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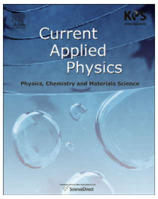

Effect of CdS deposition temperature for thermally grown Cu(In,Ga)Se_2 and two-step chalcogenized Cu(In,Ga)$(S,Se)_2$ absorbers on solar cell performances

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ABSTRACT

CdS buffer layer of varying thickness ranging from 23 to 58 nm deposited at different substrate temperature were prepared as n-type junction partner for thermally grown Cu(In,Ga)Se_2 and two-step chalcogenized Cu(In,Ga)$(S,Se)_2$ photovoltaic absorber films and the effect of deposition temperature and time on the CdS growth behavior and solar cell performance were evaluated. High deposition temperature resulted in a thicker CdS layer and more importantly lower density and shallower depth of open voids, which attributed to the improved open-circuit voltage and fill factor due to reduced interface recombination. The solar cell efficiency of thermally grown absorber saturated at about 30 nm thickness of CdS, while that of chalcogenized absorber gradually increased with CdS thickness up to 60 nm without significant loss of short-circuit current density.

1. Introduction

CdS thin film buffer layer has been known as the most suitable material for a high efficiency Cu(In,Ga)$(S,Se)_2$ (CIGSSe) solar cells [1]. When applying the chemical bath deposition (CBD) process for the material, the distinct improvement of surface properties of CIGSSe absorber layer can be attributed to the effect of surface cleaning and Cd doping [2,3]. Nevertheless, recently Zn(O,S) for CIGSSe solar cells have been widely applied as an alternative to Cd-containing CdS, and comparable efficiency of Zn(O,S)/CIGSSe solar cells has been reported [4,5]. W. Witte et al. reported the film coverage of Zn(O,S) was depending on the crystalline faces of CIGSSe, where the growth rate of Zn(O,S) on (220) oriented CIGSSe crystal plane was slower compared to that on (112) planes [6]. This is because each crystal plane has a different surface energy, and suggests that the chemistry of the absorber surface will affect the growth of the buffer layer.

The methods of manufacturing CIGSSe thin-film absorber layer include thermal co-evaporation and two step process. The thermal evaporation, which allows precise control of the film composition in real time, has been used for generating Ga compositional gradient along the thickness of Cu(In,Ga)Se_2 (CIGSe) layer. On the other hand, the two step process, in which metal precursor is selenized and/or surfurized, forms CIGSSe thin film having S/(S+Se) compositional gradient. In other words, each absorber layer will have different Ga or S content near the surface region, and therefore a suitable buffer material and/or formation process should be applied to maximize the energy conversion efficiency of CIGSSe solar cell.

In this study, CdS/CIGS and CdS/CIGSSe solar cells were compared experimentally with CdS deposition temperature as a variable. Because the deposition temperature of CdS film greatly affects growth rate as well as growth mechanism of thin films [7,8] and doping of absorber surface region [2], each solar cell will have not only a different thickness of the CdS buffer layer but also variation of electrical property of the absorber surface [9,10]. The impact of the absorber surface chemistry must be considered in achieving high efficiency solar cells, especially.

2. Experiment

CdS thin films were deposited using CBD method on both thermally evaporated CIGS (thermal_CIGSe) and two step processed CIGSSe (two-step_CIGSSe) absorber layers. The thermal_CIGSe and two-step_CIGSSe correspond to Ga-terminated CIGSe and S-terminated CIGSSe, respectively. CdS films deposited on bare

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Table 1
Physical properties of CdS thin films grown at different CBD conditions.

Sample no.	CBD condition	Thickness (nm)	Refractive index	R_Z (nm)
1	56 °C, 15 min	23.1	1.13	15.9
2	56 °C, 25 min	29.8	1.74	25.5
3	65 °C, 15 min	29.5	1.66	23.8
4	65 °C, 20 min	42.6	2.00	37.7
5	73 °C, 15 min	58.1	2.23	28.7

soda lime glass (SLG) and Si(100) wafer were also prepared to analyze the CdS thin film properties. SLG and Si wafer were chemically cleaned with mixed aqueous solution of deionized water, ammonia, and hydrogen peroxide at 85 °C for 15 min. The bath solution, used in this study for CdS preparation, is composed of deionized water, ammonium hydroxide NH_4OH (3 M), cadmium sulfate hydrate ($CdSO_4 \cdot 2.67H_2O$) (0.0015 M) as a source of cadmium and thiourea $CS(NH_2)_2$ (0.05 M) as a source of sulfide. The solution was quickly added to, and continuously mixed in a circulating water-jacketed glass reactor pre-heated to 60, 70, and 80 °C, respectively. The samples were immediately inserted vertically into the reactor, and then kept for additional 15 min after the solution temperature reached 45 °C. During the whole process, the solution was continuously circulated using a magnetic stirrer. The solution temperature gradually increased and finally reached 56, 65, and 73 °C, respectively. Another set of samples were prepared with different duration of 25 min, 20 min, 15 min for temperature setting of 60, 70, and 80 °C respectively. These samples were intended to yield identical thickness of CdS buffer layers regardless of the maximum deposition temperature. After completion of the deposition, the samples were rinsed in deionized water and air-annealed at 200 °C for 30 min. The solar cell was constructed by sequentially depositing 80 nm i-ZnO by RF-magnetron sputtering, and a 500 nm (Ga,Al):ZnO transparent conducting oxide layer by DC-magnetron sputtering. The current collecting grid of 0.1 μm Ni and 1.65 μm Ag was deposited by electron beam evaporation through a shadow mask. The optical thickness and refractive index of CdS films grown on Si wafer was obtained by single wavelength ellipsometer (LSE stokes ellipsometer, 632.8 nm). The morphology of CdS films grown on SLG was analyzed using atomic force microscopy (AFM, XE-100) and optical transmittance was measured using UV–Vis spectroscopy (Cary5000). The current density-voltage (J-V) characteristics of the CIGS solar cells were evaluated using a solar simulator (K3000, McScience) under AMG1.5, 100 mW/cm^2 illumination at 25 °C. The external quantum efficiency (QE) was measured using an incident-photon-to-electron conversion efficiency measurement system (PEC-S20, Jasco) at 25 °C.

3. Result and discussion

3.1. Characterization of CdS thin films

Table 1 presents the film thickness refractive index measured using an ellipsometer, and R_Z obtained from AFM measurements for samples deposited under varying CBD conditions. Here, R_Z is the 10-point average roughness. In this study, it was used as an indicator of the void depth existing in films. Morphology changes with the maximum deposition temperature and deposition time, which are factors influencing the growth of CdS films and the growth mechanism. For Samples 1, 3 and 5, which had the same deposition time, film thickness was found to vary with the maximum deposition temperature, due to the faster growth of CdS. Even with an increase in deposition time, there is likely to be a high void density within CdS films if the deposition temperature is not sufficiently high. For Samples 1, 2, 3 and 4, which had low deposition temperatures of 56 and 65 °C, the refractive indices were much lower than the theoretical CdS refractive index of 2.4. Meanwhile, the R_Z values, which serve as an indicator of void depth in CdS films, differed from the CdS film thickness by less than 10 nm for Samples 1, 2, 3 and 4. This implies that the films contain voids, which exist at a thickness similar to film thickness. The impact of such voids on the performance of CIGS solar cells will be discussed later.

Fig. 1 shows AFM measurements of the same samples used in the ellipsometer measurements. The sample number and deposition conditions were the same as in Table 1. The RMS value and grain size increases in the order of Sample 1, 3 and 5 as deposition temperature rises. This is because film thickness is greater at higher deposition temperatures for the same deposition time. However, a

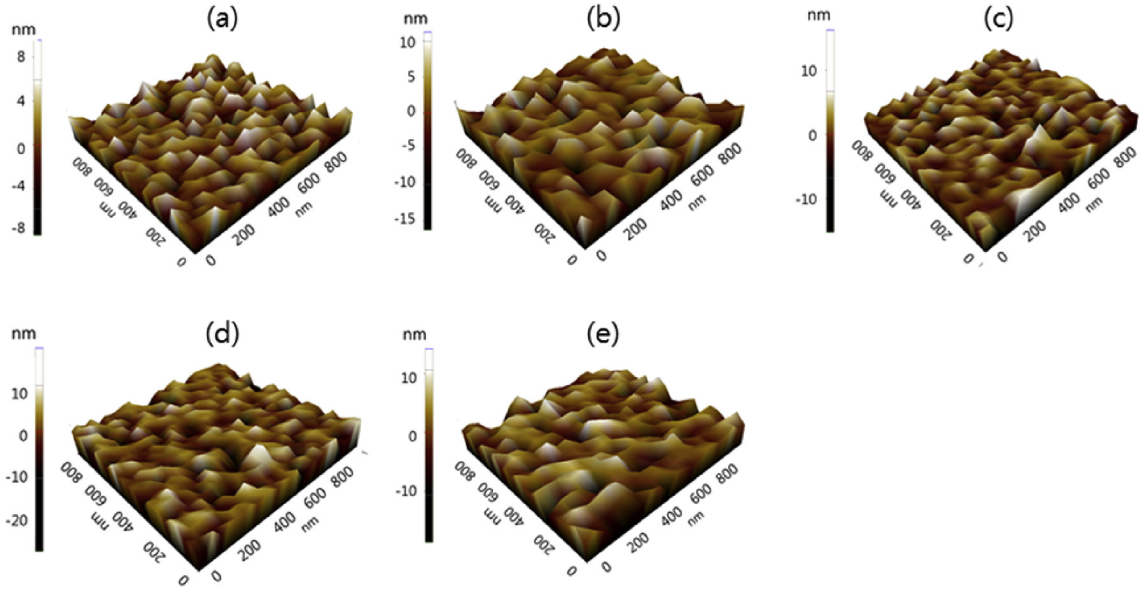

Fig. 1. AFM images of CdS films with respect to CBD condition; (a) sample 1 (56 °C, 15 min), (b) sample 2 (56 °C, 25 min), (c) sample 3 (65 °C, 15 min), (d) sample 4 (65 °C, 20 min), and (e) sample 5 (73 °C, 15 min).