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Non-toxic novel route synthesis and characterization of nanocrystalline ZnS_xSe_{1-x} thin films with tunable band gap characteristics

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ABSTRACT

An environmentally benign chemical bath deposition (CBD) route was employed to deposit zinc sulfide (ZnS) thin films. The CBD-ZnS thin films were further selenized in a furnace at various temperatures viz. 200, 300, 400, and 500 °C and the S/(S + Se) ratio was found to be dependent on the annealing temperature. The effects of S/(S + Se) ratio on the structural, compositional and optical properties of the ZnS_xSe_{1-x} (ZnSSe) thin films were investigated. EDS analysis showed that the S/(S + Se) ratio decreased from 0.8 to 0.6 when the film annealing temperature increased from 200 to 500 °C. The field emission scanning electron microscopy and atomic force microscopy studies showed that all the films were uniform, pin hole free, smooth, and adhered well to the glass substrate. The X-ray diffraction study on the ZnSSe thin films showed the formation of the cubic phase, except for the unannealed ZnSSe thin film, which showed an amorphous phase. The X-ray photoelectron spectroscopy revealed Zn—S, Zn—Se, and insignificant Zn—OH bonds formation from the Zn $2p_{3/2}$, S 2p, Se $3d_{5/2}$, and O 1s atomic states, respectively. The ultraviolet–visible spectroscopy study showed ~80% transmittance in the visible region for all the ZnSSe thin films having various absorption edges. The tuning of the band gap energy of the ZnSSe thin films was carried out by selenizing CBD-ZnS thin films, and as the S/(S + Se) ratio decreased from 0.8 to 0.6, the band gap energy decreased from 3.20 to 3.12 eV.

1. Introduction

Thin film solar cells (TFSCs) based on $Cu(In,Ga)Se_2$ (CIGS) have attracted considerable attention over the last 20 years as a potential non-silicon absorber material. CIGS solar cells exhibited record 20.3% power conversion efficiency (PCE) when the chemical bath deposited CdS (CBD-CdS) thin film was used as a buffer layer [1]. The role of a buffer layer is found to be crucial as it improves the interface quality and avoids damaging the CIGS absorber layer during ZnO window layer deposition under a vacuum. While the CBD-CdS layer has been almost universally deposited over CIGS for device fabrication, its significant disadvantage of toxicity becomes serious when the process is scaled-up industrially. For example, Cd-laden discarded water from mining operations in the Toyama Prefecture in Japan result in an outbreak of a painful and sometimes fatal affliction commonly referred to as "itai-itai" ("ouch-ouch") disease [2,3]. Similarly, CBD-CdS buffer layers have been deposited onto Cu_2ZnSnS_4 (CZTS) absorber layer based TFSCs to improve their overall performance. Recently, CZTS has also been proven to be a more economically viable option than Si and CIGS TFSCs and is on the verge of becoming commercially available [4]. Hence, it is necessary to solve the toxicity issue of the CBD-CdS buffer layer. ZnS and ZnSe have been reported to be the best options as Cd-free buffer layers for both CIGS and CZTS based solar cells [5,6]. The merits and demerits of CBD-CdS, ZnS, and ZnSe are currently being debated at length.

The CdS buffer layer has low quantum efficiency (QE) at shorter (400–500 nm) wavelengths, (QE) $\lambda_{shorter}$, but has QE fall-out at longer wavelengths, (QE) λ_{longer}, at 1.12 eV, which is better than that of ZnS and ZnSe. [7]. The CdS buffer layer also displays a

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relatively superior junction quality and small conduction band offset (CBO). While the ZnS buffer layer has the greatest advantage of harnessing λ_{shorter} due to its higher QE at λ_{shorter} (400–500 nm), its (QE) λ_{longer} is at 1.19 eV (mildly inferior to CdS), causing a lower QE at longer wavelengths [8]. Additionally, use of ZnS results in an inferior junction quality and CBO is also excessive, which increases the barrier for the photo-generated charge carriers [8]. Therefore, the problem of band-offset may partially be solved by a proper mixture of ZnO and S; however, this results in strong valence band-offset bowing, which reduces the band gap energy to 2.7 eV [8] and does not utilize the mixing of ZnO and S.

Clearly, a new Cd-free buffer layer needs to be developed that combines the advantages of both CdS and ZnS buffer layers. Thus far, ZnS and ZnSe buffer layers have been deposited using hydrazine hydrate (HH) as a complexing agent [9–11]. However, HH is a toxic, highly carcinogenic and environmentally hazardous material. Because of the use of HH, the process of avoiding the toxic Cd-free buffer layer is in itself even more toxic. Therefore, an environmentally benign process needs to be deployed for high quality buffer layer synthesis and its subsequent deposition for device fabrication. ZnS_xSe_{1-x}(ZnSSe) has been recently considered as a promising alternative candidate to CBD-CdS, ZnS, and ZnSe buffer layers [9,10,12]. Several studies on techniques such as atomic layer epitaxy, molecular beam epitaxy, vapor phase epitaxy, and CBD have reported the preparation of ZnSSe thin films for possible use as a buffer layer [9,13–15]. Although the physical techniques produce high quality layers, their maintenance, need for high quality targets, and requirement for a strong vacuum make the process expensive and time consuming. CBD is the most promising technique for large area deposition and is inexpensive. Hence, several researchers have used this technique to deposit ZnSSe thin film buffer layers. The ZnSSe thin films have been deposited using various zinc salts such as sulphates, chlorides, and their band gap tuning is also reported [9]. The band gap tuning ability of ZnSSe seems to be very attractive for the proper alignment of conduction band minima of CIGS/CZTS with a buffer layer and for minimizing CBO in order to increase the collection efficiency of the photo-generated charge carriers. However, all the solutions were prepared using the toxic complexing agent HH, which negates all of the advantages [9–11].

In this study, we have therefore undertaken the following steps: (i) synthesis of ZnS thin films using an environmentally benign Na_3-citrate route for CBD, (ii) subsequent selenization of ZnS thin films at various temperatures to examine the S/(S + Se) ratio, and (iii) analysis of the effect of selenization on the elemental, morphological, structural, compositional and optical properties.

2. Experimental details

2.1. Chemical bath deposition of ZnS thin films

Analytical grade chemicals were purchased from Sigma–Aldrich and were used for deposition of the ZnS thin films. These chemicals include zinc acetate, thiourea, liquor ammonia (25%), and the non-toxic complexing agent tri-sodium citrate (Na_3-citrate). Solutions were prepared in deionized water and ZnS thin films were deposited on 26 × 76 × 2 mm glass substrates. A reaction bath solution was prepared using 40 mL 0.2 M zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot 2H_2O$), 40 mL 0.4 M thiourea ($SC(NH_2)_2$), and 20 mL 0.2 M Na_3-citrate complexing agent. The pH of the solution was adjusted to 10 by adding 25% ammonia solution. Prior to deposition, the 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 and the temperature of the reaction bath was maintained at 80 °C. After 1 h, the glass substrates were removed, washed several times with deionized water, dried naturally, and kept in an air-tight container. The resultant films were homogenous, pin-hole free, and adhered well to the glass substrate.

2.2. Selenization of the ZnS thin films and formation of the ZnS_xSe_{1-x} thin films

The ZnSSe thin films were synthesized by using a two zone conventional furnace. A fixed amount of 3 g of Se pellets was used for all the ZnS thin films. Se pellets were kept in the first zone while the ZnS thin films were kept in the second zone. The temperature of the first zone was fixed at 300 °C and the temperature of the second zone was set at 200, 300, 400, and 500 °C. Each ZnS thin film was selenized for 1 h with the N_2 gas to carry the vaporized selenium. Formed ZnS_xSe_{1-x} thin films were cooled naturally to room temperature in an Ar atmosphere and kept in an air-tight container to avoid vigorous oxidation of the surface Se, which usually forms SeO_2 as an oxidation product.

2.3. Characterization of ZnS_xSe_{1-x} thin films

The chemical composition was examined using an energy dispersive spectrometer (EDS) system attached to a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-7500F, Japan). The morphological and surface relief studies of the ZnSSe thin films were carried out using FE-SEM (Model: JSM-6701F, Japan) and atomic force microscopy (AFM, Digital Instrument, Nanoscope III, USA) operated at room temperature, respectively. The structural properties of thin films were studied using a high-resolution X-ray diffractometer (XRD, X'pert PRO, Philips, Eindhoven, The Netherlands) which was operated using a grazing incidence diffraction mode. The chemical binding energy investigations of the ZnSSe thin films were carried out using X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Thermo Scientific, UK). The binding energies in the spectrometer were calibrated using the carbon 1 s line at 285.0 eV. The optical transmittance of thin films was observed using UV–visible spectroscopy (Cary 100, Varian, Mulgrave, Australia).

3. Results and discussion

The chemical composition of ZnS_xSe_{1-x}(ZnSSe) thin films has been investigated by EDS analysis. Fig. 1(a) shows the EDS spectrum of ZnSSe thin film annealed at 500 °C. The Zn, S, and Se atomic percentages are found to be 39.56%, 32.41%, and 28.03%, respectively. A detailed study of elemental analysis as done by EDS technique is shown in the supporting information. Fig. 1(b) shows a graph of elemental analysis for ZnSSe thin films annealed at various temperatures. From the graph, it can be seen that the atomic percentage of Zn and S for the unannealed ZnS thin film is 55.0% and 45.0%, respectively, which shows that the ZnS thin film is moderately stoichiometric. This stoichiometric Zn:S ratio can be attributed to the presence of appropriate amounts of complexing agent Na_3-citrate which forms citrate anions during chemical bath deposition (CBD). These citrate anions hold the Zn^{2+} ions securely and allow the controlled growth of Zn^{2+} ions that favor heterogeneous ZnS growth instead of homogenous growth [16]. This uniform growth shows that the hydroxide contents in the film are significantly reduced, which is crucial for a buffer layer. Furthermore, in the case of the ZnSSe thin films annealed from the temperatures of 200–500 °C, the S at% decreases from 40.94% to 32.41%, Zn at% also decreases from 53.7% to 39.56%, while Se at% increases from 5.36% to 28.03%. The ZnSSe thin film deposited at 500 °C shows a good stoichiometric ratio of Zn:S:Se, which is a key factor for ZnSSe thin films in TFSC fabrication. Our earlier results