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Double-graded bandgap in Cu(In,Ga)Se_2 thin film solar cells by low toxicity selenization process

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A low-toxic selenization with post gallium diffusion (PGD) treatment has been demonstrated to increase the bandgap in the surface Cu(In,Ga)Se_2 (CIGSe) absorbers and to form double-graded bandgap profiles to improve the cell efficiency. The CIGSe absorber with PGD for 5 min increased open-circuit voltage from 0.49 to 0.66 V and efficiency from 9.2% to 13.2%, contributed by the enhancement of carrier recombination in the space-charge region. The reduction in short-circuit current from 30.8 to 29.9 mA/cm^2, attributed to the absorption loss in long-wavelength regions, can be potentially improved by further optimization of the minimum bandgap value in gradient valley.
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$CuInSe_2$ (CISe) and its related quaternary semiconductor (incorporating gallium) have received great attention as photovoltaic absorber materials. The special characteristic of the Cu(In,Ga)Se_2 (CIGSe) material is its adjustable energy bandgap, which can be optimized to match the solar spectrum by controlling the Ga/(In + Ga) compositional ratio.[1] Lundberg *et al.*[2,3] have reported that increasing the bandgap in the space-charge region (SCR) significantly improves the open-circuit voltage (V_{OC}) for better photovoltaic performance although this accompanies a corresponding photocurrent loss to decrease short-circuit current (J_{SC}). To overcome the current loss encountered, an in-depth bandgap variation via Ga-grading has been widely studied and generally classified into two categories: normal and double grading profiles.[4,5] The normal grading of bandgap through CIGSe thin films from the surface towards the back contact can enhance carrier collection at the expense of V_{OC} decrease because of low bandgap in the SCR. The double grading, containing a "notch" profile in bandgap with a minimum value inside the CIGSe thin film and the elevated bandgap towards the bottom and surface, improves V_{OC} due to the elevated bandgap near the surface.[4]

The selenization process to fabricate CIGSe thin film exhibits elemental inter-diffusion issues in longitudinal phase inhomogeneity and low bandgap near the surface, hence, degrading its electrical properties.[6–9] Sulfurization treatment is a method that alloys sulfur into CIGSe thin films to increase the energy bandgap by using highly toxic H_2Se/H_2S gases.[10,11] Nevertheless, to investigate an environment-friendly alternative, this study addresses a low-toxic selenization process with post gallium diffusion (PGD) treatment by using selenium vapor source to fabricate CIGSe absorbers. It is worth mentioning that toxic H_2Se/H_2S reactants are excluded in this process. The PGD treatment was demonstrated to increase the bandgap near the surface of absorbers and to obtain double-graded bandgap profiles, which significantly improved the performance of the CIGSe solar cells.

Polycrystalline CIGSe thin films of ~1.9 μm in thickness were prepared in a vacuum system by a two-step selenization process without and with PGD treatment [depicted in Fig. 1(a)], respectively. A bi-layered Mo electrode of 0.9-μm-thick was deposited on soda-lime glass (SLG) substrates by a DC magnetron sputtering. In the first step, bi-layered metallic CuInGa precursors of ~0.6 μm were prepared using two ternary CuInGa alloys targets in a sputtering system.[12] A conventional CuInGa layer of Ga/(In + Ga) ratio ~ 0.28 (520 nm in thickness) was deposited on the Mo-coated SLG substrates, and subsequently covered by an ultra-thin precursor layer of Ga/(In + Ga) ratio ~ 0.60 (80 nm in thickness). The atomic compositions of bi-layered CuInGa precursors were confirmed to be the ratios of Cu/(In + Ga) ~ 0.87 and Ga/(In + Ga) ~ 0.31, respectively. Prior to the selenization, a 1-μm-thick selenium film was coated on the CuInGa layer using thermal evaporation deposition. During the second step, the selenization was performed in an evaporation system to continuously supply selenium vapors of 40 Å/s on the precursor-coated substrates, and the precursors were heated to 350 °C for 20 min and subsequently ramped up to 540 °C for 40 min to obtain the CIGSe chalcopyrite phase. To achieve double-graded bandgap distribution through CIGSe films, PGD treatment was employed at the end of annealing in the second step before the substrates were cooled down, as shown in Fig. 1(a). Elemental gallium was diffused into the surface of resulting CIGSe thin films as a flow rate of 25 Å/s, and duration was of 5 and 8 min for respective samples. Further details on the gallium diffusion are discussed below. This PGD is a treatment to directly alloy additional gallium with resulting thin films, which can be expected to increase the bandgap near the surface of CIGSe absorbers via the elevated Ga/(In + Ga) ratio.

After deposition of CIGSe thin films, the CIGSe solar cells, consisting of Al-Ni gird/AZO/i-ZnO/CdS/CIGSe/Mo multilayers on the SLG substrates, were completed to evaluate the electrical properties. Fig. 1(b) shows the structure of

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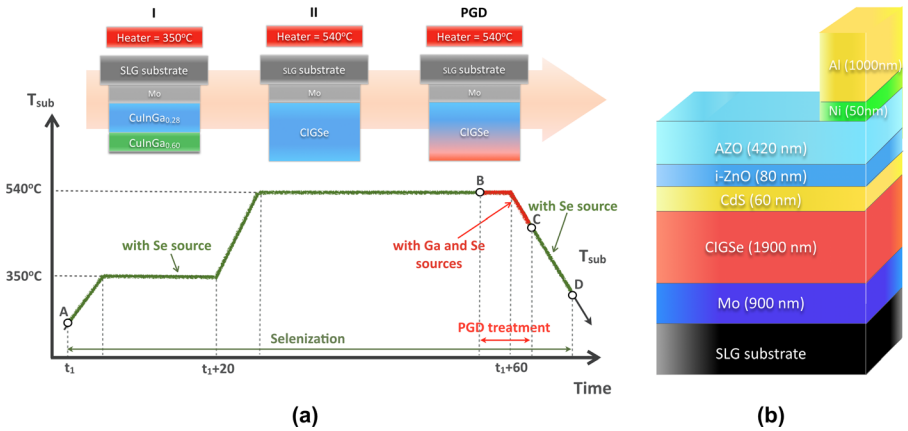

FIG. 1. (a) Scheme of the proposed two-step selenization with post gallium diffusion treatment. The green color curve denotes that the selenization is performed with selenium vapor source (from point A to point D), and the red color curve denotes with both selenium and gallium sources for PGD treatment (from point B to point C). (b) The structure of fabricated CIGSe cells for J-V characteristics.

the fabricated cell. The morphology of resulting CIGSe thin films was measured by field emission scanning electron microscopy (FESEM, Model JSM-6500F, JEOL). The crystalline phases were characterized using high-resolution X-ray diffractometer (XRD, Model Bede D1) system. Cu Kα radiation (wavelength = 1.54 Å) was used for the X-ray source and the incident angle was fixed at the angle of 1°. Atomic concentration depth profiling of elements (Cu, In, Ga, Se, and Mo) were obtained by Auger electron spectroscopy (AES, Model PHI 700, ULVAC). J-V characteristics of all fabricated cells were measured using a solar simulator at one sun illumination of 100 mW/cm^2 with AM 1.5G spectrum (Oriel class A, 91160A, Newport Co.).

Fig. 2(a) shows the top-view SEM image of surface morphology for the CIGSe film prepared by the proposed selenization with PGD for 5 min. The absorber exhibited dense, highly compact, and large-grained crystallization. The AES analysis, as shown in Fig. 2(b), revealed double-graded distribution of Ga/(In + Ga) ratios through the bulk of film. A significant increase of gallium concentration near the surface was contributed by the effect of PGD at the end of selenization procedure. It was noticed that the incorporating and alloying of gallium into CIGSe lattice should be accomplished before cooling down of the sample. Fig. 2(c) depicts the corresponding energy bandgap of the CIGSe absorber calculated from the Ga/(In + Ga) ratio.[13] This double-graded bandgap, contributed by PGD treatment, showed 1.19 eV in the gradient valley, and of 1.31 and 1.39 eV near the surface and bottom of CIGSe thin film, respectively.

The CIGSe thin film deposited by a conventional selenization method exhibited normal grading of Ga/(In + Ga) profile; nevertheless, for the effects of PGD treatment the resulting CIGSe showed double-graded gallium profile via the increase of gallium concentration near the surface, as depicted in Fig. 3. Marudachalam *et al.*[6] have demonstrated that gallium diffused towards the bottom side of absorber films during selenization process, which resulted in low gallium concentration and low energy bandgap in the SCR to degrade its cell efficiency. For the samples with PGD treatment, significant increases of Ga/(In + Ga) ratio were obtained, as well as the construction of gradient valleys (see blue and red curves in Fig. 3). It was observed that the overall Ga/(In + Ga) ratio in the CIGSe thin film with PGD for 8 min is higher than that of 5 min, while almost similar ratios of ~50% near the surface.

In CIGSe films, indium can be replaced by gallium in the CISe lattice to increase energy bandgap. The bandgap of $Cu(In_{1-x}Ga_x)Se_2$ is increased by

$$E_g(x) = (1-x)E_g(CISe) + xE_g(CGSe) - bx(1-x),$$

with a bowing coefficient (b) of 0.15 eV for $Cu(In_{1-x}Ga_x)Se_2$ thin films.[14] The bandgap of CISe and CGSe is E_g(CISe) = 1.04 eV and E_g(CGSe) = 1.68 eV, respectively.[15] The energy bandgap in the SCR near the surface of CIGSe absorber was therefore increased from 1.14 eV (x = 0.20) to 1.31 eV (x = 0.48) after employing the PGD treatment of 5 min. Schleussner *et al.*[16] have demonstrated that the increased bandgap in the SCR benefits V_{OC} via reducing the carrier recombination at the p-n junction. The gallium contents increased from the gradient valley towards the back contact induce a back-surface field (BSF) in the conduction band that reduces the recombination at the contact. However, too high bandgap in bulk of absorbers

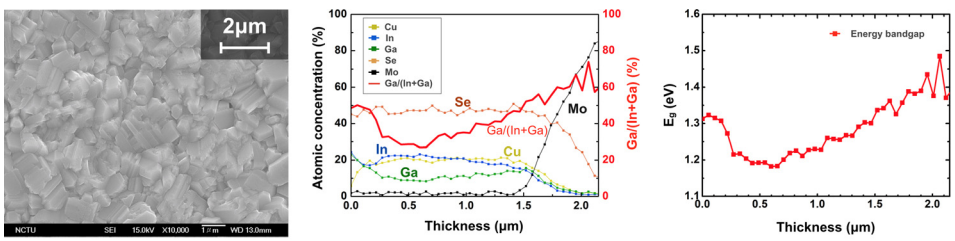

FIG. 2. Characteristics for the CIGSe thin film prepared by proposed selenization process with the effect of post gallium diffusion for 5 min. (a) Top-view SEM micrograph, (b) in-depth atomic concentration (left axis) examined by AES analysis and the calculated profile of Ga/(In + Ga) ratios (right axis), and (c) double-graded bandgap distribution with an elevated bandgap (E_g) of ~1.31 eV near the surface.

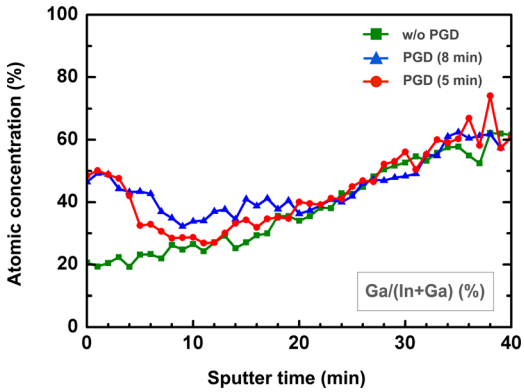

FIG. 3. In-depth AES analyses for Ga/(In + Ga) compositional ratios of resulting CIGSe thin films without and with the PGD treatment for 5 and 8 min, respectively.

exhibits detrimental impacts in photon absorption in long-wavelength regions, and a rapid or wide gallium gradient near the surface is known as a barrier for electron diffusion towards the junction.[13] Thus, we demonstrated the effects of PGD treatment for 5 and 8 min on the gallium gradients near the surface. A photocurrent improvement can be expected of the sample with PGD for 5 min since it revealed lower average bandgap in the absorber than that of 8 min.

The effect of PGD that leads to the enhanced surface energy bandgap of CIGSe absorber was characterized by XRD analysis, as shown in Fig. 4. The crystalline phase near the surface can be examined by the Grazing Incident X-ray Diffraction (GIXRD) analysis with 1° incident angle.[17] For all samples, the position of the signal reflections was compared to the powder-diffraction standard data (JCPDS) for $CuIn_{0.7}Ga_{0.3}Se_2$ and $CuInSe_2$.[18] As shown in Fig. 4(a), the dominant peaks of $CuIn_{0.7}Ga_{0.3}Se_2$ chalcopyrite phase of (112) and (220/204) preferred orientations are typically observed at 26.92° and 44.68°, respectively.[19] The XRD patterns of all CIGSe absorbers revealed pure CIGSe crystalline phase [shown in Fig. 4(a)], and there is no noticeable change after performing PGD treatment. As the peaks of (112)-orientation of $CuInSe_2$ and $CuIn_{0.7}Ga_{0.3}Se_2$ phases are located at 26.62° and 26.92°, respectively, XRD analysis is a method to identify the Ga/(In + Ga) ratio of CIGSe absorber films.[20] A blue shift of XRD peak can be observed as the increase of Ga/(In + Ga) ratio (x) of $CuIn_{1-x}Ga_xSe_2$ phase, indicating more gallium incorporated into the CIGSe lattice. The XRD patterns in the region of (112)-orientation, as depicted in Fig. 4(b), revealed more evidence that PGD treatment has alloyed gallium into the lattice of resulting film, instead just deposited on it. The absorber fabricated by the selenization with PGD treatment for 5 and 8 min revealed respective peaks of 27.01° and 27.03°, while that prepared without PGD was 26.78°. It is clearly evident that employing PGD treatment contributes to the bandgap modification of absorber film as gallium incorporation.

The effects of PGD treatment on the photovoltaic performances of CIGSe solar cells were evaluated by J-V characteristic measurement, as depicted in Fig. 5. The cell efficiency of 13.2% was achieved via a significant improvement of V_{OC} by introducing the PGD treatment for 5 min. However, the cell fabricated from the absorber without PGD treatment showed the efficiency of 9.2%, while V_{OC} and J_{SC} were of 0.49 V and 30.8 mA/cm^2, respectively, which agreed with the results of normal grading bandgap reported.[14,21] To further enhance the electrical performance, it was expected that an elevated bandgap in the SCR could increase V_{OC} and hence improve cell efficiency as the reduction of dominant recombination at the CdS/CIGSe interface.[4,22] For the samples with PGD treatment for 5 and 8 min, noticeable V_{OC} increases of 0.66 and 0.68 eV were observed, respectively; nevertheless, the increased bandgap of overall absorber films accompanied a degradation of J_{SC}. The photocurrent is strongly related to the bandgap value in the valley of double-graded distribution. A higher J_{SC} of 29.9 mA/cm^2 (5 min for PGD) was obtained in comparison to that of 26.7 mA/cm^2 (8 min for PGD), implying that lower average bandgap in the absorber increases the photon absorption. The efficiency of fabricated cells without PGD treatment was 9.2% and could be improved to 12.4% and 13.2% after employing the PGD for 8 and 5 min, respectively. In summary, the increase of V_{OC} was contributed by the elevated bandgap in the SCR, and J_{SC} loss was hence compensated by the reduction of average bandgap values in CIGSe absorber (in the case of PGD for 5 min). Consequently, the double-graded bandgap distribution, consisting of a normal grading towards the back contact and an elevated bandgap in the SCR, can improve V_{OC} at an expense of small reduction in J_{SC}.[16,23]

The photovoltaic performance of CIGSe solar cells, fabricated by the selenization process with proposed PGD treatment, exhibited substantial improvement of V_{OC} and conversion efficiency. This study explored the enhancement for electrical properties via double-graded bandgap distribution in the CIGSe absorbers under selenization-based

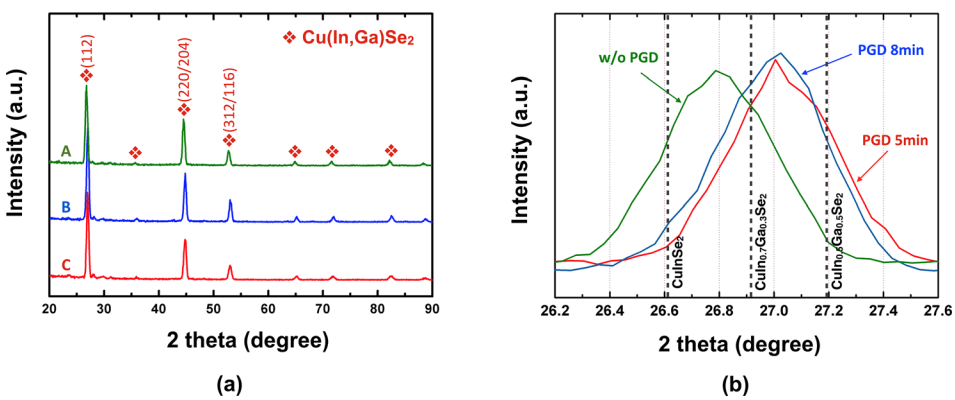

FIG. 4. (a) XRD scans for the surface of CIGSe absorbers without (curve A) and with the post gallium diffusion for 8 (curve B) and 5 (curve C) min. (b) The peaks of (112)-orientation CIGSe chalcopyrite phase for the curves A, B, and C.

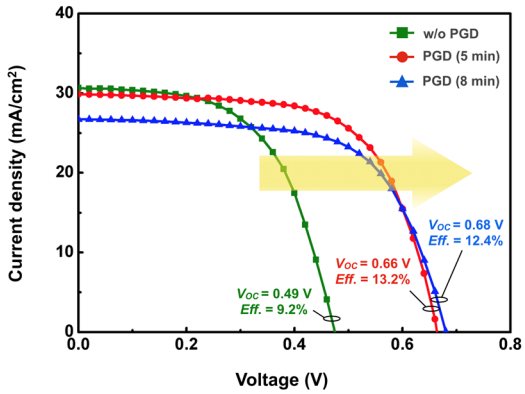

FIG. 5. J-V characteristic of the fabricated solar cells with the CIGSe absorber films prepared by the selenization process without and with the PGD for 5 and 8 min, respectively.

fabrication. Moreover, it should be noticed the highly toxic H_2Se and H_2S materials, extensively used to obtain the modified bandgap distribution to increase cell efficiency, were excluded in this process. For the sample with PGD treatment for 5 min, the increased energy bandgap in the SCR (from 1.14 to 1.31 eV) has been demonstrated to improve V_{OC} by 35% (from 0.49 to 0.66 V) and cell efficiency by 43% (from 9.2% to 13.2%), at the expense of a drop in J_{SC} (from 30.8 to 29.9 mA/cm^2). On the other hand, the sample with PGD for 5 min revealed a photocurrent enhancement (from 26.7 to 29.9 mA/cm^2) in comparison to that of 8 min by the reduction of average bandgap near the surface of absorber. It is expected that the photocurrent loss can be compensated and improved by optimizing the energy bandgap in the SCR and the bulk of CIGSe thin film. This low toxicity selenization process can potentially improve CIGSe solar cell performances and its manufacturing feasibility.

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