Research Paper

Post-Heat Treatment on Cu(In,Ga)Se₂ Solar Cells with CBD-ZnS Buffer Layers as a Function of ITO Growth Temperature

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Abstract

We fabricated Cu(In,Ga)Se₂ (CIGS) solar cells with a the chemical bath deposition-ZnS buffer layer by varying the substrate temperature for indium tin oxide (ITO) growth ($T_{\text{sub,ITO}}$) from room temperature (RT) to 200 °C. The CIGS solar cell efficiency increased with increasing $T_{\text{sub,ITO}}$. After light soaking (LS), the CIGS solar cell performance improved noticeably, with a rise in fill factor, except for $T_{\text{sub,ITO}}$ at RT, due to the high resistivity of ITO film. Post heat treatment (PHT) was carried out on the CIGS solar cells, in ambient air at 200 °C, with increasing annealing time, from 10 min to 1 h. After PHT for more than 10 min, cell performance was superior to that after LS at $T_{\text{sub,ITO}} \leq 100$ °C, with substantially increased cell efficiency. This was due to simultaneously enhancing the quality of the ITO film with supplementing thermal energy, and curing a defect at the p-n junction. At $T_{\text{sub,ITO}} \geq 150$ °C, cell performance improved after LS, compared to after PHT, regardless of the annealing time. After LS, photoexcited carriers were generated, which was beneficial for curing defects at the p-n junction, resulting in elevating cell performance. However, after PHT, excessive thermal energy was injected into the solar cell, which induced Zn diffusion into the CIGS absorber layer, forming different defect states, such as Zn_{Cu} and Zn_i , from the defect located at the p-n junction.

Keywords: Cu(In,Ga)Se₂, ITO growth temperature, Chemical bath deposition-ZnS, Light soaking effect, Post heat treatment effect

I. Introduction

The Cu(In,Ga)Se₂ (CIGS) solar cell has attracted substantial interest as a next-generation photovoltaic device, and its characteristics have been investigated for decades, due to several advantages, such as superior power conversion efficiency, controllable bandgap engineering and high absorption coefficient [1-3]. Recently, CIGS solar cell efficiency of up to ~22.9 % was reported by Solar Frontier [4], and there continues to be effort applied up to the present day in the development of CIGS solar cells with improved efficiency.

The typical structure of a CIGS solar cell involves a soda-lime-glass (SLG)/Mo/CIGS/CdS/transparent conducting oxide (TCO). The CIGS absorber layer is deposited by a 3-stage co-evaporation method, and includes various defect states [5-7]. As a buffer layer, chemical bath deposition (CBD)-CdS is widely used, although the use of toxic and harmful CdS should be avoided, for environmentally-friendly and renewable energy devices, and thus, Zn-based materials are needed, as an alternative buffer layer. In the

CIGS solar cell, the choice of TCO material for the top electrode is also considered as an important issue, in terms of cell efficiency, and for commercial products, although ZnO:Al has been adopted, indium tin oxide (ITO) is well known for its outstanding physical and electrical properties, such as wide bandgap range, from 3.5 eV to 4.3 eV, high electrical conductivity and good thermal stability [8,9].

In a previous study, we fabricated CIGS solar cells with CBD-CdS buffer layers by varying the ITO growth temperature, and investigated the relationship between cell performance and ITO film property, as a function of growth temperature [10]. The efficiency of the CIGS solar cells gradually increased with each increment of ITO growth temperature, from 25 °C to 200 °C, mainly due to improved ITO film quality, and this implied that the ITO layer had a decisive influence on cell performance.

On the other hand, the most important arbiter of cell performance is p-n junction quality, among the several CIGS solar cell interface layers. Where CBD-ZnS has been applied as a buffer layer to CIGS solar cells, there are metastable defect states at the p-n junction, which cause cell degradation owing to the lowered fill factor (FF). However, notably, FF is compensated by light soaking

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(LS) and post-annealing treatments, after which cell efficiency noticeably increased [11-13]. The study of this LS effect, of raising cell efficiency in CIGS solar cells with CBD-ZnS buffer layers, is therefore important.

In this study, we fabricated CIGS solar cells with a CBD-ZnS buffer layer, by varying the ITO growth temperature from room temperature (RT) to 200 °C, to examine the effect of ITO film quality on CIGS solar cells, and then sequentially carried out LS and post-heat treatment (PHT) on completed solar cells, to test cell performance enhancement. Cell performances were measured, after LS, under a solar simulator with air mass (AM) 1.5 spectrum, for 1 h, and PHT in an ambient air at 200 °C, with annealing time increased from 10 min to 1 h. From the results, we found that CIGS solar cell efficiency noticeably increased after LS or PHT, with the increase closely related to the growth temperature of the ITO.

II. Experiment

A 2.2 µm CIGS layer was deposited by the 3-stage co-evaporation method onto 900 nm, Mo-coated SLG [5,14]. CBD-ZnS, with a thickness of ~50 nm, was synthesized onto the CIGS layer in an aqueous solution, at 85 °C for 80 min, by dipping into a home-made water bath system [15]. The CBD processing conditions were as follows: mole concentrations of zinc sulfate, thiourea, and ammonia were 0.02 M, 0.17 M, and 2 M, respectively. ITO film was prepared on the CBD-ZnS buffer layer by radio frequency (RF) magnetron sputtering, using a sintered target ($\text{In}_2\text{O}_3:\text{SnO}_2=90:10$ wt.%) [10]. A 150 nm ITO film was deposited at various growth temperatures ($T_{\text{sub,ITO}}$), from RT to 200 °C, under fixed conditions of RF power of 100 W, Ar flow of 50 sccm, and operating pressure of 0.67 Pa. The completed solar cell consisted of Mo/CIGS/CBD-ZnS/i-ZnO/ITO/Ni/Al, and had an active area of 0.47 cm².

The CIGS solar cell parameters were deduced by measuring the current density (J)-voltage (V) curve, with a source meter (Keithley 2400), under a global AM 1.5 spectrum for 1000 W/m² at RT. To examine the LS and PHT effect on CIGS solar cells, as a function of $T_{\text{sub,ITO}}$, we carried out LS using a solar simulator, with AM 1.5 spectrum, for 1 h at RT, and PHT in an ambient air, at 200 °C, with annealing time increased from 10 min to 1 h. As CIGS solar cell efficiency can return to its initial status, after LS, if it is kept in dark conditions for several hours, PHT was carried out the day after LS. To extract the photocurrent dependence of the CIGS solar cells as a function ITO growth temperature, J - V curves were repeatedly measured, after LS and PHT, under dark and white light.

III. Results and discussion

The performance of the CIGS solar cells, as a function of

Figure 1. Performance of CIGS solar cells, as a function of $T_{\text{sub,ITO}}$, before and after LS for 1 h.

$T_{\text{sub,ITO}}$, was measured before and after LS for 1 h, as shown in Fig. 1. Cell efficiency increased with increasing $T_{\text{sub,ITO}}$. It was an interesting finding that cell efficiency was near zero in the case of $T_{\text{sub,ITO}}$ at RT, which was a result distinct from the cell efficiency of approximately 7 % achieved with a CdS buffer layer, under the same condition of $T_{\text{sub,ITO}}$ at RT [10]. After LS for 1 h, cell efficiency increased, except for $T_{\text{sub,ITO}}$ at RT, maintaining its change tendency, which was mainly due to the substantial rise in FF, rather than open circuit voltage (V_{oc}) or short circuit current (J_{sc}).

It is known that the irradiation of blue photons in the solar spectrum was the origin of the increased cell efficiency after LS [16]. In our previous study, we actually demonstrated this effect, showing increased cell efficiency with the CBD-ZnS buffer layer, by only soaking UV light into the solar cell [15,17]. According to reported results, the CIGS solar cells with Zn-based buffer layers showed noticeably increased cell efficiency after post-annealing

Figure 2. Performance of CIGS solar cells, as a function PHT time, from 10 min to 1 h, at different $T_{sub,ITO}$. PHT temperature was maintained at 200 °C.

treatment of the completed solar cells [18–21]. Unlike LS treatment, which is reversible and reproducible after several hours, post-annealing treatment is irreversible, allowing retention of improved cell performance.

In this experiment, we carried out PHT on CIGS solar cells, as a function of $T_{sub,ITO}$, by gradually increasing annealing time from 10 min to 1 h, while repeatedly measuring cell performance, as indicated in Fig. 2. Compared to as-fabricated cells, cell efficiency increased as soon as PHT was conducted for 10 min, in all cases, and became saturated after PHT for 20 min or more. For $T_{sub,ITO}$ at RT and 100 °C, the increased cell efficiency is ascribed to the increased J_{sc} and V_{oc} , while for $T_{sub,ITO}$ of 150 °C and 200 °C, it is attributed to the increased FF, which was similar to results achieved after LS; *i.e.*, we discovered that the PHT had a beneficial effect on CIGS solar cells with ITO film grown at $T_{sub,ITO} \leq 100$ °C.

Figure 3 shows the different CIGS solar cell efficiencies, after LS for 1 h (LS), PHT for 1 h (PHT) and then additional LS for 1 h after PHT for 1 h (PHT+LS). At $T_{sub,ITO}$ at RT, after LS, cell efficiency was near zero, while after PHT, cell efficiency increased, up to ~6 %. At $T_{sub,ITO}$

Figure 3. Comparison of CIGS solar cell efficiency, depending on $T_{sub,ITO}$, after LS for 1 h, PHT for 1 h and additional LS for 1 h after PHT for 1 h (PHT+LS).

Figure 4. J-V curves for CIGS solar cells at different $T_{sub,ITO}$, after LS for 1 h, PHT for 1 h, and additional LS for 1 h after PHT for 1 h (PHT+LS), under conditions of dark and white light.

at 100 °C, the increased cell efficiencies were similar for LS, PHT and PHT+LS treatments. At $T_{sub,ITO} \geq 150$ °C, the highest cell efficiency was achieved after LS, and then slightly decreased after PHT and PHT+LS. From these results, we concluded that the increase of cell efficiency at $T_{sub,ITO}$ at RT was due to the supplementary thermal energy changing the ITO film quality during PHT at 200 °C. Based on previous results on the electrical properties of ITO film, as a function of $T_{sub,ITO}$, Sn ions substituted into the In₂O₃ lattice can release more electrons and thereby increase carrier concentration, at $T_{sub,ITO} \geq 150$ °C, which facilitated the stability of the ITO film, rendering it suitable for the TCO layer [10]. In other words, ITO film quality is too poor to apply to solar cells, when grown at $T_{sub,ITO} \leq 100$ °C, and thus, PHT performed at 200 °C, for 1h, makes better quality ITO film, resulting in increased cell efficiency, similarly to the LS effect. The detailed CIGS solar cell parameters (efficiency, J_{sc} , V_{oc} and FF), after various post-treatments (LS, PHT and PHT+LS), as a

Table I. Parameters of CIGS solar cells with a CBD-ZnS buffer layer as a function of $T_{\text{sub,ITO}}$, from RT to 200 °C, after different post treatments (LS, PHT, and PHT+LS).

T_{sub} (°C)		As-fabricated	LS	PHT				PHT+LS
				10 min	20 min	40 min	60 min	
RT	V_{OC} (V)	0.20	0.18	0.39	0.46	0.49	0.50	0.49
	J_{SC} (mA/cm ²)	18.53	22.79	28.97	30.38	31.23	30.57	29.96
	FF (%)	29.90	30.00	37.90	39.30	41.40	39.70	38.70
	Efficiency (%)	1.09	1.21	4.33	5.49	6.33	6.08	5.68
100	V_{OC} (V)	0.35	0.51	0.53	0.55	0.55	0.56	0.57
	J_{SC} (mA/cm ²)	30.52	34.59	34.42	35.28	34.92	35.17	34.90
	FF (%)	35.00	49.20	46.10	47.90	48.50	48.00	51.30
	Efficiency (%)	3.69	8.62	8.43	9.27	9.34	9.36	10.17
150	V_{OC} (V)	0.54	0.58	0.57	0.58	0.57	0.57	0.58
	J_{SC} (mA/cm ²)	34.94	36.27	35.05	36.60	36.35	36.49	36.16
	FF (%)	40.40	69.50	63.50	64.10	63.50	64.00	65.30
	Efficiency (%)	7.54	14.72	12.70	13.50	13.18	13.25	13.70
200	V_{OC} (V)	0.57	0.60	0.58	0.58	0.58	0.57	0.58
	J_{SC} (mA/cm ²)	35.04	36.05	35.97	36.34	36.04	36.11	35.79
	FF (%)	41.50	68.50	59.20	60.80	61.20	60.90	62.00
	Efficiency (%)	8.34	14.89	12.35	12.89	12.72	12.62	12.93

function of $T_{\text{sub,ITO}}$, have been summarized in Table I.

To analyze differences between the LS and PHT effects on CIGS solar cells, as a function of $T_{\text{sub,ITO}}$, CIGS solar cell J-V curves corresponding to each cell of Fig. 3 were measured, under the dark and white light conditions, as shown in Fig. 4. The dark current is expressed with a black line and there was no photocurrent, as expected. With irradiation by white light, photocurrent occurred in as-fabricated solar cells, and was clearly related to $T_{\text{sub,ITO}}$. For $T_{\text{sub,ITO}}$ at RT, there was little photocurrent, due to the high resistivity of the ITO film. As $T_{\text{sub,ITO}}$ increased, although photocurrent also increased with improved ITO film quality, distorted J-V curves, called ‘kinks’ [22,23], were clearly revealed at $T_{\text{sub,ITO}} \geq 100$ °C. After LS and PHT, the kink disappeared and the FF increased, in all cases.

In a previous study, we interpreted this LS effect, raising cell efficiency in CIGS solar cells with CBD-ZnS buffer layers, as a result of the introduction of a deep acceptor ($V_{\text{Cu}}-V_{\text{Se}})^{3-}$, located near the p-n junction, as follows; in as-fabricated solar cells, the J-V curve was distorted, due to the number of electrons trapped in deep acceptor states, resulting in FF loss. After LS for 1 h, the deep acceptor states were already filled with electrons excited from the p-n junction by the blue photon injection, thus lowering the barrier height for electron transport, which enhanced cell efficiency [15]. The recovered J-V curves, after LS and PHT, signified that PHT at 200 °C for more than 10 min was sufficient to fill the deep acceptor states with thermally excited electrons, resulting in improved cell efficiency.

In this experiment, after LS, cell efficiency at $T_{\text{sub,ITO}}$, at RT, was almost zero, because the ITO film wasn’t conducting with high resistivity, blocking carrier transport to the electrode. After PHT, however, cell efficiency for

$T_{\text{sub,ITO}}$ at RT increased up to ~ 6 %, with conducting ITO film, and did not drop FF. Thus, PHT on CIGS solar cells at $T_{\text{sub,ITO}}$, at RT, improved cell performance through both ITO film quality and defect curing at the p-n junctions. These positive effects after PHT occurred in CIGS solar cells at the $T_{\text{sub,ITO}}$ of 100 °C. On the other hand, cell efficiencies were slightly less, after PHT, compared to those after LS, from 14.72 % to 13.25 % for $T_{\text{sub,ITO}}$ at 150 °C, and from 14.89 % to 12.62 % for $T_{\text{sub,ITO}}$ at 200 °C, respectively. This seemed to be due to the Zn atoms, with their monovalent atomic character, becoming easily diffused into the absorber, through the abundant V_{Cu} sites in the CIGS, which become defect point of Zn_{Cu} , occupying V_{Cu} and interstitial Zn_i [24]. The supply of additional thermal energy can cause a Zn diffusion into the CIGS layer, at $T_{\text{sub,ITO}} \geq 150$ °C, by PHT at 200 °C for 1 h, bringing about negative effects on cell performance. Actually, as $T_{\text{sub,ITO}}$ became higher, cell degradation became worse; *i.e.*, excessive post-annealing processes should be curtailed, and optimized conditions for improved cell performance should be based on the CIGS solar cell.

IV. Summary

We fabricated CIGS solar cells with a CBD-ZnS buffer layer by increasing the $T_{\text{sub,ITO}}$ from RT to 200 °C, and then investigated the effects of LS and PHT on these. As $T_{\text{sub,ITO}}$ increased, cell performance improved. After LS, cell efficiency increased in all cases with the rise of FF, excluding $T_{\text{sub,ITO}}$ at RT, which remained near zero after LS, due to the high resistivity ITO film blocking photocurrent flow. As soon as PHT time reached 10 min, at $T_{\text{sub,ITO}} \leq 100$ °C, cell efficiency improved, while at

$T_{\text{sub,ITO}} \geq 150$ °C, the improvement was similar to that from the LS process. PHT was carried out sequentially on the CIGS solar cells, with PHT time increased up to 1 h, and it was found that cell efficiency was saturated in all cases after PHT time of 20 min. Compared to cell efficiency after LS, at $T_{\text{sub,ITO}} \leq 100$ °C, it clearly increased, whereas at $T_{\text{sub,ITO}} \geq 150$ °C it slightly decreased, after PHT for 1 h.

From these results, we discovered that PHT at 200 °C had an effect on CIGS solar cells similar to the LS effect, in terms of enhanced cell performance. The change of cell performance brought about by PHT and LS can be explained by the supply of additional thermal energy. At $T_{\text{sub,ITO}} \leq 100$ °C, thermal energy by PHT facilitated both improved ITO film quality and curing of the deep acceptor defect at the p-n junction, while at $T_{\text{sub,ITO}} \geq 150$ °C, excessive thermal energy caused Zn diffusion into the CIGS layer, resulting in a degree of cell degradation.

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