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Preparation and characterization of chemical bath deposited nanocrystalline ZnSe thin films using Na_3-citrate and hydrazine hydrate: A comparative study

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ABSTRACT

In this paper, a comparative study reported on the characteristics of Zinc Selenide (ZnSe) thin films prepared by a chemical bath deposition method using the non-toxic tri-sodium citrate (Na_3-citrate) and toxic hydrazine hydrate (HH) as complexing agents. Morphological, structural, chemical, and optical properties were investigated using field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV–vis spectroscopy. FE-SEM and AFM studies revealed that the ZnSe thin film prepared using Na_3-citrate was highly uniform with very low surface roughness (3 nm) compared to those prepared using HH. XRD and XPS studies revealed formation of a cubic ZnSe phase and exhibited insignificant Zn–OH formation along with Zn–Se binding energies for both the films. UV–vis study showed that the band gap energies of ZnSe thin films prepared using HH and Na_3-citrate were 3.1 eV and 2.9 eV, respectively. These investigations show that ZnSe thin films could be grown with good optical, structural, chemical, and compositional characteristics without using a toxic HH complexing agent.

1. Introduction

Zinc Selenide (ZnSe) is an important buffer layer material for thin film solar cells (TFSCs) due to its absorption of less than 520 nm wavelength, a wide band gap of 2.7 eV, a low conduction band offset, and non-toxicity [1]. Recently, Cu(In,Ga)Se_2 (CIGS) TFSC with a chemical bath deposited ZnSe (CBD–ZnSe) buffer layer has shown high power conversion efficiency of 15.7% [1]. Reports on CBD–ZnSe thin films have presented that the uniform ZnSe thin films can be obtained if hydrazine hydrate (HH) is used as a complexing agent [2,3]. Use of a HH in CBD is necessary due to a very low reaction constant ($K_{sp}=10^{-31}$) of ZnSe which shows that it is very difficult to grow uniform ZnSe thin films [2]. In addition, several researchers have reported that the addition of HH in a reaction bath improves the film's adherence while playing a role of side complexing agent [3,4]. Although, the above discussions show that HH has a crucial role in CBD–ZnSe, highly combustible, venomous, and carcinogenic characteristics of HH pose serious limitations on industrial scale-up processing.

In our previous study, the difficult task of depositing uniform and nanocrystalline ZnS thin films by the CBD technique without using HH was carried out easily and we reported a green route deposition of ZnS thin films using tri-sodium citrate (Na_3-citrate) as a non-toxic complexing agent [5]. Na_3-citrate is a robust complexing agent, which forms strong citrate anions ($(C_6H_5O_7)^{3-}$) in an aqueous bath. In addition, Na_3-citrate has the ability to form various chelates with a variety of metal ions such as Zn^{2+}, Fe^{3+}, Ca^{2+}, Ag^{+}, Mg^{2+} etc. and it also allows a uniform deposition of thin film by a slow release of metal ions [6]. In this study we have deposited ZnSe thin films having smooth morphology using Na_3-citrate as a complexing agent.

Therefore, to the best of our knowledge, we have deposited CBD–ZnSe thin films by a complete green route using a Na_3-citrate complexing agent for the first time. We have also deposited CBD–ZnSe thin films using a HH complexing agent and morphological, structural, chemical, and optical properties of thin films were compared.

2. Experimental details

\Analytical grade chemicals from Sigma-Aldrich were used for chemical bath deposition. They include Zinc sulfate ($ZnSO_4$), selenourea ($SeC(NH_2)_2$), ammonia (25%), complexing agent tri-sodium

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citrate (Na_3-citrate), and hydrazine hydrate (HH). Solutions were prepared in deionized water and ZnSe thin films were deposited on $26 \times 76 \times 2$ mm^3 glass substrates. The first reaction bath was prepared using 10 mL of 0.5 M $ZnSO_4$, 10 mL of 0.4 M $SeC(NH_2)_2$, and 10 mL of HH complexing agent. For the second reaction bath, instead of HH, 10 mL of 0.2 M Na_3-citrate was used as a complexing agent. The pH of both solutions was adjusted to 10 by adding 25% ammonia (NH_4OH) solution. Finally, a sufficient amount of deionized water was added to make the total volume of the reaction bath 100 mL. Prior to deposition, the glass substrates were ultrasonically cleaned with acetone followed by rinsing in methanol, isopropyl alcohol, and deionized water for 10 min. The glass substrates were mounted vertically on a specially designed substrate holder. The temperature of the reaction bath was maintained at 80 °C. After 2 h, the glass substrates were removed, washed with deionized water, dried naturally, and used for further characterization.

3. Results and discussion

Fig. 1 shows plane and cross-sectional FE-SEM images of ZnSe thin films deposited with two different complexing agents HH (Fig. 1(a) and (c)) and Na_3-citrate (Fig. 1(b) and (d)). HH deposited ZnSe thin film consists of globular nano-grains with an average grain size of about 180 nm and film shows discontinuous morphology with some voids (Fig. 1(a)). Formation of ZnSe with similar nanoballs morphology was previously reported by using a HH complexing agent [7]. In case of ZnSe thin film deposited with Na_3-citrate showed very dense and smooth morphology with grains smaller than 20 nm (Fig. 1(b)). The thicknesses of ZnSe thin films deposited using HH and Na_3-citrate were ~60 nm and 95 nm, respectively. 3D AFM images showed that the root mean square (RMS) value of HH deposited ZnSe thin film is 30 nm which is higher than those prepared using Na_3-citrate which has RMS value of 3 nm (Fig. 1(e) and (f)). It seems that a low RMS value and uniform morphology of ZnSe thin film prepared using Na_3-citrate is attributed to different concentrations of Zn-[complexing agent]$^{2+}$ ions in the hot reaction bath. Generally, K_{sp} of Zn-hydrazine reaction is higher than that of Zn-citrate. These chemical behaviors indicated that all Zn^{2+} ions reacted with hydrazine and further formatted into Zn-[hydrazine]$^{2+}$ ions. Therefore, in a hot reaction bath almost all Zn^{2+} ions react with Se^{2-} ions and dominate homo-nucleation, resulting in growth of ZnSe thin films in the solution. While in case of the reaction solution prepared using Na_3-citrate, different cations

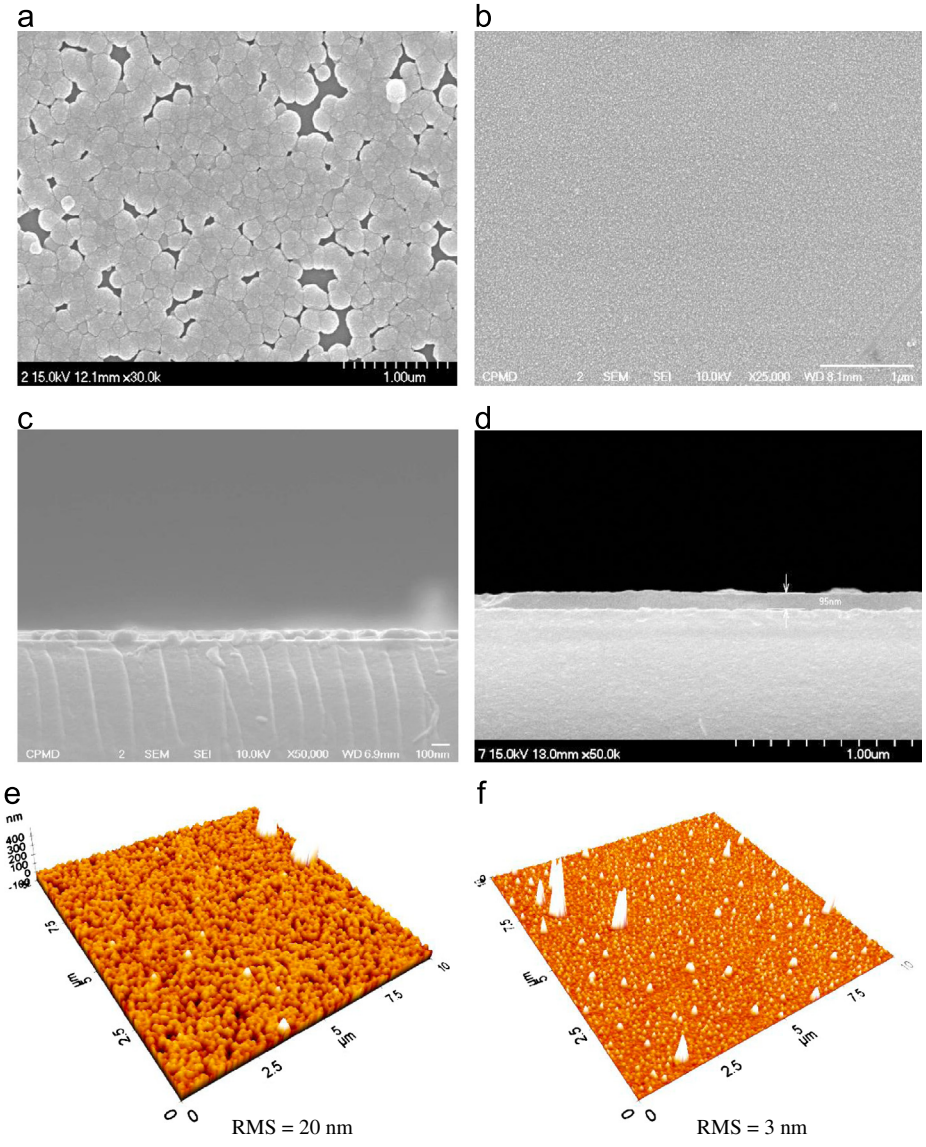

Fig. 1. Plane and cross-sectional FE-SEM images of Hydrazine hydrate (a)–(c) and Na_3-citrate (b)–(d) deposited ZnSe thin films. 3D AFM images of Hydrazine hydrate (e) and Na_3-citrate (f) deposited ZnSe thin films.