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Chemical bath deposited ZnS buffer layer for $Cu(In,Ga)Se_2$ thin film solar cell

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ABSTRACT

The dependence of Zn precursors using zinc sulfate ($ZnSO_4$), zinc acetate ($Zn(CH_3COO)_2$), and zinc chloride ($ZnCl_2$) on the characteristics of the chemical bath deposited ZnS thin film used as a buffer layer of $Cu(In,Ga)Se_2$ (CIGS) thin film solar cell was studied. It is found that the ZnS film deposition rate increases with higher stability constant during decomplexation reaction of zinc ligands, which affects the crack formation and the amount of sulfur and oxygen contents within the film. The band gap energies of all deposited films are in the range of 3.40–3.49 eV, which is lower than that of the bulk ZnS film due to oxygen contents within the films. Among the CIGS solar cells having ZnS buffer layers prepared by different Zn precursors, the best cell efficiency with 9.4% was attained using $Zn(CH_3COO)_2$ precursor due to increased V_{oc} mainly. This result suggests that $[Zn(NH_3)_4]^{2+}$ complex formation should be well controlled to attain the high quality ZnS thin films.

1. Introduction

Among the various types of solar cells, $Cu(In,Ga)Se_2$ (CIGS)-based thin film solar cell has been strongly investigated due to its cost-effective and high efficient performance. The most common CIGS device structure consists of a molybdenum (Mo) bottom contact layer, a *p*-type CIGS absorber layer, a thin *n*-type buffer layer, a zinc oxide (ZnO)-based transparent window layer and top metal contacts sequentially. The *n*-type buffer is typically with thin cadmium sulfide (CdS) formed by chemical bath deposition (CBD), which protects the absorber layer from DC sputtering damage during the ZnO:Al window layer deposition and modifies the surface of CIGS absorber layer [1]. At present, conversion efficiency of the highly efficient CIGS solar cells with chemically deposited CdS buffer layers has been reported with ~20% on the commercial scale for laboratory cells and 18% on the mini-modules [2].

The CBD process to form CdS buffer layer is simple, convenient, cost-effective, and applicable to an industrial scale. However, the usage of chemically deposited CdS thin films in the mass scale solar cell production could raise serious environmental problems. Therefore, alternative Cd-free buffer layer has been under great research interest [3–5]. Among the various materials, ZnS-based film has been suggested as the most promising candidate [6–9].

ZnS is a wide and direct band gap material having non-toxicity, earth-abundance and cheapness. Compared to the band gap energy (E_g) of CdS (2.42 eV), the wider E_g of ZnS (3.68 eV) could lead to more transparency in the short wavelength region 350–550 nm. This could achieve further improvement in the short circuit current density (J_{sc}) of the device [10,11]. ZnS thin films have been reported by the various physical and chemical techniques including metal-organic vapor phase epitaxy (MOVPE) [12], spray pyrolysis [13], magnetron sputtering [14], electrodeposition [15], sol-gel [16], thermal evaporation [17], chemical vapor deposition [18], successive ionic layer adsorption and reaction (SILAR) [19], atomic layer deposition [20] and CBD [21–23]. Among these methods, CBD is the most commonly used process to form the ZnS buffer layer. Remarkable device efficiencies have been achieved using CBD ZnS thin film as a buffer layer in the CIGS solar cells which are comparable to that of CdS [24–26]. At present, a lot of efforts have been made to obtain high quality CBD ZnS thin films by optimizing the parameters such as concentrations of various reagents [27], pH [28], temperature [29] and active deposition time [30] or by using some assisted methods including ZnS nano-particles as seed layers [31], sonication [32], and pre-treatment of substrates [33].

The CBD ZnS films have been synthesized by a zinc salt, thiourea as a sulfur source and ammonia as a complexing agent. The CBD ZnS film is formed by the condensation of slowly released Zn^{2+} and

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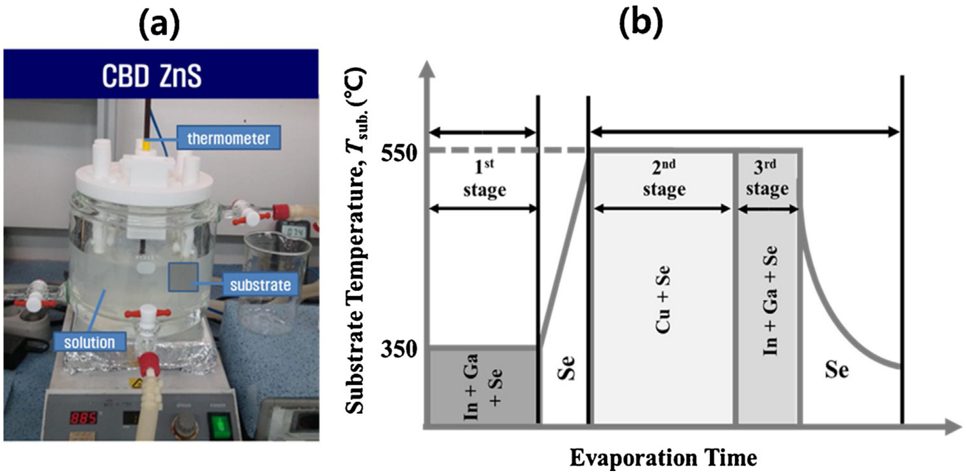

Fig. 1. The experimental set up for the CBD process (a) and a 3 stage process of co-evaporated CIGS thin film.

S^{2-} ions in the solution. In general, two recipes are used for the ZnS deposition by the CBD method. The first one was developed at Showa Shell Sekiyu, with solar-cell efficiencies of 14–15% on the 100 cm^2-sized substrates [34] while the second one by Nakada and Contreras was reported with conversion efficiency of 18.6% [35]. The difference between two processes is originated from different ammonia concentration during the CBD process. Also, the concurrent deposition of ZnS, ZnO or $Zn(OH)_2$ depending on various process conditions has been reported, which significantly affects the efficiency of CIGS solar cell [36–38]. Therefore, it is still needed to clarify the effects of chemicals such as Zn precursor on the growth mechanism further and optical properties of ZnS thin film.

In this study, we have investigated the effects of various Zn precursors such as zinc sulfate ($ZnSO_4$), zinc acetate ($Zn(CH_3COO)_2$), and zinc chloride ($ZnCl_2$) on the growth rate, morphology and optical properties of CBD ZnS thin film. In addition, we suggest the optimum CBD process condition by fabricating the CIGS solar cells employing the ZnS films.

2. Experimental details

Chemical bath deposited ZnS thin films was attained with various Zn precursor salts with $ZnSO_4$ (99.99%, Sigma-Aldrich), $Zn(CH_3COO)_2$ (99.99%, Sigma-Aldrich), and $ZnCl_2$ (99.99%, Sigma-Aldrich). Regardless ligands, zinc mole concentration, $[Zn^{2+}]$, in the precursors was fixed to 0.15 M. Ammonia ($[NH_3] = 7.5$ M) was mixed into the solution as a complexing agent. Then, thiourea ($[SC(NH_2)_2] = 0.6$ M) in de-ionized (DI) water was sequentially added to the solution as a sulfur supply. In the presence of NH_3 complexing agent, the zinc complex $[Zn(NH_3)_4]^{2+}$ was formed, leading to a slow release of the Zn^{2+} ions. Reduced deposition reaction due to $[Zn(NH_3)_4]^{2+}$ formation could enhance the ZnS film quality. The CBD ZnS thin film is formed as following process sequences: $[Zn(NH_3)_n]^{2+} \rightarrow Zn^{2+} + nNH_3$, $SC(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CN_2H_2 + 2H_2O$, $Zn^{2+} + S^{2-} \rightarrow ZnS$.

After ZnS growth on the substrates at 80 °C for 40 min with the typical CBD process, all samples were immersed into NH_3 solution with 0.5 M for 1 min to remove $Zn(OH)_2$, followed by DI-water clean and N_2 blowing. The grown films were annealed on the hot plate for 10 min at 250 °C. Fig. 1(a) shows the experimental set-up for the CBD process.

Material analysis included high resolution scanning electron microscopy (HRSEM, XL30SFEG Phillips Co., Holland at 10Kv) for the surface morphology of ZnS films, X-ray photoelectron spectroscopy (XPS, Thermo, MultiLab 2000) to understand the electronic states of each element in the surface films where spectra presented were collected using Al K Alpha source with pass energy 30 eV and step energy 0.1 eV, and a UV spectrophotometer (Shimadzu Japan, UV-vis-NIR 3101) in wavelength range from 200 nm to 2600 nm with ITO glass as a reference for attaining the optical transmittance and reflectance properties. Electrical properties were evaluated with the complete CIGS thin film solar cells processed as reported before [39,40]. 1.1 μm thick Mo as a bottom electrode on the soda-lime glass substrate was carried out by DC magnetron sputtering using Mo target with 99.95% purity. The base pressure was kept with 1×10^{-6} Torr. The 1 μm-thick *p*-type CIGS absorber layer was grown by a three-stage process involving the co-evaporation of In, Ga, Cu and Se (5N for In, Cu, Se, and 4N for Ga from Cerac Co.) from effusion cells as shown Fig. 1(b). At the 1st stage, In, Ga, Se elements were prepared at 350 °C to form In-Ga-Se precursor. Then, Cu and Se were processed at 550 °C to get Cu-rich CIGS at the 2nd state. The final 3rd stage includes In, Ga and Se co-evaporation to have Cu-poor CIGS film, followed by cooling at Se ambient. The *n*-type ZnS buffer layers were deposited onto CIGS films by CBD aforementioned. For window layers formation, 50 nm thick intrinsic and 350 nm thick Al-doped ZnO (*i*-ZnO and ZnO:Al) were prepared by RF-sputtering. Finally, Al was thermally evaporated through the mask to form metal grid contact layers. The final cell structure consists of SLG/Mo/CIGS/CdS/ZnO/Al grid. The active cell area of the solar cell is 0.4848 cm^2. Electrical characterization was performed using a solar simulator (Newport, McScience) at AM-1.5G using illumination with a total irradiance of 100 mW cm^{-2} for the current-voltage (*I*–*V*) measurements

3. Results and discussion

3.1. The effects of precursors on the growth and thickness of the ZnS films

Fig. 2 shows the cross section and surface morphologies of the ZnS films on GIGS absorber layer prepared by various Zn precursors. From the cross section images, the ZnS film thickness using $ZnSO_4$, $Zn(CH_3COO)_2$, and $ZnCl_2$ precursors turns out to be with ~90 nm, ~60 nm, and ~30 nm, respectively, as shown in Fig. 2 (a). By calculating the equivalent constant for decomplexation reaction of Zn-ligands, the stability constant values of the ZnS thin films with $ZnSO_4$, $Zn(CH_3COO)_2$, and $ZnCl_2$ precursors are attained with 0.70, 0.78, and 1.5, respectively, as presented in Table 1. The film thickness dependence on Zn sources is apparently related to the stability constants of the corresponding complex ions. Thicker film is achieved from the reaction with lower stability constant. The deposition rate is clearly affected by the degree of Zn-ligand

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