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Preparation and characteristics of chemical bath deposited ZnS thin films: Effects of different complexing agents

Seung Wook Shin[a], G.L. Agawane[b], Myeng Gil Gang[b], A.V. Moholkar[c], Jong-Ha Moon[b], Jin Hyeok Kim[b,*], Jeong Yong Lee[a,**]

[a] Department of Materials Science and Engineering, KAIST, Daejeon 305-701, South Korea
[b] Photonics Technology Research Institute, Department of Materials Science Engineering, Chonnam National University, Gwangju 500-757, South Korea
[c] Department of Physics, Shivaji University, Kolhapur 416-004, India

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ABSTRACT

Zinc sulfide (ZnS) thin films were prepared on glass substrates by a chemical bath deposition technique using aqueous zinc acetate and thiourea solutions in a basic medium (pH ~ 10) at 80 °C. The effects of different complexing agents, such as a non-complexing agent, Na_3-citrate, and a mixture of Na_3-citrate and ethylenediamine tetra-acetate (EDTA), on the structural, chemical, morphological, optical, and electrical properties of ZnS thin films were investigated. X-ray diffraction pattern showed that the ZnS thin film deposited without any complexing agent was grown on an amorphous phase. However, the ZnS thin films deposited with one or two complexing agents showed a polycrystalline hexagonal structure. No secondary phase (ZnO) was observed. X-ray photoelectron spectroscopy showed that all ZnS thin films exhibited both Zn—S and Zn—OH bindings. Field emission scanning electron microscopy (FE-SEM) images showed that ZnS thin films deposited with complexing agents had thicker thicknesses than that deposited without a complexing agent. The electrical resistivity of ZnS thin films was over $10^5\ \Omega\,\mathrm{cm}$ regardless of complexing agents. The average transmittance of the ZnS thin films deposited without a complexing agent, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA was approximately 85%, 65%, and 70%, respectively, while the band gap was found to be 3.94 eV, 3.87 eV, and 3.84 eV, respectively.

1. Introduction

Thin film solar cells based on polycrystalline Cu-chalcopyrite, such as $CuInSe_2$ (CIS), Cu(In,Ga)Se_2 (CIGS), and Cu(In,Ga)(S,Se) (CIGSSe), have attracted considerable interest for use in photovoltaic devices, owing to their relatively high efficiency in both large area and laboratory-sized solar cells [1,2]. In CIGS-based thin film solar cells, a chemical bath deposited CdS (CBD-CdS) buffer layer is placed between an absorber layer and a transparent conducting oxide (TCO) layer because of the following advantages: (i) the buffer layer protects the modification that results from chemical species in the sensitive surface of the absorber and junction regions, (ii) the damage caused by physical deposition during the subsequent TCO deposition process, and (iii) the appropriate interface charge adjusted during the deposition process [3,4]. In addition, the n-type doping effect on the surface region of an absorber layer can be caused by metal ions implanted into the CBD-buffer layer on a Cu-deficient absorber, which improves the electrical resistivity in the absorber layer [5]. CIGS-based thin films with a CBD-CdS buffer layer have achieved the best efficiency of 19.9% over a small area ($0.5\ \mathrm{cm}^2$) [6] and 16.6% on a mini module ($16\ \mathrm{cm}^2$) [2]. However, the fabrication of a Cd-based buffer layer in CIGS-based thin film solar cell can create serious environmental problems due to the large amount of Cd-containing waste generated during the deposition process [5,7–10]. This problem has stimulated research into developing a Cd-free buffer layer. Different buffer layers, such as ZnS, In_2S_3, ZnSe, Zn(S_x,Se_{1-x}), SnS, and $Zn_xIn_{1-x}Se$, have been examined, and their effect on the solar cell efficiency has been investigated [7,9,11,12]. Unfortunately, the efficiencies of Cd-free CIGS-based thin film solar cells fabricated from these materials are not as high as those fabricated from CBD-CdS buffer layers [4]. Among these alternative buffer layers, ZnS is considered to be the most promising buffer materials because a CIGS-based thin film with a CBD-ZnS buffer layer achieved the best efficiency of 18.6% over a small area compared to the other buffer materials, and it is less toxic and cheaper [12]. In addition, the band gap of ZnS (~3.6–3.8 eV) is wider than that of CdS (2.4 eV), which improves the short-circuit current of thin film based solar cells [3]. These practical facts suggest that

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* Corresponding author. Tel.: +82 62 530 1709; fax: +82 62 530 1699.
** Corresponding author. Tel.: +82 42 350 4216; fax: +82 42 350 3310.
E-mail addresses: jinhyeok@chonnam.ac.kr (J.H. Kim), j.y.lee@kaist.ac.kr (J.Y. Lee).

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CIGS thin film solar cells consisting of a CBD-ZnS buffer layer can achieve an efficiency beyond 20% [5]. ZnS is also an important II–VI compound semiconductor because of its higher transmission, high refractive index, and linear and nonlinear absorption, indicating that it finds wide applications in optoelectronic fields as deep-blue light emitting devices or a base material for phosphors [13–15].

The CBD-ZnS thin films are generally deposited from aqueous solutions of Zn salts, thiourea, or thioacetamide (as a S source) in a hot basic medium using one or more complexing agents, which allows control of the Zn^{2+} ions concentration [8,16,17]. Hydrazine hydrate and ammonia are generally used as complexing agents [18–20]. Oladeji et al. and Dona et al. reported that the adhesion, crystal quality, homogeneity, and growth rate of ZnS thin films are improved by adding hydrazine hydrate as a complexing agent [9,21]. However, hydrazine hydrate is a highly flammable, carcinogenic, and toxic material [21]. Therefore, in order to solve these problems, several research groups have examined ZnS thin film deposition using less toxic complexing agents, such as tri-sodium citrate (Na_3-citrate) [9] and ethylenediamine tetra-acetate (EDTA) [22]. Johnston et al. and Goudariz et al. reported the growth of 100 nm-thick ZnS thin films with high transmittance in the visible region using Na_3-citrate or EDTA as a less toxic complexing agent [10,22]. Although ZnS thin films were deposited successfully using one less toxic complexing agent, the deposited films had poor crystallinity, rough morphology, discontinuous microstructure, and thin thickness during long deposition times. These characteristics suggest the low efficiency in the thin film solar cells [6]. One possible alternative is the addition of an another complexing agent in order to improve the crystallinity of ZnS thin films deposited with one of these complexing agents in the reaction bath, which demonstrate that the increase in growth rate and more dense microstructure (continuous thin films) of ZnS thin films could be improved while keeping the smooth morphology by the proper use of the mixed complexing agent. Previous studies on CBD-ZnS thin films deposited with less toxic complexing agents focused mainly on the growth of ZnS thin films. However, there are no reports for a direct comparison of the structural, chemical, morphological and optical properties, and the detailed growth mechanism of CBD-ZnS thin films using different complexing agents in a basic bath.

The purpose of this study is to improve the growth rate and to compare the effect of different complexing agents, such as those without a complexing agent, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA on chemical-bath deposited ZnS thin films. The effects of the different complexing agents on the structural, chemical, compositional, morphological, and optical properties and the growth mechanism of ZnS thin films were investigated.

2. Experimental details

ZnS thin films were prepared on glass substrates by a CBD method using aqueous solutions of zinc acetate, thiourea, and different complexing agents in a hot alkaline medium. Na_3-citrate and a mixture of Na_3-citrate and EDTA were used as the complexing agents. The reaction bath solutions were prepared using 40 mL of a 0.2 M zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) solution and 60 mL of a 0.2 M Na_3-citrate ($Na_3C_6H_5O_7$) and a mixture containing 60 mL of 0.2 M Na_3-citrate ($Na_3C_6H_5O_7$) and 20 mL of 0.4 M of EDTA ($C_{10}H_{16}N_2O_8$). Subsequently, 80 mL of a 0.4 M thiourea ($SC(NH_2)_2$) solution was added, and the pH was adjusted to 10 by adding an ammonia (NH_4OH) solution. Finally, the required quantity of deionized water was added to make a 200 mL solution in the reaction bath. Prior to deposition of the ZnS thin films, the glass substrates were cleaned ultrasonically with acetone, methanol, isopropyl alcohol, and deionized water for 10 min, sequentially. The substrates were dried in air, and the cleaned substrates were then located vertically in a jig, which was then immersed in a reaction bath maintained at 80 °C for 4 h. After deposition, the substrates were removed from the reaction bath, rinsed with distilled water, dried in air, and preserved in an airtight plastic container. The deposited thin films were found to be uniform, pin-hole free, and well adhered to the glass substrates.

The structural properties of the thin films were examined by high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, The Netherlands) operated using a grazing incidence diffraction mode. The microstructures of the deposited thin films were analyzed by conventional transmission electron microscope (HR-TEM, TECNAI G^2F30 ST, FEI, and The Netherlands). The chemical binding energy of the films was examined by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, ThermoVG Scientific, UK) at room temperature. The binding energies in the spectrometer were calibrated using the carbon 1s line at 285.0 eV. The surface and cross-sectional morphology of the thin films were examined by field emission scanning electron microscopy (FE-SEM, Model: JSM-6701F) operated at room temperature. The optical transmittance of the thin films was measured by UV-visible spectroscopy (Cary 100, Varian, Mulgrave, Australia) at room temperature. The electrical properties of the deposited thin films were characterized using a Hall measurement (M/N #7707_LVWR, Lake Shore Cryotronics Inc., USA) at room temperature.

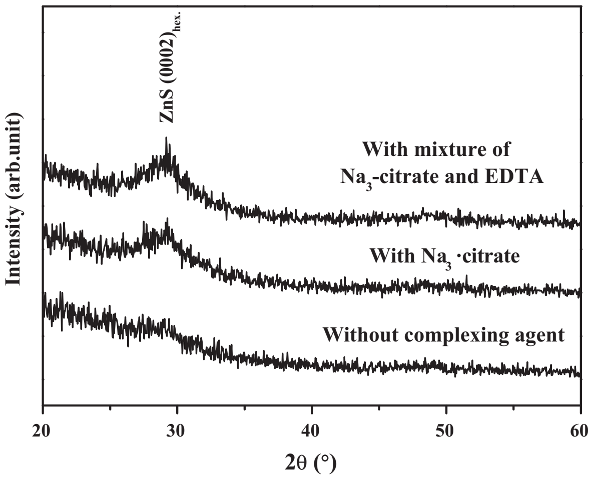

Fig. 1. XRD patterns of the ZnS thin films deposited without complexing agents, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA.

3. Results and discussion

3.1. Characterization of ZnS thin films

The ZnS thin films consisted of hexagonal (wurtzite-type structure) and cubic (zinc blende-type structure) phases. Previous literature surveys indicated the growth of cubic and hexagonal phases of ZnS thin films [8,19,22,23]. Fig. 1 shows the XRD patterns of the ZnS thin films deposited without a complexing agent and with complexing agents, such as Na_3-citrate and a mixture of Na_3-citrate and EDTA. The X-ray diffraction patterns showed that no strong peaks corresponding to cubic or hexagonal ZnS planes were observed for the thin film deposited without complexing agents. This confirmed the amorphous nature of ZnS thin film deposited without complexing agents. However, the ZnS thin films deposited with one complexing agent or with a mixture of complexing agents showed a broad peak at approximately 28.8°, corresponding to the cubic (1 1 1) plane or hexagonal (0 0 0 2) plane [JCPDS data file No.: 65-0309 (ZnS/Cub.) and 72-0163 (ZnS/Hex.)]. Unfortunately, they cannot be distinguished clearly into cubic or hexagonal planes because their angle positions are similar. In order to confirm the crystal structure of ZnS thin films deposited with one or mixture of complexing agents, the *d*-spacing value of the ZnS thin films deposited with different complexing agents were measured by high-resolution TEM (Fig. 2). Fig. 1 also shows that the intensity of the XRD peak of the ZnS thin film deposited with a mixture of Na_3-citrate and EDTA was relatively strong compared to that deposited with Na_3-citrate. No characteristic peaks resulting from the secondary phase (ZnO) were detected.

Fig. 2 shows the bright field (BF) – (a) and high-resolution (HR) – (b) TEM images of ZnS thin film deposited with a mixture of Na_3-citrate and EDTA. The inset in Fig. 2(b) presents the corresponding selected area electron diffraction (SAED) patterns obtained from the films and glass substrate interface. From BF- and HR-TEM image,

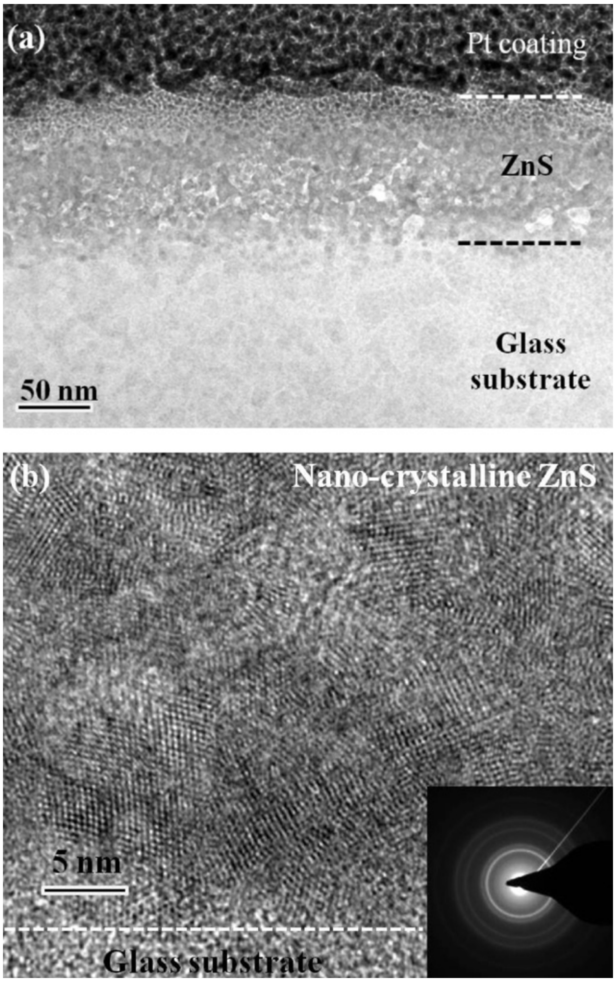

Fig. 2. Cross-sectional tilt bright field TEM image (a) and high-resolution TEM image (b) of ZnS thin film deposited with a mixture of Na_3-citrate and EDTA.

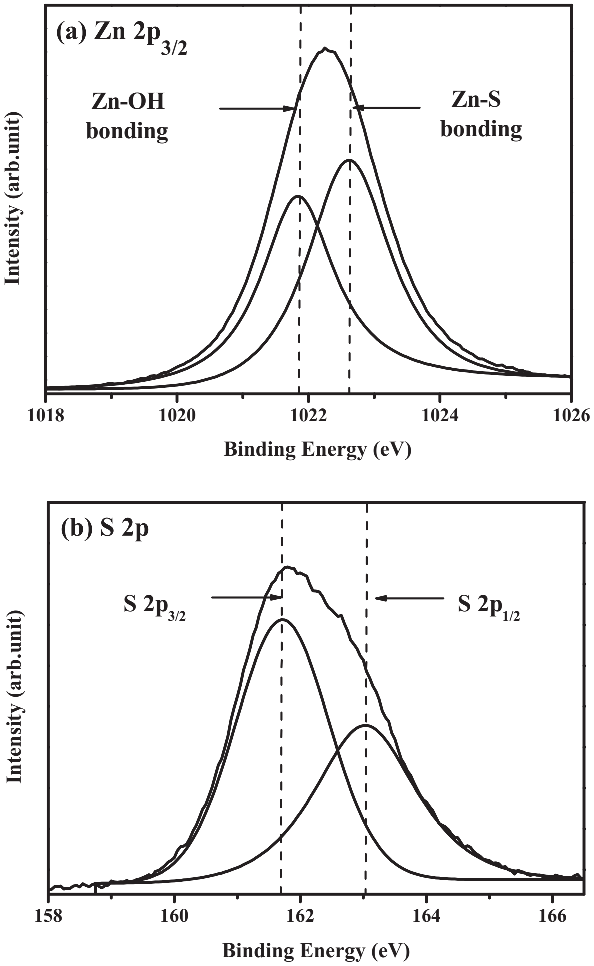

Fig. 3. High-resolution XPS spectra of Zn 2p (a) and S 2p (b) in ZnS thin film deposited with a mixture of Na_3-citrate and EDTA.

it was shown that the ZnS thin film consisted of many nanosized grains (below 5 nm), and it is observed that the interface between the ZnS thin film and the glass substrate was very sharp, without any indication of interfacial reaction or any formation of interfacial compounds. From the atomic lattice image (Fig. 2(b)), the *d*-value of ZnS thin films was 0.312 nm, which confirm the (0 0 0 2) plane for the ZnS hexagonal structure. The SAED pattern in the inset in Fig. 2(b) showed a typical polycrystalline ring pattern. These TEM images were quite similar to those of the ZnS thin films deposited with Na_3-citrate.

The chemical state of the constituent elements and binding energy in the ZnS thin films was examined by XPS. Fig. 3 shows the high-resolution XPS spectra of Zn 2p (a) and S 2p (b) of the ZnS thin film deposited with a mixture of Na_3-citrate and EDTA. The binding energy of Zn $2p_{3/2}$ (Fig. 3(a)) consisted of two binding energies positioned between 1021.9 eV and 1022.6 eV, which correspond to Zn—OH and Zn—S bonds, respectively [24]. It is well known that the Zn—OH bonding in CBD-ZnS thin films has been easily formed in basic aqueous solutions [24]. The S 2p binding energies in the ZnS thin film (Fig. 2(b)) were 161.8 eV and 163 eV, respectively [16]. The first binding energy was assigned to the S $2p_{3/2}$ core level, and the second binding energy corresponds to S $2p_{1/2}$ core level, respectively. These XPS spectra were very similar to the ZnS thin films deposited without complexing agents and with Na_3-citrate, and similar results of CBD-ZnS thin films were reported by several authors deposited in a basic medium [24–27].

Fig. 4 shows the cross-sectional FE-SEM images of the ZnS thin films deposited without complexing agent (a), those with Na_3-citrate (b), and those with a mixture of Na_3-citrate and EDTA (c). The cross-sectional FE-SEM images also showed that the thicknesses of the ZnS thin films deposited with one or mixture of complexing agents were thicker than that of the film deposited without a complexing agent. This increase in film thickness of the ZnS thin films was attributed to the higher concentration of Zn-complexing-agent bonded ions that may have exhibited Zn—S bonding in the hot reaction bath and thus increased the thickness of the ZnS thin film. The ZnS thin films deposited without any complexing agents showed a smoother morphology than that deposited with the complexing agents. The ZnS thin film without any complexing agents showed holes and a microstructure consisting of small spherical-shaped grains with a size of about 30 nm. However, both the ZnS thin films deposited with one or mixture of complexing agents showed uniform, continuous, and dense microstructures consisting of very small-sized grains (below 5 nm as observed by HR-TEM (Fig. 2)) and spherical-shaped grains of sizes ranging from 30 to 100 nm. These different morphological properties of ZnS thin films were attributed to easier nucleation in reaction baths with one or more complexing agents than in that without any complexing agents. In the case of the reaction solution without comlexing agents, the growth process of ZnS was dominant compared to that of the nucleation process because of a lower presence of Zn-complexing-agent bonded ions, where thus, the ZnS thin film formatted the spherical-shaped grains. In contrast, the nucleation process of ZnS was dominant

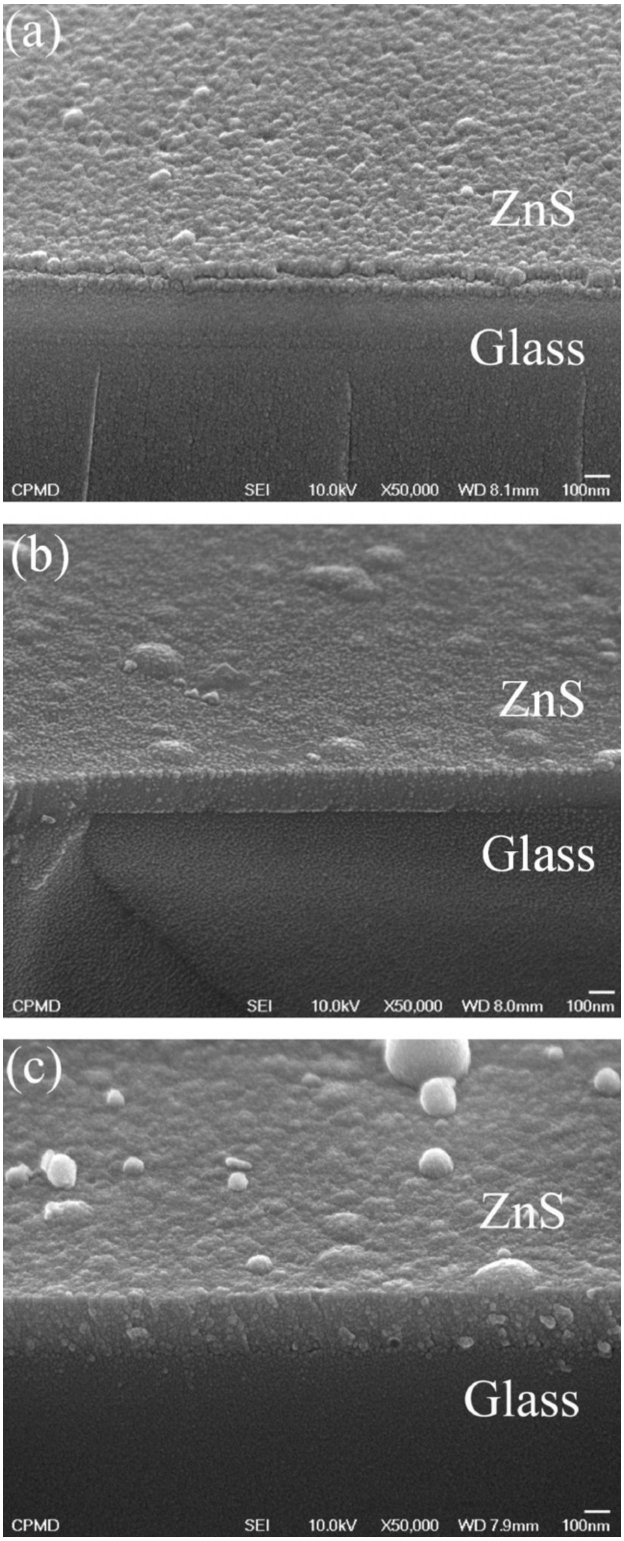

Fig. 4. Cross-section FE-SEM images of the ZnS thin films deposited without complexing agents (a), those with Na_3-citrate (b), and those with a mixture of Na_3-citrate and EDTA (c).

compared to that of the growth process in hot reaction solution with one or mixture of complexing agents. Many small-sized grains were easily formed, and uniform, continuous, and dense ZnS thin films were deposited. In addition, the thicknesses of the ZnS thin films without complexing agents, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA were about 50 nm, 110 nm and 130 nm, respectively.

Table 1
Results of compositional analysis of the ZnS thin films deposited without complexing agents, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA.

Elements	Without complexing agent	Na_3-citrate	Mixture of Na_3-citrate and EDTA
Zn (at%)	46.45	48.47	51.14
S (at%)	53.55	51.53	48.86

Table 2 shows the electrical properties of the ZnS thin films deposited without complexing agents, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA examined by the Hall measurement system at room temperature. The 200 nm-thick Au was deposited by electron beam evaporation technique to improve the ohmic condition between Au grid and ZnS thin films. Hall measurement results for the ZnS thin films indicated that the ZnS thin films showed n-type semiconductor characteristics regardless of the complexing agents. The electrical resistivity of ZnS thin films was over $10^5\ \Omega\,\text{cm}$. The electrical resistivity, carrier concentration, and mobility of the ZnS thin were $1.74 \times 10^6\ \Omega\,\text{cm}$; $9.62 \times 10^9\ \text{cm}^{-3}$; and $2.23\ \text{cm}^2\ \text{V}^{-1}\ \text{S}^{-1}$ (without complexing agent); $2.27 \times 10^5\ \Omega\,\text{cm}$; $7.23 \times 10^{10}\ \text{cm}^{-3}$; and $4.57\ \text{cm}^2\ \text{V}^{-1}\ \text{S}^{-1}$ (with Na_3-citrate); and $1.69 \times 10^5\ \Omega\,\text{cm}$; $9.12 \times 10^{10}\ \text{cm}^{-3}$; and $5.98\ \text{cm}^2\ \text{V}^{-1}\ \text{S}^{-1}$ (with a mixture of Na_3-citrate and EDTA), respectively. The lower electrical mobility of the ZnS thin film deposited without complexing agents is attributed to the rougher surface morphology of the ZnS thin film deposited with one mixture of complexing agents. This rough morphology resulted in the low mean free path for electron leading to a deterioration of electrical mobility. In addition, the increase in carrier concentration of ZnS thin films deposited with one or more complexing agents, as compared to that deposited without a complexing agent resulted from the decrease in compositional ratio of S. From previous literature on it is known that in chalcogenide-based thin films, the electrical properties deteriorated with the compositional ratio of chalcogenide [27,28].

Fig. 5(a) shows the UV–visible transmittance spectra in the wavelength region from 300 nm to 800 nm. Fig. 5(b) shows the plots of $(\alpha h\nu)^2$ vs photon energy of the ZnS thin films deposited without and with the complexing agent Na_3-citrate and of that with a mixture of Na_3-citrate and EDTA. The average transmittance of the films without complexing agents, those with the complexing agent Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA was approximately 85%, 65%, and 70%, respectively. The low transmittance in the visible region for the ZnS thin films with one or more complexing agents compared to that without a complexing agent was attributed to the thicker thickness. It is well known that the transmittance of thin film is strongly related to the thickness and surface condition of the film [28]. From Fig. 4, the ZnS thin films with one or mixture of complexing agents showed greater thicknesses, compared to that deposited without a complexing agent, and the spherical-shaped grains with sizes ranging from 30 to 100 nm. These thicker thicknesses and the presence of spherical-shaped grains resulted in a scattering out of the beam in the spectrophotometer. Therefore, the transmittance of the ZnS thin film with a mixture of Na_3-citrate and EDTA is higher than that with Na_3-citrate.

All ZnS thin films with and without complexing agents showed a sharp absorption feature. This sharp absorption feature was attributed to the good homogeneity in the shape and size of the grains and low defects in the film. The sharp absorption edge was observed near 300 nm. This absorption edge of the ZnS thin films deposited with one or more complexing agents shifted toward a shorter wavelength as compared to that deposited without

Table 2
Electrical resistivity, carrier concentration, and mobility of the ZnS thin films deposited without complexing agent, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA.

	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} S^{-1}$)
Without complexing agent	1.74×10^6	9.62×10^9	2.23
With Na_3-citrate	2.27×10^5	7.23×10^{10}	4.57
With mixture of Na_3-citrate and EDTA	1.69×10^5	9.12×10^{10}	5.98

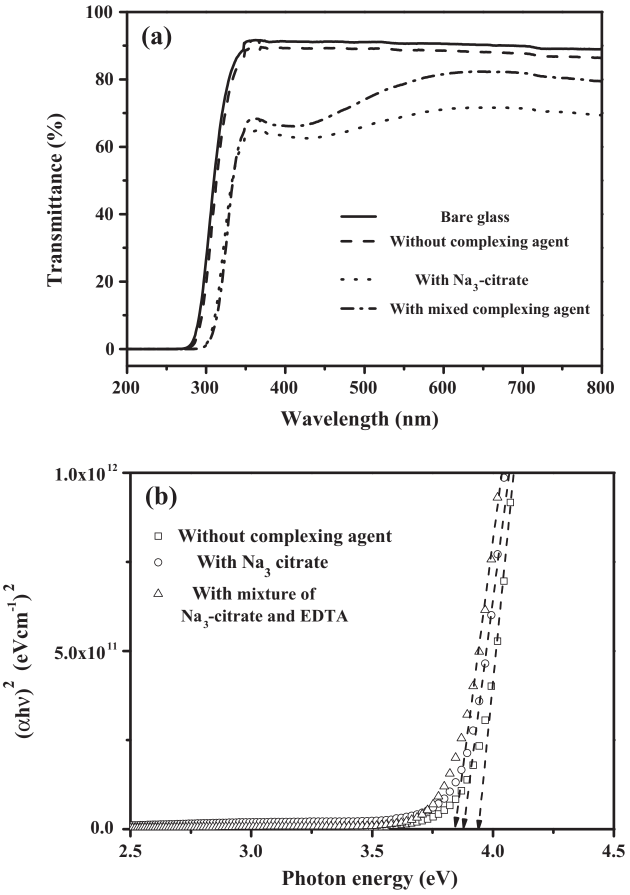

Fig. 5. UV–visible transmittance spectra in the wavelength region from 300 nm to 800 nm (a) and the plot of $(\alpha h\nu)^2$ vs photon energy (b) of the ZnS thin films deposited without complexing agents, those with Na_3-citrate and those with a mixture of Na_3-citrate and EDTA.

complexing agents. Based on the optical transmittance for ZnS thin films, the values of the optical absorption coefficient (α) were determined by using this equation [23]:

$$I_t = I_0 \exp(-\alpha t), \quad (1)$$

where t is the thickness of film, and I_t and I_0 are the intensities of transmitted light and initial light, respectively. In order to determine the direct band gap energy, the Tauc relationship was used as follows [29]:

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

where A is a constant, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap energy, and n is 1/2, respectively. The optical band gap energy of the ZnS thin films deposited without complexing agents, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA, which was obtained from the $(\alpha h\nu)^2$ vs photon energy plots by extrapolating the line portion of the curves at $\alpha = 0$, were found to be 3.94 eV, 3.87 eV, and 3.84 eV, respectively (Fig. 5(b)).

3.2. Discussion: effects of different complexing agents

These results showed an improved crystallinity, greater thicknesses, and a higher Zn atomic ratio in the ZnS thin films deposited with complexing agents compared to that deposited without complexing agents. Generally, the growth mechanism of ZnS thin film has been known to be such that the Zn-[complexing agent]$^{2+}$ ions react with S^{2-} ions at the solution or substrate surface [30]. Therefore, a suitable complexing agent plays a very important role in the stable deposition of ZnS thin films because complexing agents reduce the release rate of Zn metallic ions in a reaction bath [8,16]. In addition, a suitable complexing agent is used to bind Zn ions to avoid homogenous precipitation [30].

In a reaction solution without added complexing agents, there is only NH_3 to act as a complexing agent. While heating a solution without a complexing agent, NH_3 reacts with Zn^{2+} ions, which produces $[Zn(NH_3)_n]^{2+}$ ions in the reaction bath. However, in the absence of enough ammonia, the NH_3 does not fully react with the Zn^{2+} ions, and there are free Zn^{2+} ions in the reaction bath, where the $Zn(OH)_2$ can be easily precipitated in the basic solution [31]. The ZnS film deposited without an added complexing agent is formed at relatively high concentrations of Zn—$(OH)_2$ binding and low concentrations of Zn—S binding, indicating that the film has finally been grown as an amorphous phase (Fig. 1). The relatively low concentrations of Zn—S ions in the bath resulted in a low growth rate (Fig. 3) in the ZnS thin film deposited without complexing agents.

In contrast, in a reaction bath with one or mixture of complexing agents, there are many Zn-[complexing agent]$^{2+}$ ions, such as $[Zn(NH_3)_n]^{2+}$, $[Zn(Na_3\text{-citrate})_n]^{2+}$, and $[Zn(EDTA)_n]^{2+}$, as well as a small amount of Zn^{2+} ions compared to that without complexing agents. This leads to the formation of high concentrations of Zn—S bonds. The high concentrations of formatted Zn—S binding can react easily with the substrate surface, resulting in improved crystallinity (Fig. 1) and the high Zn atomic ratio (Table 1) of ZnS thin films with complexing agents.

The ZnS thin films deposited with a mixture of Na_3-citrate and EDTA showed improved crystallinity, higher transmittance in the visible region, and greater thicknesses than that deposited with Na_3-citrate. A possible reason for this may be attributed to the different binding force between Zn ions and the complexing agent ions with different complexing agent types. The solubility product of Zn-[EDTA] is higher than that of Zn-[Na_3-citrate], indicating greater binding between the Zn ions to Na_3-citate compared to that with the mixture of Na_3-citrate and EDTA [22]. The concentration of Zn-complexing ions in the solution with a mixture of Na_3-citrate and EDTA is higher than that deposited with Na_3-citrate. Therefore, the growth rate and morphology of the ZnS thin films deposited with a mixture of Na_3-citrate and EDTA are greater than that deposited with Na_3-citrate.

4. Conclusions

Thick ZnS films were successfully prepared by a chemical bath deposition technique in a basic medium (pH ~ 10) at 80 °C, using different complexing agents. The crystal quality of the CBD-ZnS thin films deposited with one or mixture of complexing agents was superior to that of the films deposited without the complexing agent. The ZnS thin films deposited with one or mixture of complexing agents had a thicker thickness (over 100 nm) and smoother morphology than the films deposited without the complexing agent (below 50 nm). The electrical resistivity of the ZnS thin films was over 10^5 Ω cm regardless of complexing agents. The optical band gap energy of the ZnS thin films deposited without the complexing agent, those with Na_3-citrate, and those with a mixture of Na_3-citrate and EDTA was found to be 3.94 eV, 3.87 eV, and 3.84 eV, respectively. The growth mechanism, thickness, and properties of chemical bath deposited ZnS thin films were strongly related to the complexing agents. These characteristic could be easily applied to TFSCs as a Cd-free buffer layer and could improve the conversion efficiency of TFSCs.

Acknowledgments

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