleting a toxic element (Cd) has directed the research in the field to study different synthesis parameters to optimize the CBD process (e.g., the effect of temperature, chalcogenide and metal source, complexing agents, pH, stirring). The main reports studied the physical–chemistry properties in thin films with only one coating (one layer) [40]. In this paper, we studied the effect of the number of buffer layers on the optical and structural properties of Zn(O;OH)S coatings deposited by CBD.

2. Materials and Methods

2.1. Thin Film Deposition by the CBD Process

Although the CBD process has been used in thin-film semiconductor synthesis for several decades, most reports do not explain the mechanism of film formation. Thus, different explanations have emerged, and two models are discussed in the literature to explain this process: (i) the ion–ion mechanism, which is a process that occurs by the direct reaction of the ions present in the solution on the surface of the substrate; and (ii) growth via cluster–cluster collisions. Figure 1a shows the ion–ion mechanism. In the first stage, the diffusion processes of metal ions (e.g., Zn$^{2+}$ or In$^{3+}$) and S$^{2–}$ ions occur on the surface of the substrate (Figure 1(a1)). In the second stage, the first semiconductor nuclei are generated on the surface of the substrate (Figure 1(a2)). In the third stage, the nuclei grow by adsorbing more ions, while new semiconductor nuclei are generated (Figure 1(a3)). Finally, the crystals grow and adhere to each other to generate the film (Figure 1(a4)) [41,42].

Figure 1b shows the cluster–cluster mechanism. In the first stage, colloidal size particles are generated in metal sulfide solution (e.g., ZnS or In$_2$S$_3$) or a possible intermediate (Zn(OH)$_2$ or In(OH)$_3$); then, these particles diffuse onto the substrate (Figure 1(bi)). In the second stage, the first nuclei are generated on the surface of the substrate (Figure 1(bii)). In the third stage, the nuclei grow by adsorbing more Zn$^{2+}$ and S$^{2–}$ ions, and the reaction continues until the possible intermediates transform into the respective sulfide through interchange reactions (Figure 1(biii)). Particle growth occurs both inside the solution and on the substrate surface. Finally, the particles adhere to each other on the surface of the substrate and form the film [41,42]. In the CBD process, both mechanisms may be present, generating the film and allowing the addition of colloidal aggregates for the subsequent growth of the film. The control of one of the two mechanisms is established by the extent of homogeneous and heterogeneous nucleation.
In the Zn(O;OH)S thin film deposition process, we used Thiourea as the S^{2+}-ions source (150 mM), Zn acetate as the Zn^{2+}-ions source (15 mM), and ammonia (350 mM) and sodium citrate (30 mM) as a complex agent with a temperature at 80 °C and pH at 10.5. In the CBD, soda-lime glass was used as substrate (SLG; 2 cm × 1.5 cm). After 45 min, the CBD was stopped, and the substrate was withdrawn and washed with distilled water. The thin layer was dried at ambient temperature. This first layer was immersed in a new chemical bath system, and the deposition process was repeated using this first layer as substrate to the second layer. This process was repeated to obtain different numbers of layers. Finally, the Zn(O;OH)S thin films were annealed in air at 400 °C for 30 min.

2.2. Thin Film Characterization

The thickness of the films was measured using a Veeco Dektak 150 profilometer (Plainview, NY, USA). The optical properties of the thin films were studied through transmission measurements between 300 and 800 nm (Perkin Elmer Lambda 2S spectrophotometer, Waltham, MA, USA). The structural assay was carried out using a Shimadzu 6000 diffractometer (Tokyo, Japan) with a source of CuKα radiation (λ = 0.15418 nm) within the 2θ range of 20°–60°. Finally, the chemical surface assay was carried out using a Perkin-Elmer ESCA/SAM model 560 (Waltham, MA, USA).

3. Results and Discussion

3.1. Thin Film Deposition

Figure 2 shows the Zn(O;OH)S thin-film thickness as a function of the deposition time. In the typical growth trend during CBD, two regions are distinguished: (a) linear growth, a stage in which the film thickness increases linearly with time, and (b) the saturation zone, a stage in which the growth rate decreases significantly as a consequence of consumption of the reagents inside the solution [43,44]. In our case, the data on thin film thickness within a 60 min time were suitable with linear fitting (R^2 = 0.993); after this time, it is typical, in the CBD process, that linear kinetics change to due to the consumption of the reagents.

![Figure 1](image-url)
inside the solution. We performed the deposition of each layer within a 45-min deposition time (linear growth, Figure 2). Table 1 lists Zn(O;OH)S thin film thickness as a function of the number of layers. The results show a typical trend: as the number of layers increases, so does the thickness of the films. After the second layer, the coating thickness exceeds 100 nm. The typical thickness used to reduce the mechanical stress between the absorbent layer and the transparent conductor oxide (TCO) in thin-film solar cells is smaller than 100 nm. For three and four layers, the thickness values are 350 and 480 nm, respectively. The next sections will present the effect of the number of layers on the optical and structural thin films.

![Figure 2. Zn(O;OH)S thin-film thickness as a function of CBD deposition time. White squares represent data and the red line represents the linear fitting. Fitting data: R² = 0.993. Fitting equation: y = 3.38(x) − 18.5.](image)

**Table 1.** Optical and structural properties of the thin films, varying the number of layers deposited by CBD.

| Number Layers | Thickness (nm) | Energy Band Gap (eV)¹ | Crystal Properties                |
|---------------|----------------|-----------------------|-----------------------------------|
| 1             | 90             | 3.81                  | Amorphous                         |
| 2             | 190            | 3.77                  | Amorphous                         |
| 3             | 350            | 3.70                  | Cubic/hexagonal phases            |
| 4             | 480            | 3.65                  | Cubic/hexagonal phases            |

¹ Value as a result of extrapolating the linear portion of the graph onto the x-axis in Figure 5b.

Although CBD is widely studied as a film deposition method, most reports are limited to exposing the different deposition parameters of the coatings; few reports show analytical studies about the chemical systems used during the deposition of the coatings. In a recent study, Gonzales et al. [45] reported the species distribution diagrams for CDB-ZnS film deposition. Due to chemical conditions (e.g., reagent concentration, pH, temperature), they did not report the formation of a ternary complex. It is known that the use of complexing agents reduces the homogeneous precipitation to obtain uniform and adherent coatings. The typical complexing agents in CBD include ammonia, hydrazine, ethanolamine, triethanolamine, tartaric acid, sodium citrate, and EDTA [46–49]. In the present study, we used sodium citrate to replace hydrazine in the CBD process. After CBD begins, the sulfide ion is generated as a free species in the solution due to hydrolysis of thiourea in a basic medium [50]:

\[
\text{SC(NH}_2)_2 + \text{OH}^- \rightarrow \text{NCNH}_2 + \text{SH}^-(\text{aq}) + \text{H}_2\text{O}. \tag{1}
\]
Once the dissociated species of hydrogen sulfide (HS\textsuperscript{-}) is formed in the medium, the \( S^{2-} \) ion is formed as follows \([50]\):

\[
\text{SH}^- + \text{OH}^- \rightleftharpoons S^{2-}\text{(aq)} + \text{H}_2\text{O}.
\] (2)

In the CBD solution, two solids can precipitate \([50]\):

\[
\text{Zn}^{2+}\text{(aq)} + S^{2-}\text{(aq)} \rightleftharpoons \text{ZnS(s)} \quad K_{sp} = 10^{-24.7}
\] (3)

\[
\text{Zn}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)} \rightleftharpoons \text{Zn(OH)}_2\text{(s)} \quad K_{sp} = 10^{-16}
\] (4)

where \( K_{sp} \) is the solubility product constant (the equilibrium constant for the chemical equilibrium of solid dissolving in aqueous solution) \([51]\). The presence of a complexing agent is necessary to prevent the excessive formation of ZnS/Zn(OH)\(_2\). The complex formation reactions are as follows \([52,53]\):

\[
\text{Zn}^{2+} + 3\text{Cit} \rightleftharpoons [\text{Zn(Cit)}_3]^7^- \quad \beta = 10^{5.5}
\] (5)

\[
\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Zn(NH}_3)_4]^{2+} \quad \beta = 10^{9.46}
\] (6)

\[
\text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons [\text{Zn(OH)}_4]^{2-} \quad \beta = 10^{15}
\] (7)

\[
[Zn(NH}_3)_4]^{2+} + \text{Cit} \rightleftharpoons [Zn(NH}_3)_3\text{Cit}]^- + \text{NH}_3 \quad \beta = 10^{15}
\] (8)

\[
[Zn(NH}_3)_3\text{Cit}]^- + \text{Cit} \rightleftharpoons [Zn(NH}_3)_2(\text{Cit})]^{4-} + \text{NH}_3 \quad \beta = 10^{10}
\] (9)

\[
[Zn(NH}_3)_2(\text{Cit})]^{4-} + \text{Cit} \rightleftharpoons [Zn(NH}_3)(\text{Cit})]^{7-} + \text{NH}_3 \quad \beta = 10^{7.46}
\] (10)

where Cit represents citrate anion ([C\(_6\)H\(_5\)O\(_7\)]\(^{-3}\)), \( \beta \) is the stability constant (the equilibrium constant for the formation of the complex between metallic-ion and complexing agent) \([51]\). Based on the chemical equilibrium Equations (1)–(10) and single complexing equilibrium, we simulated the species distribution diagram for Zn(O;OH)S synthesized by the CBD. We calculated the fraction molar (\( x_i \)) for each species at equilibrium, with the \( x_i \) value being determined by physical–chemical conditions of the mixture (e.g., pH, reagent concentration, temperature). The theory and details of the methodology used to simulate the distribution diagram can be found in previous reports \([54,55]\). In the equation, \( x_i \) represents the molar fraction of each species under specific chemical conditions, for which case we studied the pH effect on the \( x_i \) value \([45]\):

\[
x_i = \frac{[s_i]}{\sum [s_i]}
\] (11)

where \( S_i \) is the concentration of the species \( i \) at a specific pH. Regarding the stability constants of ternary compounds (4–6), Figure 3a shows the distribution diagram of the species involved in the thin films deposited by CBD in the pH range 2–14. Figure 3a shows that the hydroxyl complexes are important from pH values higher than 12. Furthermore, the complexing agent used (sodium citrate) participates in the generation of ternary complexes. Figure 3b shows that when under the pH conditions used during CBD (pH = 10–11), the ternary complexes (ammonium-Zn-citrate) are present (near 70% of the species in the CBD solution). Conventionally, CBD processes use hydrazine as a reducing and/or complexing agent due to its chemical and physical properties \([56]\). However, this compound poses serious risks for the environment and health. The challenge is to combine inexpensive and green chemical routes for semiconductor fabrication and to direct synthetic routes to develop hydrazine-free chemical bath depositions \([57]\). The results show that the chemical reagents used in CBD are suitable for Zn(O;OH)S thin-films synthesis; furthermore, the simulation indicates that the citrate complex acts as a complexing agent during CBD.
Figure 3. Species distribution diagram for Zn(O;OH)S synthesized by the CBD method under experimental conditions. (a) pH range 2–14. (b) Zoom range pH 10–12. Inside figure, Cit represents citrate anion ([C$_6$H$_5$O$_7$]$^{3-}$). ($\chi$) represents fraction molar for each species at equilibrium.

3.2. Structural Characterization

The effect of the number of thin film layers on structural properties was studied by X-ray diffraction. After the annealing procedure, the coatings with one and two layers did not show signals in the diffraction pattern (patterns are not shown), suggesting that these coatings could be formed by small-sized grains (on a nanoscopic scale); besides, the coatings with three and four layers were polycrystalline. Figure 4 shows the X-ray diffraction patterns for Zn(O;OH)S thin films (three and four layers).

Figure 4. X-ray diffraction patterns of Zn(O;OH)S-thin film thickness as a function of the number of the layers. (a) Zn(O;OH)S coatings three layers. (b) Zn(O;OH)S coatings four layers. Inside figure: (*) The signal could be assigned to Wurtzite and/or Zincblende structure. (i) The signal could be assigned to Zn(OH)$_2$ structure.

Due to the chemical conditions of CBD, (i) the signals located at 2$\theta$ = 28.8°, 31.6°, 47.2°, and 58.2° were assigned to reflections of two different crystalline phases: (i) (002), (011), (110), and (0.21) planes of the hexagonal structure (Wurtzite; JCPDS 79-2204), and (ii) the signals located at 2$\theta$ = 28.8° and 47.2° were assigned to reflections of (111), (022) planes of the cubic structure (Zincblende; JCPDS 77-2100)) [58]. Furthermore, the signals located at 2$\theta$ = 34.4° and 58.22° were assigned to reflection $\beta$-Zn(OH)$_2$ (JCPDS 77-2100) [59], and the presence of this signal suggests the formation of Zn(OH)$_2$ or ZnO inside the buffer layer. The possible mechanism of generation and growth of the film occurs according to the formation of Zn(OH)$_2$ (Equation (4)). This process is not eliminated from the reaction medium despite the fact that a low concentration of the metal ion and the addition of the complexing agent were used during CBD [50]. The competition between the formation of ZnS and Zn(OH)$_2$ during the Zn-buffer layer deposition by CBD has been previously reported [45,60]. In a previous work [61], we identified that the Zn$^{2+}$, sulfur, and oxygen were present inside the Zn(O;OH)S-thin films deposited by CBD, suggesting that ZnS and ZnO could be generated during the CBD process. Sáez-Araoz et al. [62] reported that in
the early Zn-buffer layer deposition by CBD, a very thin film of ZnS is generated, which is followed by a mixture of ZnS and ZnO. Finally, other authors report the generation of a mixture of chemical phases during Zn-based buffer layers synthesized by CBD [63–65].

3.3. Optical Characterization

Figure 5a shows the transmittance curves of the Zn(O;OH)S films deposited on SLG by the CBD process. The number of layers significantly affected the spectral transmittance. In general, for one (90 nm) and two (190 nm) layers, transmittances are greater than 80% in the visible region of the electromagnetic spectrum (zone of low absorbance $\lambda > 310$ nm). Such a high transmittance value indicates that these coatings are optically suitable for use as a buffer layer. Furthermore, Figure 5a shows a deterioration in the optical transmittance for three and four layers, reducing until 60–70% (three layers) and 50–60% (four layers). High optical transmittance in the visible range of the electromagnetic spectrum is a critical requirement for buffer layers inside solar cells. The band-gap energy value was determined for all samples using the Tauc model. For films with reduced thickness and that do not present sufficient interference patterns, the absorption coefficient of each layer can be determined using the following equation [66,67]:

$$\alpha(h\nu) = \frac{1}{d} \ln \frac{1}{T(h\nu)}$$

(12)

where $\alpha$ is the absorption coefficient, $d$ corresponds to the thickness of the buffer layer and, $T$ corresponds to the spectral transmittance as a function of the wavelength. The absorption coefficient is related to the band gap according to the following equation [68]:

$$\alpha(h\nu) = A(h\nu - E_g)^2$$

(13)

where $E_g$ corresponds to the band gap of the material, and $A$ is a constant. The value of $E_g$ can be obtained by extrapolating the linear portion of the graph of $(\alpha h\nu)^2$ vs. $(h\nu)$ to zero. This method was used to determine the $E_g$ of the buffer layers. Figure 5b shows plots $\alpha^2$ versus $(h\nu)$ for the transmittance spectra of Figure 5b. The optical band gap of the films was determined by extrapolating the linear portion of the graph onto the x-axis [68]. Table 1 lists the optical properties of the thin films. During the chemical bath deposition of semiconductors, it is common to produce a mixture of different chemical compounds [41,42]. In the case of Zn-buffer layers, depending on experimental parameters, the mixture of compounds (e.g., sulfide, hydroxide, and oxide) could be generated [69,70]. Furthermore, the semiconductor thin films band gap is affecting by thickness, crystalline structure, and physical–chemical composition [71,72]. The ZnO has a wide and direct band gap ($\approx 3.37$ eV) [73]. In the case of ZnS thin films, this is a semiconductor with a wide optical band gap ($\approx 3.6$ eV) [74,75]. However, the thin films band gap is affected by the deposition method and the post-treatment process. Mursal et al. [76], reported the optical band gap of ZnO thin films varying between 3.82 and 3.69 eV deposited by the sol–gel spin-coating method after changed the sintering temperature. The difference in the experimental and theoretical band gap is attributed to the intrinsic defects in ZnO (e.g., O vacancy ($V_O$), Zn vacancy ($V_{Zn}$), Zn interstitial ($Zn_i$), O interstitial ($O_i$) and anti-site Zn ($Zn_O$)) [77–79]. Table 1 shows that the coating’s band gap changes between 3.65 and 3.81 eV. The band-gap energy of the Zn(O;OH)S coating synthesized by CBD has values between the band gap of ZnS and ZnO. This result could be related to the possibility of the generation of a mixture of chemical phases during buffer layers deposition (Section 3.2).
Figure 5. (a) Zn(O;OH)S thin-film transmittance as a function of the number of layers deposited by CBD. (b) Tauc plots and band-gap energy estimation for the Zn(O;OH)S thin films as a function of the number of layers deposited by CBD.

Furthermore, Table 1 shows that reducing the layer thickness affects the bulk properties and changes the optical properties, and that the thinner layers have a higher band-gap energy value, which is consistent with other reports. Das et al. reported band-gap variation with thickness for CdS thin films deposited by CBD and found that the band gap decreased from 3.2 eV (CdS thin films of 153 nm in thickness) until 2.54 eV (CdS thin films of 205 nm in thickness) [80]. Hossain et al. studied the In2S3 buffer layer band-gap variation from 2.0 to 2.9 eV to observe the effects thereof on electrical performance, and they reported that the band gap increased up to 2.9 eV with a layer of 50 nm in thickness, and this value decreased to 2.0 eV with a layer of 1 µm in thickness [81]. Such results verified that the number of layers in the coatings determines the physical–chemical properties of buffer layers (e.g., band gap, crystalline structure). Although all the coatings had energy values higher than 3.65 eV (requirement for the buffer layer in solar cells), only the coatings with one and two layers were suitable for use as buffer layers.

4. Conclusions

In this paper, we studied the structural and optical properties of Zn(O;OH)S coatings grown by CBD with different numbers of layers. We presented the simulation of the species distribution diagram for the Zn(O;OH)S synthesized by CBD. The thickness of the buffer layer films varied from 90 to 480 nm. The Zn(O;OH)S thin films with three and four layers represented a mixture of the cubic and hexagonal phases. Furthermore, the species diagram simulation indicates that the citrate complex could play an important role as a complexing agent during CBD. Finally, optical properties indicate that only the coatings with one and two layers were suitable for use as buffer layers, since these coatings had higher transmittance values. Furthermore, although all coatings had energy values higher than 3.65 eV, the coatings with three and four layers showed reduced transmittance in the visible region (50–70%).

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