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Improvement of bandgap homogeneity in Cu(In,Ga)Se$_2$ thin films using a modified two-step selenization process

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A modified two-step selenization has been demonstrated to overcome inhomogeneous gallium distribution, an issue to lower energy bandgap in the space-charge region as well as cell efficiency. It was found that incorporating selenium into conventional precursors could accelerate the formation of CuInGaSe$_2$ phase in the selenization to accordingly suppress the diffusion effect of gallium. By introducing a pre-heating treatment, this selenization enhanced the bandgap distribution with a back-surface field and an increase of bandgap in the space-charge region, consequently improving open circuit voltage (V$_{OC}$) by 25% and cell efficiency by 55%, respectively. © *2013 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4824762]

Polycrystalline CuInGaSe$_2$ (CIGSe) thin film has been demonstrated as a promising material for high efficiency solar cell applications.[1–4] Wei *et al.*[5–7] have reported that energy bandgap and open circuit voltage (V$_{OC}$) increase according to the ratio of Ga/(In + Ga) through absorbers. A CIGSe absorber with high gallium contents in the space-charge region can reduce the carrier recombination and improve V$_{OC}$. The selenization of sputtered CuInGa precursors has emerged as a large-scale process to fabricate CIGSe thin films for industrial manufacturing.[8–10] However, a critical issue of elemental interdiffusion during selenization process results in longitudinal inhomogeneity in CIGSe phase and low gallium contents in the space-charge region, consequently restricting conversion efficiency.[8,9,11] The highly toxic H$_2$Se material is a reactive material to empirically suppress the inhomogeneity of CIGSe crystallization.[8,12,13] However, this study addresses a two-step selenization method to improve the bandgap homogeneity by controlling gallium diffusion effects. Introducing a pre-heating treatment to incorporate selenium into conventional precursors accordingly accelerates the formation of chalcopyrite phase and benefits CuInGaSe$_2$ crystallization near the surface of absorbers. The bandgap in the space-charge region was substantially increased, consequently improving V$_{OC}$ by 25% and efficiency by 55%. Surface free energy, elementary interdiffusion coefficient, and reaction kinetics of chalcopyrite phase are discussed. It is worth mentioning that proposed selenization is a safe process by substituting selenium vapors for toxic H$_2$Se gas.

CIGSe absorber films were prepared by a conventional and a two-step selenization (depicted in Fig. 1), respectively, of stacked selenium and CuInGa (Se/CuInGa) precursor films. Cu$_{0.7}$Ga$_{0.3}$ alloy and Cu$_{0.2}$In$_{0.8}$ targets were utilized as sputtering sources to prepare 0.6-μm-thick CuInGa precursors on 1-μm-thick Mo-coated soda-lime glass substrates, and selenium pellets were thermal evaporated to deposit a 1-μm-thick selenium layer on CuInGa precursors. The atomic compositions of CuInGa precursors were confirmed to be the

ratios of Cu/(In + Ga) = 0.92 and Ga/(In + Ga) = 0.28, respectively. A conventional selenization process was utilized to fabricate CIGSe absorbers by heating the Se/CuInGa films for about 60 min at 350 °C in the first-stage and 550 °C in the second-stage.[7]

The proposed two-step selenization consists of a low-temperature pre-heating treatment (Step I) and subsequent annealing (Step II). Prior to the selenization process, 1-μm-thick selenium film was coated on CuInGa precursors. The pre-heating treatment in Step I, heating the stacked Se/CuInGa layers, is to incorporate selenium into the CuInGa precursors before the annealing (Step II) and recrystallization for CIGSe phase. It should be mentioned that pre-heating was carried out at the pressure of about 700 Torr by introducing Ar gas flow. The effect of pre-heating on selenium diffusion of the Se/CuInGa layers at 130 °C and 200 °C was examined, respectively. Additionally, the annealing (Step II) was performed by supplying a constant selenium vapor flow of about 15 Å/s rate on the pre-heated Se/CuInGa films that were heated to about 350 °C and 550 °C in succession for the formation of CIGSe phase. The duration of two-step selenization procedure is 60 min for pre-heating (Step I) and 60 min for annealing (Step II), respectively. Phase of CIGSe films was observed by a high-resolution x-ray diffraction (XRD) system with CuKα (k = 1.54) radiation. ULVAC PHI 700 Auger electron microscope (AES) operating at 10 KV was used to measure compositional depth profiles of all films. The effect of selenium contents on gallium homogeneity was examined by AES, XRD, and SEM analyses for pre-heated Se/CuInGa layers and its resulting CIGSe films, respectively.

AES analysis for respective Se/CuInGa layers without and with pre-heating at 130 °C and 200 °C revealed that more selenium diffused into the CuInGa layer as a result of pre-heating temperature increase, as shown in Fig. 2(a). On the other hand, the Se/CuInGa film pre-heated at 200 °C exhibited high gallium concentration near the bottom and low near the surface significantly in comparison to both as-deposited one and after pre-heated at 130 °C, as shown in

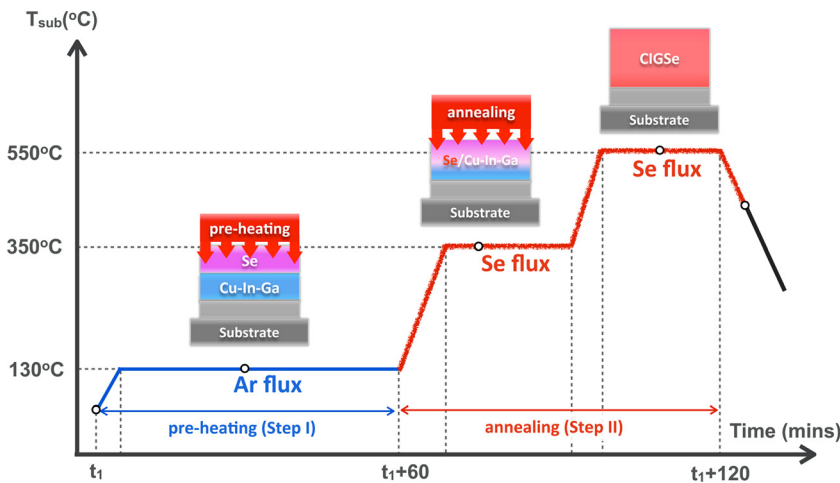a)E-mail: easonwang.eo98g@g2.nctu.edu.tw. Tel.: 886-3-5712121 ext. 59456

FIG. 1. Scheme of the proposed two-step selenization process.

Fig. 2(b). Gallium has diffused to the bottom of the film pre-heated at 200 °C; namely, inhomogeneous gallium distribution was being induced as the Se/CuInGa film was heated at 200 °C. After pre-heating at respective temperatures, the resulted Se/CuInGa films were subsequently annealed in Step II for the recrystallization of CIGSe phase. The comparison of Ga/(In + Ga) ratios for all CIGSe films is plotted in Fig. 2(c). The film, prepared by the conventional selenization without pre-heating, showed low gallium contents in the bulk regions and dramatic increase near the bottom. It was suggested that inhomogeneous chalcopyrite phases were segregated in the film, resulting low conversion efficiency (5.35% in this case). On the other hand, the film prepared by two-step selenization with 130 °C pre-heating exhibited homogeneous gallium distribution; the gallium, however, slightly accumulated near the bottom in the case of pre-heating at 200 °C, attributed to gallium movement in the Se/CuInGa film after pre-heated at 200 °C [see red curve in Fig. 2(b)]. The ratio of Ga/(In + Ga) was, respectively, improved to about 20% and 12% in the space-charge region of the absorber fabricated by the two-step selenization with pre-heating at 130 °C and 200 °C, and of less than 7% in the absorber prepared by the conventional selenization. In CIGSe films, indium is replaced by gallium in the $CuInSe_2$ (CISe) lattice to increase the bandgap from 1.04 eV to 1.68 eV. 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.[8] The bandgap of $CuInSe_2$ and $CuInGaSe_2$ is $E_g(CISe) = 1.04$ eV and $E_g(CIGSe) = 1.68$ eV, respectively.[12] The energy bandgap in the space-charge region near the surface of CIGSe absorber prepared by the two-step selenization with pre-heating at 130 °C was calculated to be 1.14 eV (x = 0.2), while that prepared by the conventional selenization was 1.08 eV (x = 0.07). Fig. 3(a) is the SEM images of both cross-sectional and top-view analyses for the CIGSe film fabricated by two-step selenization with pre-heating at 130 °C. The absorber exhibited smooth morphology in surface and large-grains in crystallization. AES analysis revealed slight-graded in-depth distribution of gallium through the CIGSe absorber, as shown in Fig. 3(b). On the other hand,

Fig. 3(c) shows the corresponding energy bandgap of the absorber calculated from the in-depth Ga/(In + Ga) ratio.[14] It should be noted that a normal-graded bandgap ranged from 1.14 to 1.28 eV through the absorber was contributed by employing the pre-heating treatment. The open circuit voltage (V_{OC}) and cell efficiency significantly depend on the bandgap in the space-charge region.[8]

The crystallization of CIGSe phase, carried out by XRD scans, exhibited that pre-heating treatment enhanced the chalcogenic CIGSe phase near the surface of absorbers, as shown in Fig. 4. CIGSe phase near the surface was examined
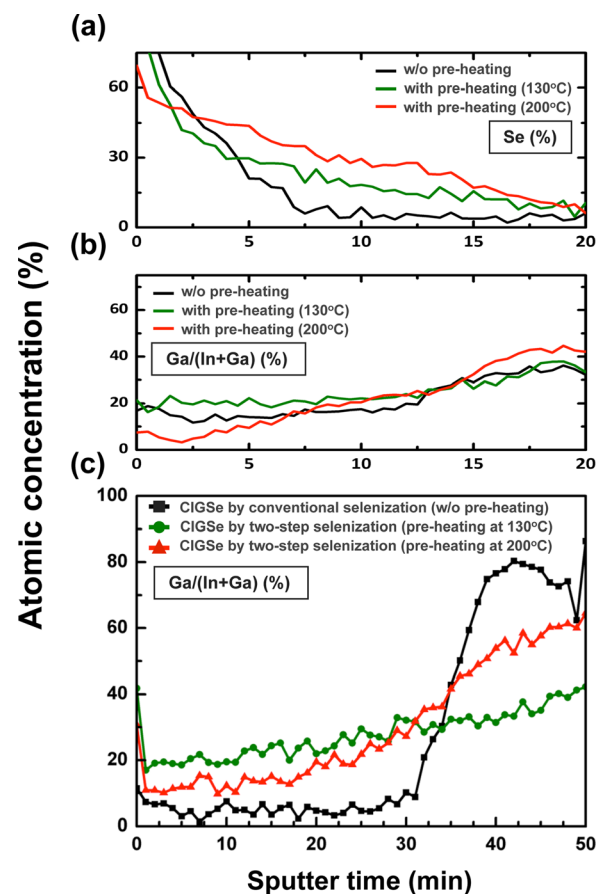

FIG. 2. In-depth distributions of (a) Se and (b) Ga/(In + Ga) for stacked Se/CuInGa layers with and without pre-heating, and (c) Ga/(In + Ga) for CIGSe absorbers after selenization.
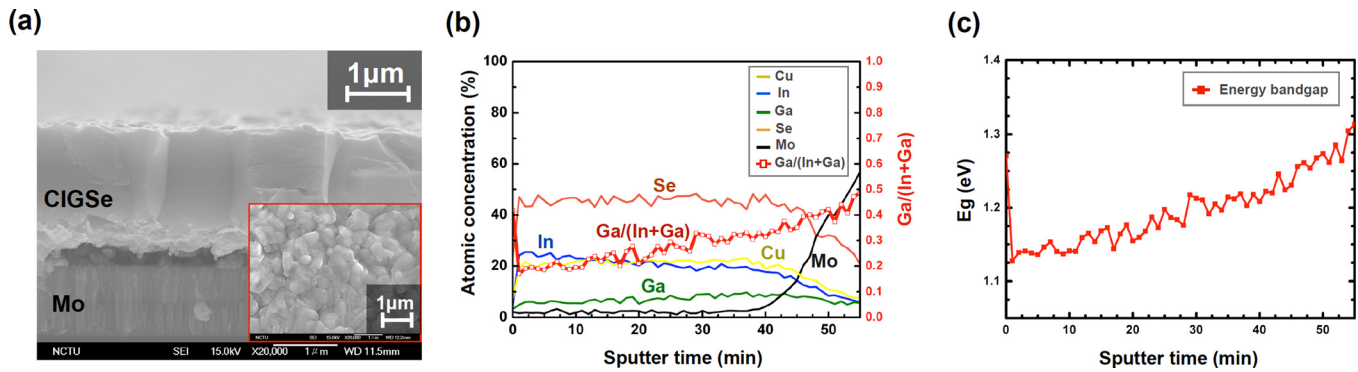
FIG. 3. Characterization for the CuInGaSe$_2$ thin film prepared by two-step selenization with the effect of pre-heating at 130 °C. (a) Cross-sectional and top-view (see inset) SEM micrographs. (b) In-depth atomic concentration (left axis) measured by AES analysis and calculated Ga/(In + Ga) ratio profile (right axis). (c) Bandgap distribution with an enhanced energy bandgap (E$_g$) ∼1.14 eV near the surface.

by the Grazing Incident X-ray Diffraction (GIXRD) analysis with 1° incident angle. For each sample, the position of the x-ray reflections was compared with the powder-diffraction standard data (JCPDS) for CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ and CuInSe$_2$. The peaks of (112)- and (220/204)-orientation are typically observed in CIGSe absorber films.[15,16] The absorbers prepared by proposed two-step selenization with the effect of pre-heating (Step I) at 130 °C and 200 °C revealed respective (112)-orientation peaks of 26.82° and 26.74°, while the peak of the film prepared by the conventional selenization was 26.65°. This blue shift was attributed to the increase of gallium concentration near the surface that enhances the replacement of gallium in the CISe lattice. On the other hand, the peak at 30.9° revealed CISe phase in the film prepared by conventional selenization, attributed to low gallium contents near the surface. In addition, the (112) peaks were close to 26.91° in the XRD patterns of 5° incident angle, indicating that the phase of CuIn$_{0.7}$Ga$_{0.3}$Se$_2$ was obtained in the bulk regions of all films. Consequently, the proposed two-step selenization with the effect of pre-heating contributed to the homogeneity of gallium distribution through CIGSe absorbers.

Increasing selenium concentration accelerates the formation of CIS-based chalcopyrite phase and suppresses gallium diffusion effects in selenization. Marudachalam et al.[11] have reported that the formation temperature of CIGSe is relatively higher than that of CISe, and the CISe phase forms much faster than CuGaSe$_2$ (CGSe) phase. Moreover, the reaction kinetics in terms of activation energy of CISe phase

(∼124 KJ/mol), given by the Avrami model, is lower in comparison to that of CIGSe (∼144 KJ/mol).[17] CISe phase has lower surface free energy than CGSe. Therefore, there is a tendency for the CISe to segregate towards the surface, implying that CISe phase is preferentially formed relative to CIGSe, and gallium diffuses towards the bottom through grain boundaries or selenium vacancies in the selenization of CuInGa precursors.[10,11] Moreover, the interdiffusion coefficient of gallium (D$_{Ga}$ = 4.0 × 10^{-11} cm^2/s) was reported to be higher than that of indium (D$_{In}$ = 1.5 × 10^{-11} cm^2/s) in CIGSe films at 650 °C.[11] The presence of selenium vacancies, which easily occur in the films prepared by selenization from selenium vapors, critically contribute to gallium accumulation near the bottom of absorber.[5,11] In summary, the increase of selenium contents in the CuInGa precursors can accelerate the formation of CIGSe phase in selenization and further enhance homogeneous crystallization, agreed with our experimental results.

The J-V measurement, shown in Fig. 5, revealed that the conversion efficiency of the CIGSe device fabricated by proposed two-step selenization with pre-heating at 130 °C was higher than that of conventional one (an improvement from 5.35% to 8.27%). A dominant recombination against the cell efficiency was suppressed by increasing the barrier height via the increase of bandgap in the space-charge region, benefiting the open circuit voltage.[18,19] The increase of the bandgap should decrease the absorption of the long wavelength light; however, a back-surface field (BSF) improved the short-circuit current (J$_{SC}$), contributed by the normal
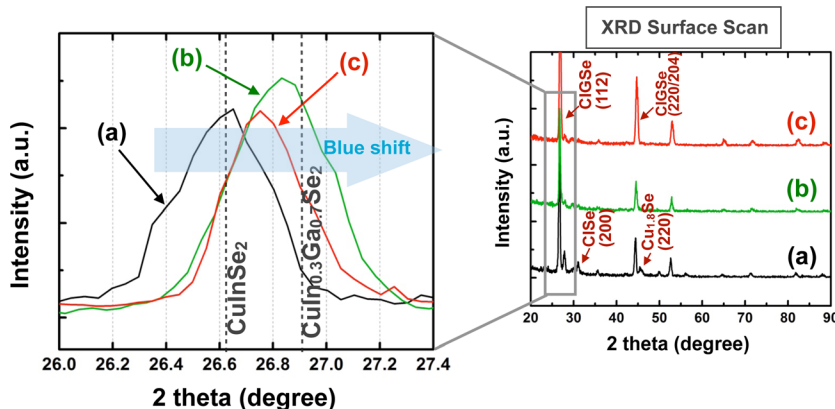

FIG. 4. XRD scans for the surface of CuInGaSe$_2$ films prepared by (a) the conventional (without pre-heating) and proposed two-step selenization process with the effect of pre-heating at (b) 130 °C and (c) 200 °C.
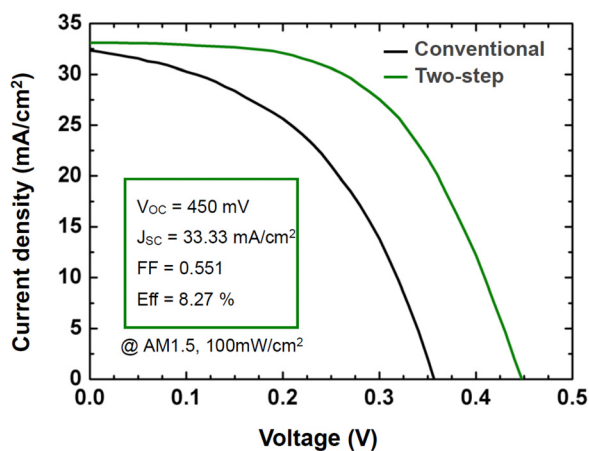
FIG. 5. J-V characteristic of solar devices with the CIGSe absorber prepared by the conventional (without pre-heating) and two-step selenization (with pre-heating treatment at 130 °C).

grading of bandgap [shown in Fig. 3(c)].[19] It was concluded that the bandgap in the space-charge region was improved from 1.08 to 1.14 eV by employing proposed two-step selenization, and V_{OC} was substantially increased from 360 mV to 450 mV.

This work presents a modified selenization to improve V_{OC} and device efficiency with a safe fabrication process by the substitution of selenium vapors for toxic H_2Se gas. As CISe is more preferentially formed than CIGSe, gallium tends to diffuse towards the bottom of films during conventional selenization, resulting in inhomogeneous bandgap distribution. Consequently, incorporating selenium into conventional CuInGa precursors effectively accelerated the formation of CIGSe chalcopyrite phase to suppress the inter-diffusion of gallium. The absorber with a normal-graded gallium distribution and homogeneous CIGSe crystallization was demonstrated. The increased energy bandgap (from 1.08

to 1.14 eV) in the space-charge region accordingly improved V_{OC} from 360 mV to 450 mV and efficiency enhancement by 55%.

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