

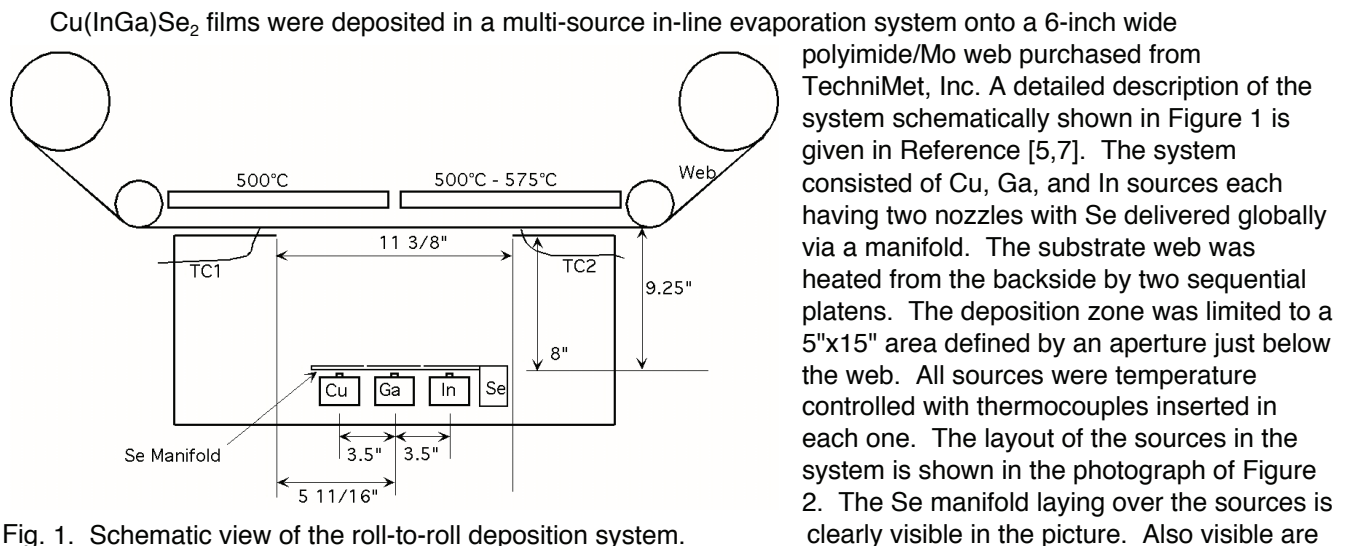
CRITICAL ISSUES FOR $\text{Cu}(\text{InGa})\text{Se}_2$ SOLAR CELLS ON FLEXIBLE POLYMER WEB

Erten Eser, Shannon Fields, William Shafarman, Robert Birkmire
Institute of Energy Conversion
University of Delaware, Newark, DE 19716

Introduction

Elemental in-line evaporation on glass substrates has been a viable process for the large-area manufacture of CuInSe_2 -based photovoltaics, with module efficiencies as high as 12.7% [1]. However, lightweight, flexible CuInSe_2 -based modules are attractive in a number of applications, such as space power sources. In addition, flexible substrates have an inherent advantage in manufacturability in that they can be deposited in a roll-to-roll configuration allowing continuous, high yield, and ultimately lower cost production. As a result, high-temperature polymers have been used as substrates in depositing CuInSe_2 films [2]. Recently, efficiency of 14.1% has been reported for a $\text{Cu}(\text{InGa})\text{Se}_2$ -based solar cell on a polyimide substrate [3]. Both metal foil and polymer webs have been used as substrates for $\text{Cu}(\text{InGa})\text{Se}_2$ -based photovoltaics in a roll-to-roll configuration with reasonable success [4,5]. Both of these substrates do not allow, readily, the incorporation of Na into the $\text{Cu}(\text{InGa})\text{Se}_2$ film which is necessary for high efficiency devices [3]. In addition, polymer substrates, can not be used at temperatures that are optimum for $\text{Cu}(\text{InGa})\text{Se}_2$ deposition. However, unlike metal foils, they are electrically insulating, simplifying monolithically-integrated module fabrication and are not a source of impurities diffusing into the growing film. The Institute of Energy Conversion (IEC) has modified its in-line evaporation system [6] from deposition onto glass substrates to roll-to-roll deposition onto polyimide (PI) film in order to investigate key issues in the deposition of large-area $\text{Cu}(\text{InGa})\text{Se}_2$ films on flexible polymer substrates. This transition presented unexpected challenges that had to be resolved. In this paper, two major problems, spitting from the Cu source and the cracking of Mo back contact film, will be discussed and the solution to each will be presented.

Experimental



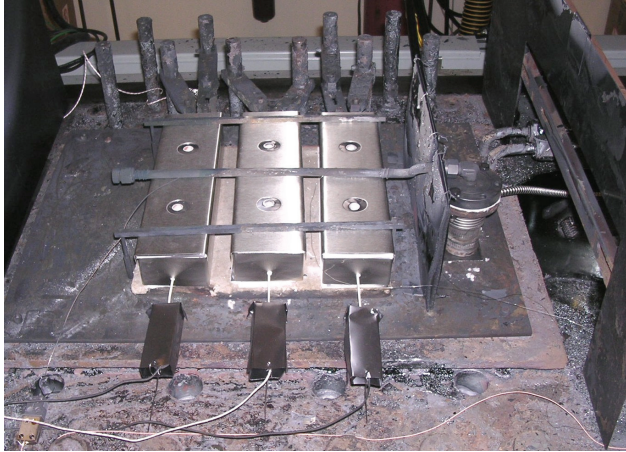


Fig. 2. Evaporation sources in the Cu(InGa)Se_2 deposition system: from left Cu, Ga, In, and Se on the right of the thermal shield.

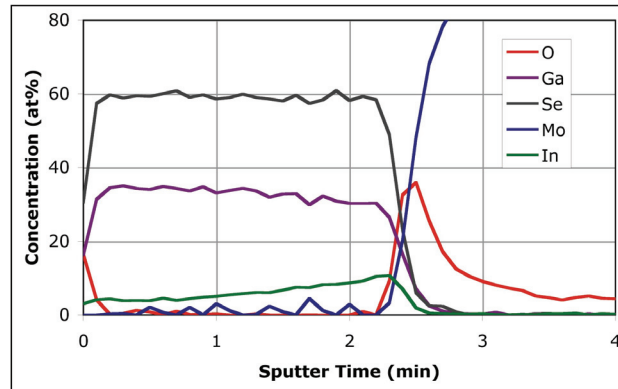


Fig. 3. Auger depth profiling of the 200 Å adhesion promoting layer of $\beta\text{-(Ga}_{0.8}\text{In}_{0.2})_2\text{Se}_3$.

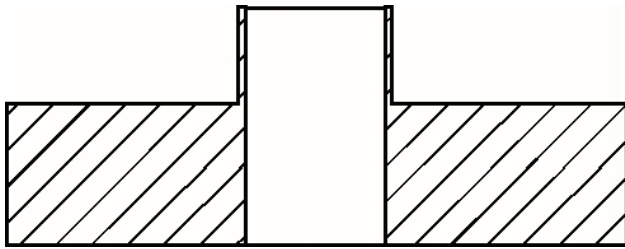
the control thermocouples in the foreground and the power feed-troughs in the back. During the operation, the manifold is heated by the sources to approximately 400°C , which is always higher than the temperature of the Se source, visible on the far right. As a result, no condensation takes place in the manifold. This configuration where sources are placed sequentially, gives, nevertheless, uniform Cu distribution through the thickness of the film due to the high diffusivity of Cu atoms. The distribution of Ga relative to In, however, will change as the film grows. This produces a band gap gradient in the film that can be engineered, giving another level of control in optimizing the performance of the devices based on these films.

The deposition of the Cu(InGa)Se_2 film was performed in two steps. The web was initially coated with an adhesion improving Ga-In-Se film deposited by moving it through In-Ga source sequence at a substrate temperature of approximately 350°C . A 200 Å thick $\beta\text{-(Ga}_{1-x}\text{In}_x)_2\text{Se}_3$ layer, as determined by glancing incidence X-ray diffraction [5,7], is deposited during this step. Auger depth profiling, Figure 3, of this layer gives $x=0.2$. The web was then moved through the Cu-Ga-In source sequence at a speed of $0.75''/\text{min}$. and at a web temperature between 400 to 450°C . This yielded approximately $2.2 \mu\text{m}$ Cu(InGa)Se_2 film in 15 min. ($0.15 \mu\text{m}/\text{min}$). With this source sequence, the Cu(InGa)Se_2 film initially grows Cu-rich, followed by a Cu-deficient growth stage.

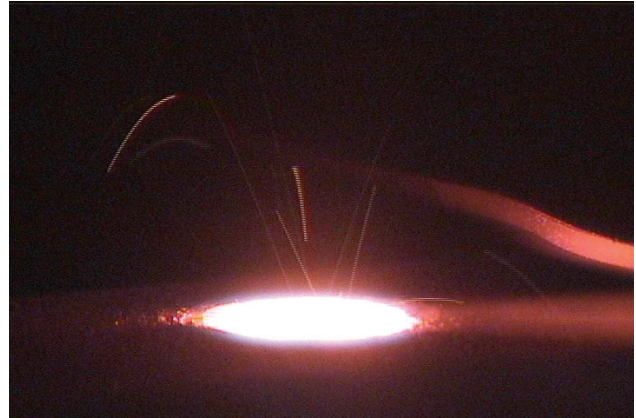
Results

Cu Spitting

The metal evaporation sources are narrow boron nitride boats with a lid having two protruding effusion nozzles. The boats are heated with resistive heater placed near the lid. The nozzle-to-nozzle distance has been determined to give uniform material flux at the substrate web using the evaporation model described previously [7]. Initially, the nozzles were cylindrical and for low deposition rates, the sources performed well. However, at high effusion rates, Cu source showed heavy spitting which was visible, and resulted in Cu inclusions in the Cu(InGa)Se_2 film, ultimately causing shorting of the devices fabricated on the Cu(InGa)Se_2 film. The schematic of this standard nozzle and the photograph of the spitting action at an effusion rate of 2.8 g/hr are shown in Figure 4. The effusion rate, in this case, is equivalent to a Cu(InGa)Se_2 film deposition rate of $0.5 \mu\text{m}/\text{min}$. It was also observed that the spitting was totally suppressed when the effusion nozzle was reduced to a hole on the lid. This observation seemed to indicate that the temperature drop along the nozzle is responsible for the spitting. In order to reduce the temperature gradient, a lid with conical nozzles was designed and fabricated. The conical shape, schematically shown in Figure 5(a), allows more heat flow to the tip and thus reduces the temperature gradient along the internal wall. As can be seen from Figure 5(b) Cu source with conical nozzle lid operated at up to 15 g/hr effusion rate, corresponding to a deposition rate of $2.8 \mu\text{m}/\text{min}$, without any spitting action. The absence

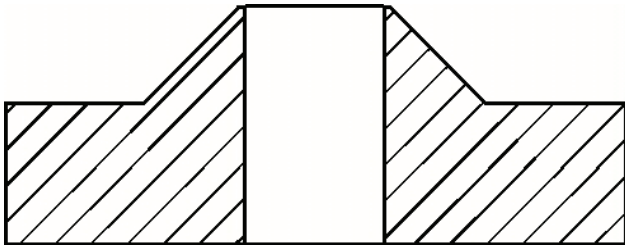


(a)

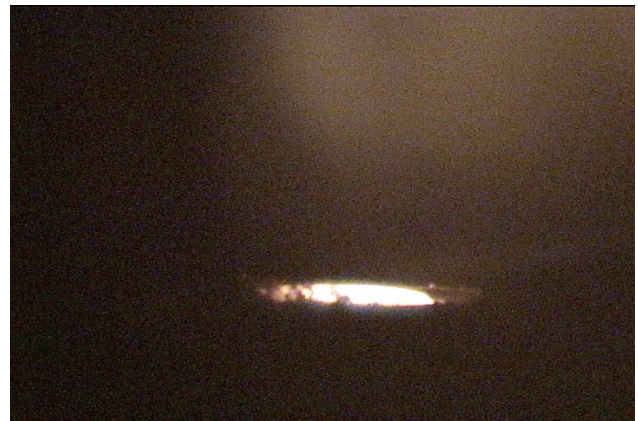


(b)

Fig. 4. Schematic of the standard cylindrical nozzle (a), and spitting from the Cu source operating at 2.8 g/hr.



(a)



(b)

Fig. 5. Schematic of the conical nozzle (a), and spitting from the Cu source operating at 15 g/hr.

of spitting was also confirmed by the fact that devices fabricated on the Cu(InGa)Se_2 film from such a source did not show shorting typical of Cu inclusions due to spitting. It should be emphasized that though a solution to the source spitting has been found, the actual mechanism responsible is still not well understood. The photograph of the lid with conical nozzles that is now the standard for all the sources in the system is shown in Figure 6 below.



Fig. 6. Standard source lid with conical nozzles used for all the metal evaporation sources in the system.

Mo Film Cracking

Formation of cracks in the Mo and Cu(InGa)Se₂ film during the deposition of the latter on Mo/polymer web in a roll-to-roll system has been a constant problem without solution. These cracks on Mo would severely impede lateral current collection, resulting in poor device performances. The scanning electron micrographs of Figure 7 illustrate typical such cracks on Mo, black areas, and on Cu(InGa)Se₂ film, white areas. These cracks can develop in the reactor prior to the deposition of the Cu(InGa)Se₂ film or after. They can be tensile or compressive cracks labeled "A" and "B" in Figure 7(a). The latter is shown at high magnification in Figure 7(b). It should be

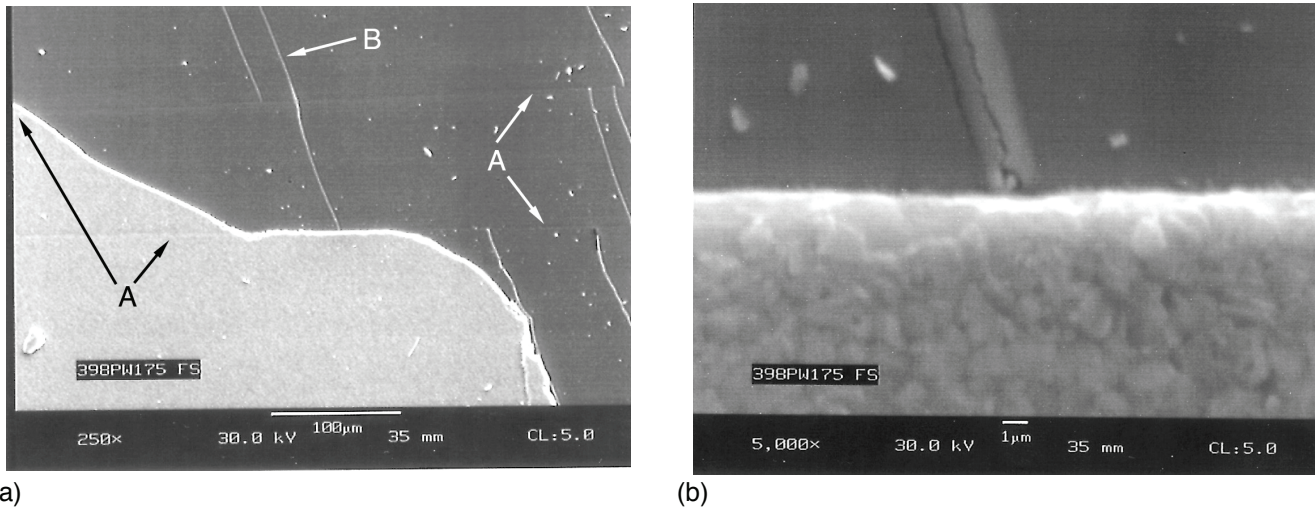


Fig. 7. Typical cracks in Cu(InGa)Se₂-on-Mo/polymer system: (a) low magnification view showing different types of cracks, and (b) high magnification view of a compressive crack.

pointed out that cracking was only observed when Cu(InGa)Se₂ film was deposited on Mo/polymer substrate in roll-to-roll system. Deposition of Cu(InGa)Se₂ film on the same substrate in a stationary system would not show any cracking.

While investigating the cracking behavior of Mo sputter deposited under different conditions, it was observed that crack density decreased with decreasing amount of Se usage for similar Cu(InGa)Se₂ depositions. Since it was also observed that Cu(InGa)Se₂ films deposited under reduced Se condition showed better adhesion to Mo films, it was postulated that reaction between Mo and Se was the process responsible in reducing mechanical strength of the Mo layer. Though such a reaction was never directly observed, it was decided to reduce chemical reactivity of Mo to Se by adding oxygen into the Mo. This is because the Gibbs free energy of formation of the most stable molybdenum selenide, Mo₃Se₄, is -363kJ/mole, while that of the least stable molybdenum oxide, MoO₂, is -467kJ/mole. As a result, TechniMet, the supplier of Mo/polymer substrate, was asked to prepare a Mo/polymer roll of substrate while using a mixture of oxygen/argon over the second target of their Mo sputtering system. The thickness of Mo layer was maintained at 2000 Å which was the standard thickness used. The back of the substrate was coated with 200 Å Mo, as it was, again, the standard practice. The only difference was that the top 1000 Å of the Mo layer contained oxygen. Figure 8 gives Auger depth profiles of the standard Mo layer and the Mo layer deposited with oxygen addition into the sputtering gaz over the second target. In the standard Mo layer, oxygen level is around 3 at% in both top (2nd target) and bottom (1st target) half of the film. A slight increase in oxygen is seen in the middle of the film probably due to adsorption from the background, while the web was transiting between targets. In the case of the oxygenated film, the top layer contains around 8 at% oxygen while the bottom layer has only 3 at% oxygen similar to the standard film. The oxygen signal in the middle of the film is much larger since the background oxygen is now quite high.

A number of Cu(InGa)Se_2 films were deposited onto these substrates to evaluate the cracking behavior. In each case, oxygenated substrate showed no cracks while the standard substrate was heavily cracked. Confirming these observations, devices made on the Cu(InGa)Se_2 film deposited on oxygenated Mo have shown superior performance and the ones on standard substrate were uniformly poor.

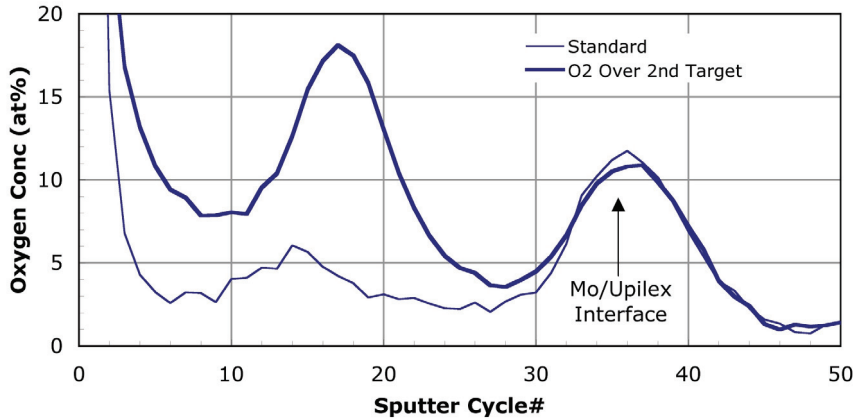


Fig. 8. Auger depth profile of the standard and oxygenated Mo layer.

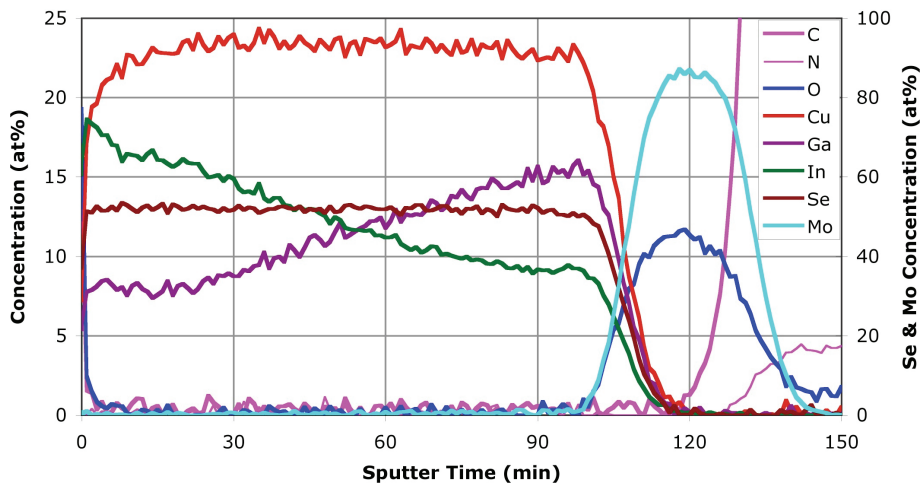


Fig. 9. Auger depth profile of a typical Cu(InGa)Se_2 film deposited on oxygenated Mo layer

It should be pointed out that these observations support the view that there is a threshold in oxygen concentration above which cracks are not formation is inhibited. Below that threshold, oxygen has no effect. This threshold may depend on the Cu(InGa)Se_2 reactor and on the characteristics of the Mo layer. Actually the situation is more complicated than simply the amount and distribution of oxygen in the as-deposited Mo layer. This is highlighted in the Auger depth profile of Figure 9 of a typical Cu(InGa)Se_2 film deposited on the oxygenated Mo layer with an as-deposited oxygen profile as given in Figure 8. Figure 9 shows that during the deposition of Cu(InGa)Se_2 there is diffusional redistribution of oxygen in the Mo layer giving a substantially more uniform oxygen. It is worth noting that the oxygen adsorbed during the transit between targets accounts for the substantial part of the oxygen in the Mo film.

Figure 9 also shows constant Cu concentration throughout the film and gradients in Ga and In as discussed earlier in a section describing deposition process.

Conclusion

Two of the major challenges encountered during the development of roll-to-roll process for depositing Cu(InGa)Se_2 films onto a continuous polyimide/Mo web has been discussed. The first issue was related to the operation of sources, particularly Cu, which produced heavy spitting at high effusion rates. The problem was found to be related to the temperature gradient along the internal wall of the nozzle. Modifying the nozzle geometry that reduced this gradient solved the problem. The second issue was a material problem and involved cracking of the Mo back contact layer during the deposition of Cu(InGa)Se_2 films. In this case, the problem was

tracked down to the reaction of Mo with Se within the reactor, which is thermodynamically favored at the deposition temperatures. The solution implemented was to reduce this chemical reactivity by adding oxygen into the Mo film. More stable oxides suppress the reaction with Se. Analysis also showed that oxygen concentration in the Mo film redistributes itself, by diffusion at Cu(InGa)Se₂ deposition temperatures, to give nearly constant concentration irrespective of the starting profile.

References

1. M. Powalla, and B. Dimmler, *Thin Solid Films* 361-361, 540 (2000).
2. B. M. Basol, V.K. Kapur, C.R. Leidholm, A. Halani, and K. Gledhill, *Solar Energy Materials and Solar Cells* 43, 93 (1996).
3. D. Rudmann, D. Bremaud, H. Zogg, and A. N. Tiwari, *J. Appl. Phys.*, 97, 084903 (2005)
4. M. E. Beck, S. Wiedeman, R. Huntington, J. VanAlsburg, E. Kanto, R. Butcher, and J. S. Britt, 31st IEEE Photovoltaic Specialists Conf., 211 (2005).
5. G. M. Hanket, U. P. Singh, E. Eser, W. N. Shafarman, and R. W. Birkmire, 29th IEEE Photovoltaic Specialists Conf., 567 (2002).
6. G. M. Hanket, P. D. Paulson, U. P. Singh, S. T. Junker, R. W. Birkmire, F. J. Doyle III, E. Eser, and W. N. Shafarman, 28th IEEE Photovoltaic Specialists Conf., 499 (2000).
7. R. W. Birkmire, E. Eser, S. Fields, and W. N. Shafarman, *Prog. Photovolt: Res. Appl.* 2005; 13: 1-8