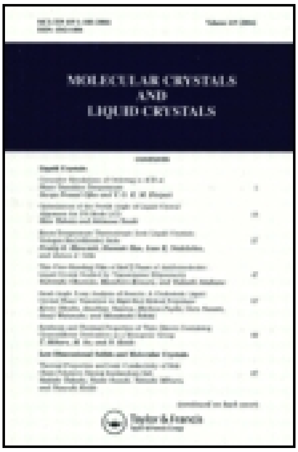

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Property of $Cu(In,Ga)Se_2$ Absorption Layer Produced using a Proximity Selenization Method

Sang-Hwan Lee [a], Eun-Woo Lee [b], Yun-Su Lee [b], Bo-Sung Kim [c], Sang-Wook Park [d] & Chan-Wook Jeon [d]

[a] Doosan Corporation, Electro-Materials, Development 1 Team, Gyeonggi-Do, Korea

[b] Advanced Display Manufacturing Research Center., Kyungpook National University, Daegu, Korea

[c] Mobile Display Research Center, Kyungpook National University, Daegu, Korea

[d] Department of Chemical Engineering and Technology, Yeungnam University, Gyeongsan, Korea

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Property of $Cu(In,Ga)Se_2$ Absorption Layer Produced using a Proximity Selenization Method

SANG-HWAN LEE,[1] EUN-WOO LEE,[2] YUN-SU LEE,[2]
BO-SUNG KIM,[3] SANG-WOOK PARK,[4]
AND CHAN-WOOK JEON[4,*]

[1]Doosan Corporation, Electro-Materials, Development 1 Team, Gyeonggi-Do, Korea
[2]Advanced Display Manufacturing Research Center., Kyungpook National University, Daegu, Korea
[3]Mobile Display Research Center, Kyungpook National University, Daegu, Korea
[4]Department of Chemical Engineering and Technology, Yeungnam University, Gyeongsan, Korea

$Cu(In,Ga)Se_2$ thin films were prepared using co-sputtering and proximity selenization. This new method supplies Se by closely attaching opposite a metal precursor. $CuInSe_2$ thin film was produced at 280°C, and consisted of small structures. As the temperature was increased, more Ga was substituted in place of In, while the X-ray peak of the $CuInSe_2$ shifted to the right. A thin film with a Cu:In:Ga:Se ratio of 1:0.7:0.3:2 was obtained at 480°C, which is comparatively lower than the temperature needed when using Se vapor. This grew into crystals with a diameter of 3–5 μm.

Keywords CIGS; photovoltaic; thin film solar cell; selenization; metal precursor; sputtering

Introduction

Solar cells based on the Cu(In,Ga)Se2 (CIGS) compound semiconductor have recorded the highest conversion efficiency among thin film solar cells technologies. Many processes to synthesize high quality CIGS absorber have been suggested including vacuum methods such as the co-evaporation method and sputtering/selenization and non-vacuum methods such as the nano-powder method, electro-deposition and solution method [1–4]. So far, vacuum methods are known to have higher perfection for mass production technology. Especially, the 2-step process consisted of the precursor deposition and subsequent thermal processing under the selenium atmosphere, has been known for its advantage in producing large area modules. The selenization process normally uses H_2Se gas due to very high reactivity, however, its severe toxicity and corrosiveness requires additional safety facilities. While the use of Se vapor evaporated from elemental Se source is relatively free from the safety

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[*] Address correspondence to Chan-Wook Jeon, Department of Chemical Engineering and Technology, Yeungnam University, Dae-dong, Gyeongsan-si, Gyeongbuk 712-749, Korea (ROK). Tel.: (+82)53-810-2513; Fax: (+82)53-810-4631. E-mail: cwjeon@ynu.ac.kr

issue, it suffers from the difficulty of uniform supply and low reactivity. In this paper, a new Se supply method named "proximity selenization" is proposed as an alternative to existing methodologies. In proximity selenization, Se-covered glass is laid tightly against a metal precursor. This method is designed to provide uniform Se flux over a large area.

Experimental

Fabrication of Cu(In,Ga)Se_2 Absorber

The Cu-In-Ga metal precursor were prepared on Mo coated glass at room temperature by rf-dc magnetron co-sputtering system equipped with a tilted sputter gun. The pure In and CuGa (Ga, 24wt%) dual targets of 3 inch diameter and 3 mm thickness were used. The base pressure was 1×10^{-6} torr, and working pressure was maintained at 1 mtorr. The substrate was rotated at 10 rpm for better uniformity of film thickness. The Se film were prepared on glass at room temperature by evaporator. The Cu-In-Ga metal precursor and the selenium were laid face-side together and selenized using a two-zone furnace. The precursor was annealed at temperatures varying between 280 and 580°C. Once the target temperature was reached, it was maintained for 60 minutes. After annealing, the thin film was placed in a KCN solution consisting of 0.5 g KCN and 50 g D.I. water and etched over a period of one minute.

Measurements

The thickness of Cu-In-Ga metal precursor and Se film was measured from the a-step, and the crystalline properties were characterized by X-ray diffractometer (PANalytical, Cu-Ka = 1.54178 A). The surface and cross sectional morphology of each film was analysed at acceleration voltage of 5 kV by scanning electron measurement (Hitachi, s-4800). The composition of metal precursor were calculated from inductively coupled plasma atomic emission spectroscopy(ICP-AES, ICPS-8100, SHIMADZU).

Results and Discussion

Figure 1 shows the pre- and post-etching SEM images of the CIGS thin film selenized at 280°C. KCN solutions are typically known to be effective in removing secondary phases [5]. Upon completing selenization, a thick film of indiscernible shape was observed on the surface, while small grains were found distributed across the bottom layer. After KCN etching, the thick amorphous film on the upper layer could no longer be seen, but the small grains below as well as the relatively larger grains, which had been observed as protrusions in the upper layer prior to KCN etching, were left unremoved.

From the XRD curve of the thin film selenized at 280°C, it could be seen that the CuSe peak, which had been detected strongly at 31.3° before KCN etching, was almost completely eliminated after etching (Fig. 2). Prior to KCN etching, a broad X-ray curve was obtained between 20° and 35°; this is a situation that occurs when amorphous selenium is deposited [6,7]. However, KCN etching only affects the surface, leaving the secondary phases inside the thin film unremoved. This means that the peaks of the secondary phases can still be detected. The peaks at 26.6°, 44.3°, and 52.4° showed no changes in intensity even after KCN etching; these peaks are generally known to be (112), (220), and (312) crystal peaks of $CuInSe_2$. Because the selenium was attached closely to the metal precursor in thin film form, more of it was diffused into the precursor or involved in the reaction than

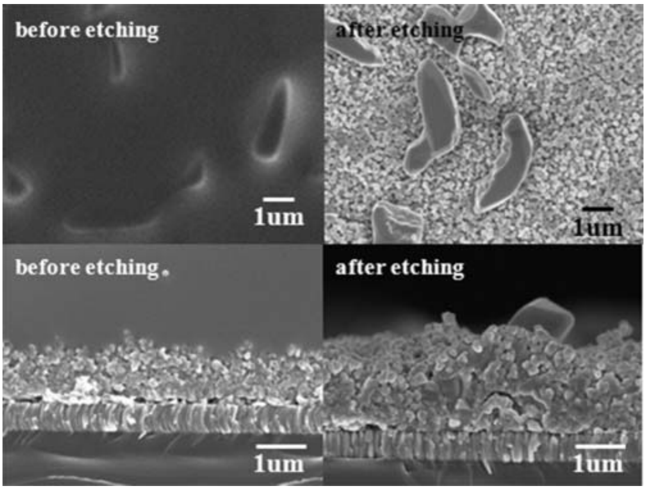

Figure 1. SEM morphology of the selenized thin film before and after KCN treatment.

was lost externally. As can be seen in the phase diagram of In_2Se_3-Cu_2Se, it is sufficiently possible to acquire the $CuInSe_2$ phase at 280°C [8].

Figure 3 shows the surface and cross section SEM images of thin films selenized at various temperatures. All of the thick, amorphous selenium that was present at 280°C took part in the reaction and grew into large structures. Large plate crystals of hexagonal shape existed on the surface; these are CuSe crystals, which take a hexagonal structure. Small grains that did not take part in the reaction were distributed between the $CuInSe_2$ and Mo, which were slightly detached due to insufficient junction with the lower layer. At a temperature of 480°C and higher, the $Cu(In,Ga)Se_2$ grew into crystals with a diameter of 3–5 μm. No additional changes in crystal size were observed, and there were no gaps at the interface due to good junction with the lower layer. $MoSe_2$ was produced at 380°C, which

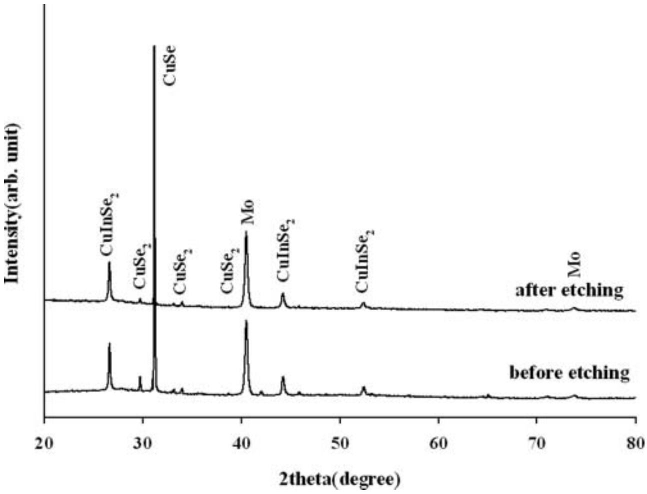

Figure 2. XRD curve of the selenized thin film before and after KCN treatment.

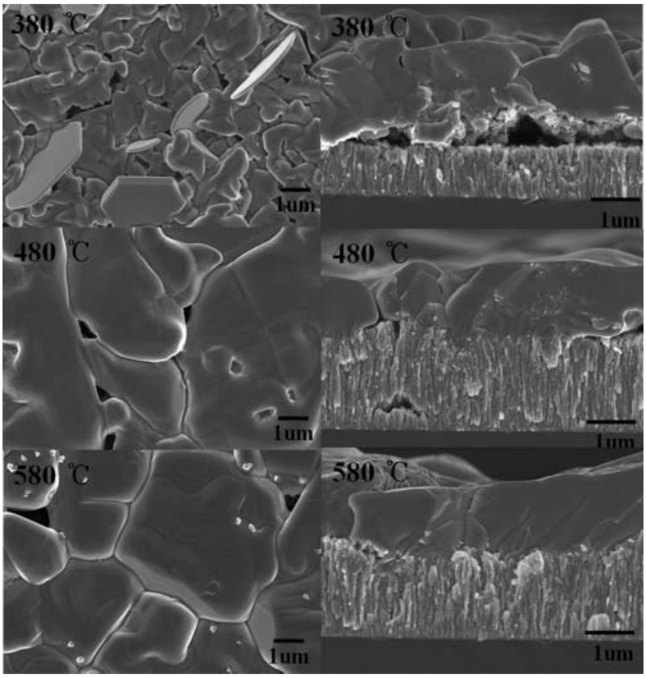

Figure 3. surface and cross section SEM morphology as a variety annealed temperature.

is lower than the generally reported temperature, and grew to a thickness of up to 1.5 μm when the temperature was 480°C or higher [9].

Figure 4 shows the X-ray curves of thin films selenized at various temperatures. As could be seen in the 380°C image in Fig. 3, peak of hexagonal CuSe was detected at 31°. At temperatures of 480°C or higher, the CuSe peak could no longer be seen. At all temperatures,

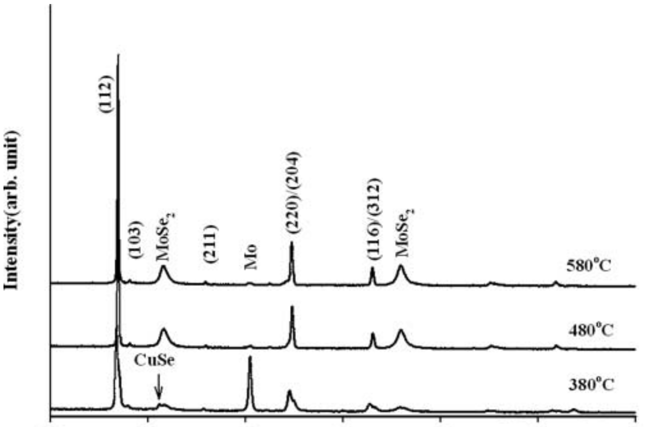

Figure 4. XRD curve as a variety annealed temperature.

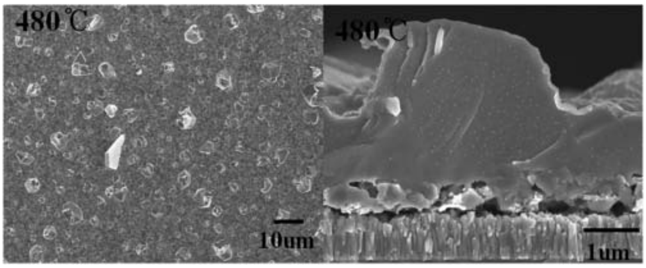

Figure 5. SEM morphology of selenized thin film using Se vapor.

the Cu(In,Ga)Se_2 phase had a preferred orientation toward (112). In the case of the thin film selenized at 380°C, the Cu(In,Ga)Se_2 peak appeared more to the left than in the case of high temperature selenized thin film. The higher the temperature of selenization, the more active intermixing becomes. This leads to an increase in the amount of In substituted by Ga. Because Ga has a smaller atom, the interface distance becomes smaller, which in turn enlarges the angle of x-ray diffraction. Due to this situation, the X-ray peak moved toward the right, and ultimately achieved a chalcopyrite crystal structure with a composition of $Cu_1In_{0.7}Ga_{0.3}Se_2$ [10]. At 380°C, FWHM (Full Width at Half Maximum) was 0.2598°; at 480°C and 580°C, it was 0.1948°, showing improved crystallinity. When the temperature was 480°C or higher, no additional improvement in crystallinity occurred. The Mo peak seen at 40.5° disappeared as the temperature exceeded 480°C, and, as can be seen at 31.6° and 55.9°, all reaction progressed toward $MoSe_2$.

Figure 5 shows the SEM images of the thin film selenized at 480°C using selenium vapor. Unlike the 480°C SEM image in Fig. 3, hexagonal CuSe secondary phases are present on the surface, which shows a considerable roughness as well. Compared to supplying Se from immediately above, this method did not allow for an efficient supply of Se and thus did not lead to the production of $MoSe_2$, but large pores appeared in the interface with Mo.

Conclusions

In this study, selenium was deposited on a separate glass, and joined closely with a Cu-In-Ga metal precursor for selenization. A $CuIn_{0.7}Ga_{0.3}Se_2$ phase with good crystal growth was obtained at 480°C, which is lower than the generally reported selenization temperature. In this case the crystals measured 3–5 μm in diameter. The Cu(In,Ga)Se_2 had a preferred orientation toward (112), but Se flux became excessively high compared to the method using Se vapor, which led to a thickening of the $MoSe_2$ layer. This problem is expected to be easily resolvable by shortening the selenization time and optimizing the Se thin film thickness. Continued research is needed to devise new low-temperature selenization methods using safe Se sources.

References

[1] Contreras, M. A., Gabor, A. M., Tennant, A. L., Asher, S., Tuttle, J., & Noufi, R. (2007). *Progress in Photovoltaics: Research and Applications*, *2*, 4, 287–292

[2] Palm, J., Probst, V., Stetter, W., Toelle, R., Visbeck, S., Calwer, H., Niesen, T., Vogt, H., Hernandez, O., Wendl, M., & Karg, F. H. (2004). *Thin Solid Films*, *451–452*, 544–551

[3] Friedfeld, R., Raffaelle, R. P., & Mantovani, J. G.(1999). *Solar Energy Materials & Solar Cells*, *58*, 375–385

[4] Basol, B. M. (2000). *Thin Solid Films*, *361–362*, 514–519

[5] Hashimoto, Y., Kohara, N., Negami, T., Nishitani, M., & Wada, T. (1996). *Japanese Journal of Applied Physics*, *35*, 4760–4764

[6] Bandyopadhyay, A. K., & Ming, L. C. (1996). *The American Physical Society, Physical Review B*, *54*, 17

[7] Chandra Shekar, N. V., Yousuf, M., Ch Sahu, P., Mahendran, M., & Govinda Rajan, K. (1993). *Pramana Journal of Physics*, *40*, 5, 367–376

[8] Park, J. S., Dong, Z., Kim, S., & Perepezko, J. H. (2000). *Journal of Applied Physics*, *87*, 8

[9] Nishiwaki, S., Kohara, N., Negami, T., & Wada, T. (1998). *Japanese Journal of Applied Physics*, *37*, L71–L73

[10] Marudachalam, M., Hichri, H., Klenk, R., Birkmire, R. W., Shafarman, W. N., & Schultz, J. M. (1995). *Applied Physics Letter*, *67*, 26