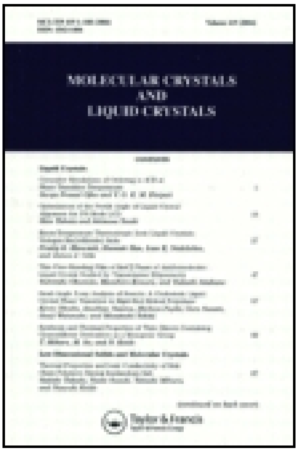

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The Effect of Post-Deposited Na on Cu(In$_x$,Ga$_{1-x}$)Se$_2$ Solar Cells by using the Na$_2$S Solution

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The Effect of Post-Deposited Na on $Cu(In_x,Ga_{1-x})Se_2$ Solar Cells by using the Na_2S Solution

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It is known that even mixing only a small amount of Na has effect on electrical and structural property of the CIGS absorber layer and, as a result, device efficiency is improved. In this study, unlike the conventional method where Na diffuses from SLG while CIGS absorber is growing, a new method was applied. In the new method, Na precursor is deposited on the CIGS absorber layer grown on Al_2O_3/SLG to incorporate Na. The effect of Na on the absorber layer was observed using secondary ion meass spectroscopy, Hall measurement system, scanning electron microscopy, and x-ray diffraction. As a result, it was found that, in the post deposition treated CIGS absorber layer, Na has effect mostly on the electrical property of CIGS without significant change of the microstructure.

Keywords: Cu(In; Ga)Se_2; CIGS absorber layer; Na diffusion; Na effect; PDT; post deposition treatment

Introduction

The high-efficiency Cu(In,Ga)Se2 (CIGS)-based polycrystalline thin film solar cell is an attractive target for research. since it can obtain stable and high conversion efficiency at a relatively low cost [1]. The most efficient CIGS solar cells were produced only by the combination of soda-lime glass (SLG) and a high growth temperature [2–4]. It is considered that the high performance of CIGS absorber layer grown in a high growth temperature with SLG substrate is due to the Na diffused from SLG to the growing CIGS film [5–10]. In general, Na of about 0.1 at.% diffuses to the absorber layer and stays at the grain boundary affecting the electrical (for example, passivation of defects or introduction of acceptor states) and structural (for example,. larger grain size, more pronounced texture, or suppression of defect formation) properties of the CIGS absorber. As a result, mainly, the open-circuit voltage (Voc) and fill factor(FF) increase, improving efficiency in turn [11].

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Of the methods for Na introduction, the most common method is the direct usage of Na diffused naturally from SLG, because the Na amount contained in SLG is high enough as much as 28%. However, since Na in the form of Na_2O is distributed non-uniformly across the glass substrate, it is hard to obtain uniform Na distribution across the large area CIGS absorber layer. Na may increases efficiency in small area cells, however, in making large area module, undesirable lateral nonuniformity and irreproducibility of cell performance may be caused. And, the flexible sollar cells that must utilize the metal or the polyimide foils as substrate material, which doesn't contain Na source, require a separate process to add an optimized Na to improve the device efficiency. Therefore, other methods are being considered to control Na amount easily and uniformly.

One of the alternative methods is depositing Na precursor on Mo, however, the weak adhesion of CIGS and Mo might be another problem to be solved. Another alternative is depositing the Na precursor layer after growing CIGS absorber layer. Recently, this method is grabbing attention since it controls the thickness of the Na precursor layer without causing adhesion problems and easily controls Na amount by adjusting the thickness of the Na precursor layer. And, at the same time, the method also diffuses Na uniformly, as a result, improving efficiency [12,13].

In this study, post-deposition treatment (PDT) using Na_2S solution was performed. Unlike the existing method of forming Na precursor by vacuum process, it is a solution-based method where process control is very simple. Therefore, it is expected that the method is advantageous in the aspect of the cost to produce photovoltaic modules.

Experimental

In order to examine the electrical and structural effect of Na on the $Cu(In,Ga)Se_2$ (CIGS) absorber layers by the PDT method, the Mo-deposited Mo/SLG sample that Na diffusion is allowed from the bare soda-lime glass (SLG) and the Al_2O_3 -deposited Al_2O_3/SLG sample which prevents diffusion of Na elements from SLG substrate, were used.

On all the samples of Mo/SLG and Al_2O_3/SLG, the 2.5um-thick CIGS absorber layer, whose Cu/(In+Ga) ratio is between 0.85 and 0.95, was deposited by co-evaporation method at the maximum substrate temperature of 530°C (CIGS/Mo/SLG and CIGS/Al_2O_3/SLG). It is known that the high-efficiency CIGS solar cells are mostly made within the narrow range of Cu/(In+Ga) ratio between 0.85 and 0.95. The PDT was applied to some of the CIGS/Al_2O_3/SLG samples in order to observe the electrical and structural effect of Na introduced by PDT not from SLG.

In this study, PDT method was applied by performing dip-coating in the aqueous Na_2S solution precursor and annealing of the Na_2S -coated samples. The PDT process was carried out under atmospheric pressure after the CIGS absorber layer was grown.

Since the Na_2S aqueous solution used as Na precursor is strongly alkaline, surface of the CIGS absorber layer may be etched depending on the concentration and sample dip time [14]. It is necessary to set the optimum concentration and dip time with which a proper amount of Na diffuses and undesirable etching does not occur. In this study, CIGS/Mo/SLG and CIGS/Al_2O_3/SLG samples were dipped in the Na_2S aqueous solution of 0.1M at the room temperature for 10 seconds, and, then samples were taken out and dried for annealing at 400°C for 20 minutes.

The secondary-ion-mass spectrometry (SIMS) depth profile was analyzed to check that whether the Na content is sufficiently diffused by the Na_2S -PDT method. Also, to examine the effect of Na on the electrical property of CIGS absorber layer, Hall measurement was used. Meanwhile, the effect on structural properties was examined by scanning electron microscope (SEM) images and X-ray diffraction (XRD) patterns.

Results and Discussion

The Na diffusion from SLG substrate begins with the CIGS absorber layer growth and has both of the structural and the electrical effects on the CIGS quality as an photovoltaic absorber. However, in the case of PDT, it is known that it has effect mainly on electrical properties of CIGS absorber since Na diffuses to the already grown CIGS absorber layer [11, 16].

According to the results of Hall measurement (for the group of the treated CIGS/Al_2O_3/SLG samples and the group of the non-treated CIGS/Al_2O_3/SLG samples), hole concentration largely increased as much as 4 times while the resistivity decreased from 1.76×10^2 to 3.96, showing considerable difference after PDT.(Table 1) The reduced resistivity and increased hole concentration is known to increase both of the open circuit voltage and the fill factor [16, 17]. The as-deposited CIGS absorber layer may have large amount of V_{Se}, which is major donor in this material system, due to the high vapor pressure of Se, especially along the grain boundaries. Na is known to promote the oxidation of the Se-deficient surfaces and hence reduce the donor compensation, which resulted in the increased hole concentration and the resistivity [18].

SIMS measuring was carried out to check whether the resistivity was reduced because of the Na diffused by the PDT. As shown in Figure 1, in the PDT-treated depth profile, a larger amount of Na was found. Regarding the depth profile of Al, which is the element of Al_2O_3 inserted as an alkali barrier layer of the CIGS/Al_2O_3/SLG sample, one can know it is Al_2O_3 layer since there is the characteristic peak like the Mo layer of CIGS/Mo/SLG sample. Near the Al peak position, the Na peak of the non-treated CIGS/Al_2O_3/SLG sample with a high intensity exists together. This proves that the Na from SLG cannot diffuse to the CIGS absorber layer due to Al_2O_3. Therefore, the sample can be considered as Na-free. Na depth profile of the CIGS/Al_2O_3/SLG sample can be considered as the background for the CIGS/Mo/SLG samples. Since PDT method includes the deposition of Na precursor layer and the annealing of the sample as well, it is necessary to confirm that the annealing treatment doesn't induce a significant change in the Na profile of CIGS/Mo/SLG. Figure 1b was obtained from the annealed CIGS/Mo/SLG without Na2S dip coating. Obviously the PDT-CIGS/Mo/SLG shows much higher Na concentration compared to the annealed one, which means that the Na incorporation is indeed a result of the PDT rather than the low temperature annealing itself.

The Na diffused by PDT method mostly stays at grain boundaries and act there passivating defects such as hole trap, reducing resistivity to the level lower than that of the Na-free sample [18–19–20]. Looking into the depth profile of CIGS/Mo/SLG samples,

Table 1. Hole concentration and resistance of the PDT-treated sample and the non-treated sample of CIGS/ Al_2O_3/SLG

	resistivity (ohmcm)	hole concentration (/cm^3)
CIGS/Al_2O_3/SLG	1.76e+2	1.99e17
CIGS/Al_2O_3/SLG after PDT	3.96	7.96e17

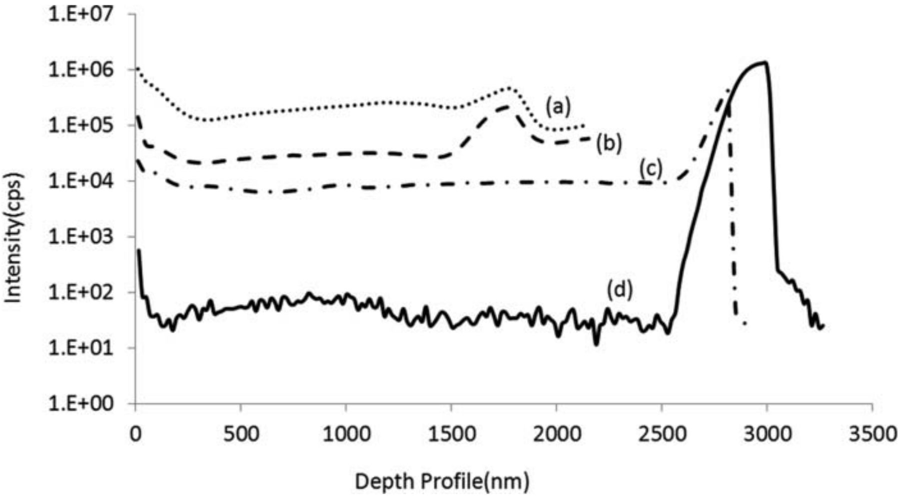

Figure 1. SIMS depth profiles. (a) [Na]; after PDT of CIGS/Mo/SLG, (b) [Na]; after the annealing of CIGS/Mo/SLG, (c) [Na]; from SLG of CIGS/Al2O3/SLG, (d) [Al]; from Al_2O_3 of CIGS/Al_2O_3/SLG.

a high Na concentration is found in the surface of CIGS absorber layer and the interface of CIGS/Mo, which suggests that most of grain boundaries of CIGS layer is saturated with enough Na since the grain boundaries are the main paths for Na diffusion. The above Na distribution together with the Hall measurement results, strongly supports that the Na supplied by the PDT existing at grain boundaries enhanced the electrical properties of CIGS absorber. However, the effect of the acceptor states created by the small amount of Na dissolved in the crystalline grains on the electrical properties cannot be completely excluded [15].

Figure 2 shows SEM images for the non-treated and the PDT CIGS/Al2O3/SLG. This analysis was intended to investigate the structural effect of Na on the CIGS absorber layer. Both samples don't show any significant difference in the morphology and the grain size. Although the cross-sectional SEM image contains the artifacts induced by breaking the sample, it is generally accepted as a tool to see the grain size distribution. The morphological behavior is well consistent with other report, where CIGS was annealed at 400°C under Na environment [11], In fact, it is known that CIGs is very stable at this low temperature

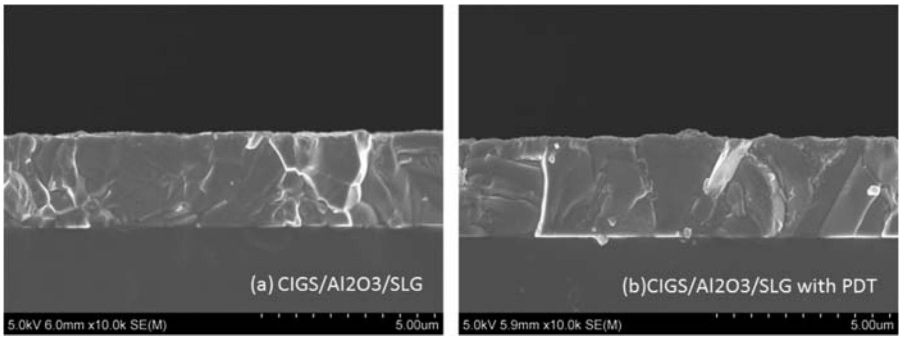

Figure 2. SEM images of (a) PDT-treated and (b) the non-treated CIGS/Al_2O_3/SLG.

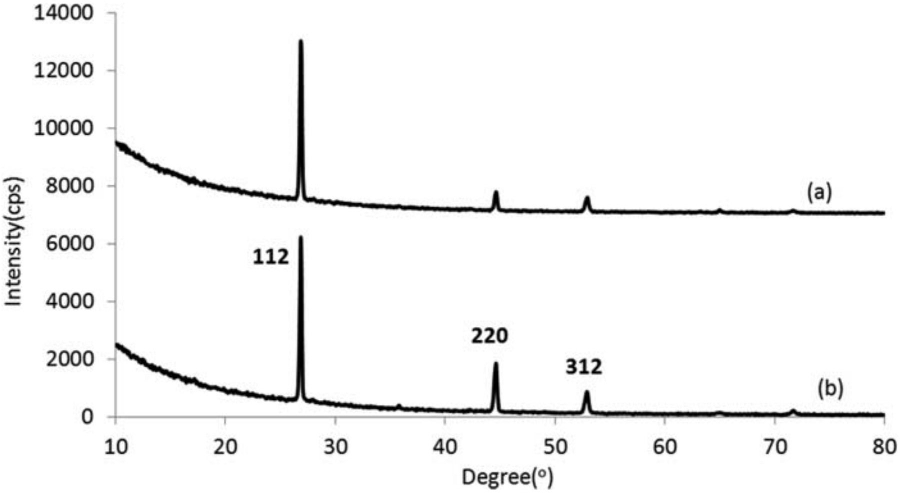

Figure 3. XRD pattern of (a) the non-treated group and (b) PDT-treated group of CIGS/Al_2O_3/SLG samples.

range near 400°C and the recrystallization is observable only from long-time annealing at the temperature of higher than 500°C [21]. Also, XRD diffraction patterns do not show a texture change and no other peak was not found after the PDT, as shown in Figure 3. This means that the other new crystalline phase is not formed by the Na_2S aqueous solution based PDT. Therefore, it can be concluded that the Na incorporated in CIGS absorber by PDT is distributed mostly along grain boundaries causing changes in electrical properties without affecting the microstructural properties of CIGS absorber layer.

Conclusions

The PDT method using Na_2S solution on the Na-free CIGS absorber layer grown was applied. The Na-free sample without PDT and the sample with PDT were compared and following results were obtained. It was found that Na diffuses sufficiently through the CIGS absorber layer to Mo by the PDT process at 400°C for 20 minutes. The PDT sample showed increased hole concentration and reduced resistivity compared to the Na-free sample. Both of the PDT and the non-treated sample did not show changes in the grain size and texture. Therefore, Na by PDT has effects only on the electrical properties without affecting structural properties of the CIGS absorber layer.

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