

Effects of sulfur incorporation into absorbers of CIGS solar cells studied by numerical analysis

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Abstract— The performance of Cu(In,Ga)Se₂ (CIGS) solar cells with the incorporation of sulfur into the surface region of the absorbers has been studied by numerical simulation. The impacts of sulfur contents and thickness of sulfurized layers in the surface region of absorbers on the performance were evaluated. The results show that the incorporation of sulfur in the CIGS films enhances the open-circuit voltage (V_{OC}), but concurrently leads to the reduction in short-circuit current density (J_{SC}). The S/(S+Se) ratios of below 0.2 could improve the cell performance for all thickness of sulfurized layers in this study. For S/(S+Se) ratios of 0.1–0.5, the thickness of 200nm was suggested to enhance the efficiency of devices.

Keywords— CIGS solar cells; Surface sulfurization; Thin films; Selenization

I. INTRODUCTION

Thin-film Solar cells based on polycrystalline CIGS materials are regarded as the most promising alternative to the silicon-based solar cells due to the high conversion efficiency, low cost, large-area production, and the great potential for developing high-efficiency flexible solar cells [1]. The high efficiency of over 20% for CIGS solar cells has been demonstrated at the laboratory scale [2]. The selenization of CuGa/In metallic bi-layer precursors to prepare CIGS absorbers is a cost-effective method for the large-area production. However, it has been found that most of the Ga is accumulated near the Mo/CIGS interface. This could result in a decrease in V_{OC} due to the shrinkage of band gap near the space charge region (SCR), being ascribed to the lower Ga concentration in SCR. The surface sulfurization of CIGS absorbers has been studied to improve the performance of CIGS solar cells [3], [4], enlarging the band gap near SCR by substituting sulfur for selenium. Their results showed that the incorporation of sulfur into the surface region of CIGS absorbers did not necessarily enhance the cell performance, and even deteriorated the cell efficiencies. In order to investigate the factors impacting cell performance for the incorporation of sulfur into absorbers as well as its benefits, the effects of sulfur distribution profile, including sulfur contents and the depth of sulfur diffusion, on the performance of CIGS solar cells are evaluated with numerical simulation.

II. DEVICE MODELING

The baseline device structure of CIGS solar cells consists of Mo back contact, p-CIGS absorber, CdS buffer layer, and i-ZnO/ZnO:Al window layer. The thickness of CIGS film is

2 μ m and the overall Ga/(Ga+In) ratio is 0.25. The thicknesses of CdS, i-ZnO, and ZnO:Al are 60, 50, and 300nm, respectively. For the CIGS films prepared by selenization of metallic precursors, the Ga concentration of CIGS films near the CdS/CIGS interface is as low as negligible, and its maximum value is located near Mo back contact. In the simulations, we consider that the surface sulfurization of CIGS films results in the linear decrease of sulfur concentrations from the surface of absorbers. The device structure of CIGS solar cells with the sulfurized Cu(In,Ga)(S,Se)₂ (CIGSS) layer on the top of CIGS layer is shown in Fig. 1. The device simulation tool of wxAMPS [5], an update of one-dimensional solar cell simulation program AMPS-1D, was employed for the numerical study. The sulfur concentration near the surface region of CIGS films and the sulfur diffusion depth were varied. All other input parameters for the i-ZnO/ZnO:Al window layers, CdS buffer layers, and un-sulfurized CIGS absorbers were kept constant throughout all simulations as shown in Table 1. The additional deep defect levels, acting as the recombination centers, were located in the middle of band gap for all three layers.

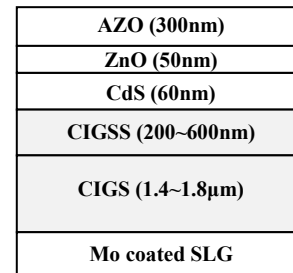


Fig. 1 Device structure of CIGS solar cells for numerical simulation

TABLE I
INPUT PARAMETERS OF EACH LAYERS FOR SIMULATIONS

Layer properties	ZnO:Al	i-ZnO	CdS	CIGS
Permittivity	9	9	10	13.6
E_g (eV)	3.3	3.3	2.4	1.167
N_C (cm ⁻³)	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}
N_V (cm ⁻³)	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}
μ_e (cm ² /V- s)	100	100	100	100
μ_h (cm ² /V- s)	25	25	25	25
Carrier density (cm ⁻³)	n: 1×10^{19}	n: 5×10^{16}	n: 5×10^{17}	p: 2×10^{16}

E_g : band gap energy; N_C : effective density of states in conduction band; N_V : effective density of states in valence band; μ_e : electron mobility; μ_h : hole mobility;

III. RESULTS AND DISCUSSION

The simulation results of conversion efficiency, open-circuit voltage, short-circuit current density, and fill factor (F.F.) for the baseline CIGS solar cells are 17.4%, 0.566V, 40.3mA/cm², and 76.2%, respectively. With the incorporation of sulfur into the surface region of CIGS absorbers, the valence band edge shifts together with the shift in conduction band edge as the band gap increases due to the formation of CIGSS layers near the surface region of absorbers [6]. The impacts of sulfur concentration and diffusion depth on the device performance are illustrated in Fig. 2. The value of V_{OC} increases with the increase of sulfur concentration and diffusion depth, attributed to the enlargement of band gap near SCR, resulting in the reduction of recombination in SCR. At the same time, however, the value of J_{SC} decreases with the increase of sulfur concentration and diffusion depth, corresponding to the increase of minimum band gap, which results in the reduction of light absorption. When the diffusion depth of sulfur is greater than the SCR width (~0.3μm), a higher sulfur concentration will result in a notch shape in conduction band edge (shown in Fig. 3), leading to the recombination of electrons in conduction band and holes in valence band [7]. And thus, the current collection was impaired. With the thick sulfurized layer, the F.F. and the efficiency deteriorate dramatically as the S/(S+Se) ratio is more than 0.3. For thin sulfurized layer of 200nm, there are only small variations in cell performances despite the sulfur concentration.

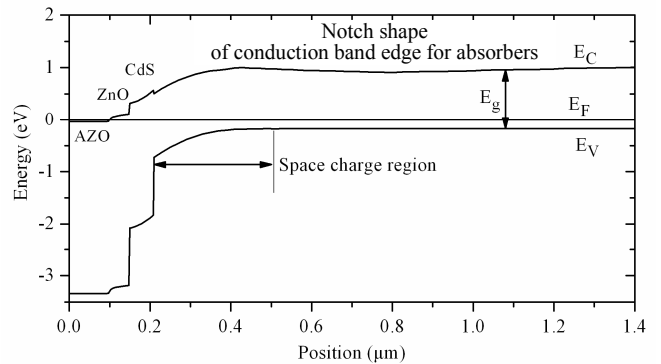


Fig. 3 Schematic energy band diagram of a CIGS solar cell with sulfurized layer thickness of 600nm and S/(S+Se) ratio of 0.5 under equilibrium condition

IV. SUMMARY

Numerical simulations of CIGS solar cells with the surface sulfurized CIGS absorbers have been carried out using the wxAMPS simulation program. The impacts of the sulfur concentration near the surface region of absorbers and the depth of sulfur diffusion on the performance of devices were investigated. It is found that the sulfurized absorber layers can improve the cell performance as the sulfur diffusion depth is less than the SCR width. With the greater depth and high sulfur concentration, the performance of devices decreases, which could be ascribed to the low F.F. and the reduction in current collection due to the formation of notch in conduction band edge of absorbers. It is concluded that both the thickness of sulfurized layer less than SCR width and the small S/(S+Se) ratios (≤ 0.2) are beneficial to the enhancement of cell performance.

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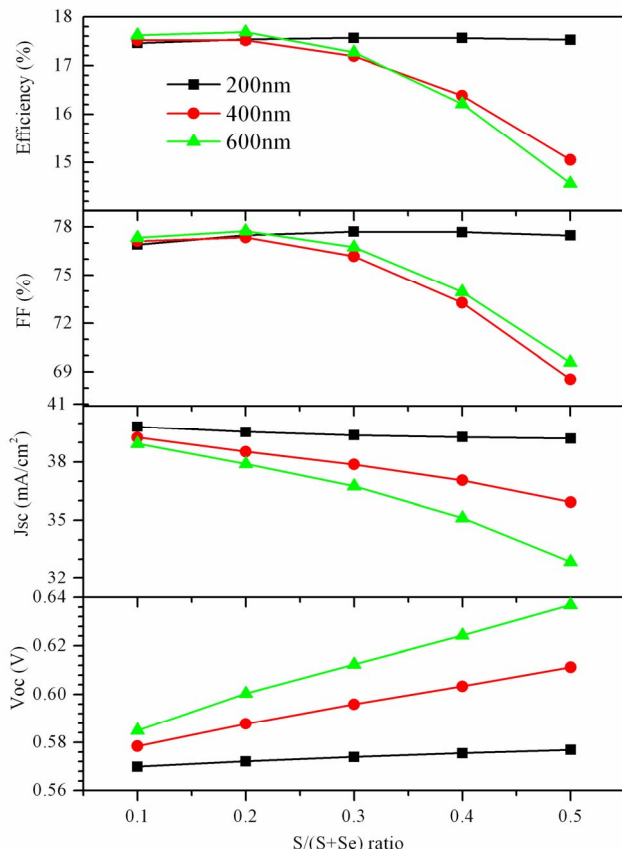


Fig.2 Performance parameters of CIGS solar cells calculated as the functions of sulfur concentration near surface region of absorbers and depth of diffusion