

# Chemical Kinetics and Equilibrium Analysis of I-III-VI Films

Robert Birkmire and Michael Engelmann

*Institute of Energy Conversion  
University of Delaware, Newark, DE 19716 USA*

**Abstract.** Preliminary results are presented on the growth and characterization of Cu-In-Se-S thin films formed by reaction of Cu-In layers with a H<sub>2</sub>Se/H<sub>2</sub>S gas mixture. The approach was to first develop a process to grow device quality CuInS<sub>2</sub> films by reaction of a Cu-In layer in H<sub>2</sub>S. This process was then modified to form alloyed CuIn(Se,S)<sub>2</sub> films. A quantitative model for the reaction of Cu-In films in a CVD reactor with a mixed H<sub>2</sub>S-H<sub>2</sub>Se flowing gas was developed and verified. The composition of the CuIn(Se,S)<sub>2</sub> film can be controlled by the concentration H<sub>2</sub>Se + H<sub>2</sub>S and/or Se<sub>2</sub> + S<sub>2</sub> in the gas phase. Graded films can be made by annealing either CuInSe<sub>2</sub> or CuInS<sub>2</sub> films in a controlled Se and/or S containing atmosphere. Expanding this to include Ga in the films will provide a basis for engineering film compositions and bandgaps.

## BACKGROUND

CuInSe<sub>2</sub> based solar cells and modules have demonstrated the highest performance of any of the thin film PV technologies, with small area cell efficiency over 17% and module efficiency over 11% [1]. These results should be viewed as proof of concept, pointing to the manufacturing potential of this material. However, 15 years after Mickelsen and Chen reported the first 10% cell [2], there is no large scale manufacturing facility. The translation of laboratory results to first-time manufacturing has been much more difficult than expected due to the complexity of the processes involved for making thin film polycrystalline PV modules. This is compounded by the limited scientific basis to complement R&D, since CuInSe<sub>2</sub> based thin films are primarily used for PV. Further, most of the research activities were driven by the need to improve device performance and not to develop the fundamental scientific and engineering base required to properly engineer manufacturing equipment.

The primary issues that have inhibited the development of manufacturing processes for copper indium gallium diselenide based PV modules are: 1) the design, operation & control of commercial scale equipment required for the deposition of the CuInSe<sub>2</sub>; 2) analytical instrumentation for monitoring film growth; and 3) the difficulty of maintaining uniformity over large areas.

To address these issues, research at IEC has been directed towards developing quantitative models relating processing parameters and film growth chemistry to provide the scientific and engineering basis for effective design of commercial equipment. The research has focused on the Cu-In-Ga-Se-S materials system since all high efficiency

CuInSe<sub>2</sub> based solar cells use Cu(In,Ga)(Se,S)<sub>2</sub> films. Further, wider bandgap materials are needed for improved module performance and for next generation multijunction devices. However, solar cell performance drops in CuInGaSe<sub>2</sub> devices when Ga/(Ga+In) is above ~50%, where E<sub>g</sub> > 1.3 eV [3, 4]. The goal of the research is to alloy CuInSe<sub>2</sub> with appropriate amounts of Ga and S to control the bandgap of the material and maintain the broad 'single' phase regime of CuInSe<sub>2</sub>. The bandgap of the ternaries are:

CuInSe <sub>2</sub>	1.0 eV	CuGaSe <sub>2</sub>	1.7 eV
CuInS <sub>2</sub>	1.5 eV	CuGaS <sub>2</sub>	2.5 eV.

Since these materials form solid solutions with each other, there is the potential for 'engineering materials' with a bandgap from 1.0 to 2.5 eV.

Previously we reported on reaction analysis of the Cu-In-Se materials system where the reaction chemistry was evaluated and the rate constants and activation energies were determined [5]. A process for forming single phase CuInGaSe<sub>2</sub> films by selenization was developed and the Cu-In-Ga-Se materials system characterized [6]. A reactor analysis for a multiple source PVD system was performed and the mathematical models developed were used for the design of commercial scale equipment [7]. In this paper, preliminary results are present on the growth and characterization of Cu-In-Se-S thin films formed by reaction with H<sub>2</sub>Se and H<sub>2</sub>S. The approach was to first develop a process to grow CuInS<sub>2</sub> films by reaction of a Cu-In layer in H<sub>2</sub>S which was suitable for fabricating moderately efficient solar cells. This process was then modified and quantitatively characterized with respect to growth of mixed Se-S films.

## EXPERIMENTAL

Cu and In precursor layers were deposited by sputtering on Mo coated Corning 7059 glass substrates. About 2500Å of Cu were deposited followed by In to give a Cu-In ratio of about 1 and a final film thickness of about 2µm. The precursors were reacted in a laminar flow CVD tubular reactor described previously [8] which had been upgraded to allow delivery of both H<sub>2</sub>Se and H<sub>2</sub>S. The growth parameters used were:

Flow rate: 1320 sccm	H <sub>2</sub> S + H <sub>2</sub> Se = 0.5% - 2.0% in Ar
Velocity: 76 cm/min.	O <sub>2</sub> /(H <sub>2</sub> S+H <sub>2</sub> Se) = 0.01
Holding time: 1 min.	T <sub>reaction</sub> = 350°C to 450°C
Reaction Time: 5 to 120 min.	

The films were evaluated by scanning electron microscopy (SEM) to characterize their morphology and by energy dispersive x-ray spectroscopy (EDS) to determine elemental composition. The films were analyzed by x-ray diffraction (XRD) to identify chemical species present in the films and to estimate the S/Se+S in the CuIn(Se,S)<sub>2</sub> film. The sensitivity of the EDS and XRD methods used was ±1%.

## RESULTS AND ANALYSIS

CuInS<sub>2</sub> films suitable for solar cells were grown in a two-step process. The Cu-In layer was reacted at 350°C for 30 min. in a 0.5% H<sub>2</sub>S gas concentration followed by a 60 min. reaction at 450°C. The two-step process results in denser films than in a single step process at 450°C. Films were slightly Cu rich, from 25 to 27 atomic % of Cu. It is important to note that CuInS<sub>2</sub> has a narrow single phase regime extending ~2% from stoichiometry towards Cu<sub>2</sub>S [9]. Before fabricating devices, the film was etched in 0.2 molar solution of KCN at 40°C for 1 min. to remove Cu-S phases. CdS /ZnO was used as the window layer to fabricate the devices. Solar cells were made with efficiencies over

8% and the best cell had a  $V_{oc} = 0.65$  V,  $J_{sc} = 19.7$  and  $FF = 65.5\%$ . This was used as a validation of the process for growing the films.

The reaction of the Cu-In layer at  $450^\circ\text{C}$  for times from 5 to 120 min. in mixed  $\text{H}_2\text{Se}-\text{H}_2\text{S}$  flows was analyzed by XRD and the results can be qualitatively summarized as follows: 1) for time less than 10 min. binary indium selenides and sulfides are formed along with what appear to be ternary copper selenide-sulfide; 2) for intermediate times of 10 to 20 min. mixed Cu-In-Se-S phases are present; and 3) for 120 min. *uniform*  $\text{CuIn}(\text{Se},\text{S})_2$  films in steady state equilibrium with  $\text{H}_2\text{S}/\text{H}_2\text{Se}$  gas composition are formed. This is consistent with previous work where the precursors and any intermediates occurring in the formation of  $\text{CuInSe}_2$  [8] and  $\text{CuInS}_2$  [10] are consumed within 10 to 15 min. In addition to the existing proposed reaction paths for the formation of  $\text{CuInSe}_2$  [11] and  $\text{CuInS}_2$  [12], replacement reactions with  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  may occur resulting in a film composed of  $\text{CuInSe}_2$ ,  $\text{CuInS}_2$  and/or  $\text{CuIn}(\text{Se},\text{S})_2$ . If these constituents are taken to be a continuous solid solution of  $\text{CuInSe}_2$  and  $\text{CuInS}_2$ , it is proposed that they will react with the hydride gases according to the reversible reaction,



The equilibrium constant,  $K$ , is given by the ratio of the rate constants,  $k_1$  and  $k_2$ , for the reaction

$$K = \frac{k_1}{k_2} = \frac{[\text{H}_2\text{S}]^2 [\text{CuInSe}_2]}{[\text{H}_2\text{Se}]^2 [\text{CuInS}_2]} = \frac{x^2}{1-x} \frac{y}{y} \quad (2)$$

where

$$x = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{H}_2\text{Se}]} \quad (3)$$

and

$$y = \frac{S}{\text{Se} + S} \quad (\text{in the film}). \quad (4)$$

The equilibrium constant is calculated from the Gibbs free energy using,

$$K = \exp(-G/kT). \quad (5)$$

The free energy for each component of the reaction was calculated from published data shown in Table 1. The resulting total Gibbs free energy for the reaction was found to be -12.90 kcal/mol, resulting in an equilibrium constant of 7957 for a temperature of  $450^\circ\text{C}$ , which implies an equilibrium favoring the presence of  $\text{CuInSe}_2$ .

**TABLE 1.** Gibbs Free Energies for Reaction Constituents at  $450^\circ\text{C}$ .

Constituent	Free Energy @ $450^\circ\text{C}$ (kcal/mol)	Reference
$\text{CuInS}_2$	-89.71	[13]
$\text{CuInSe}_2$	-83.43	[14]
$\text{H}_2\text{S}$	-42.31	[15]
$\text{H}_2\text{Se}$	-32.73	[15]
$\text{S}_2$	-10.46	[15]
$\text{Se}_2$	-11.58	[15]
$\text{O}_2$	-37.00	[15]
$\text{H}_2\text{O}$	-84.44	[15]

Experimentally,  $x$ , the fractional concentration of  $H_2S$ , can be set and  $y$ , the fractional concentration of  $S$  in the film, measured. Figure 1 shows the predicted solid-vapor phase equilibrium based on the above analysis.

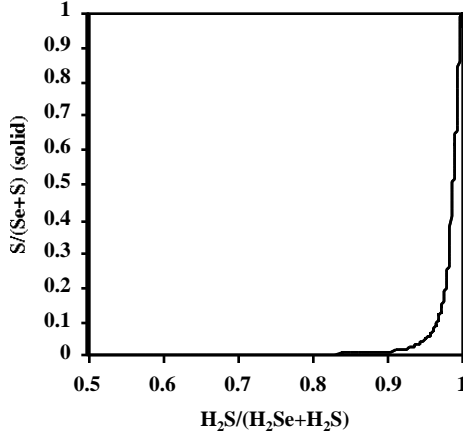


FIGURE 1. Steady state model for  $H_2Se + H_2S$

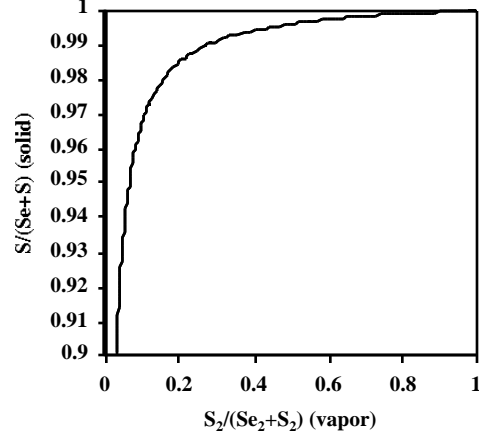
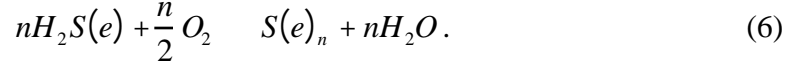
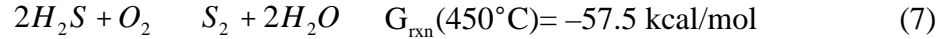


FIGURE 2. Steady state model for  $Se_2 + S_2$ .

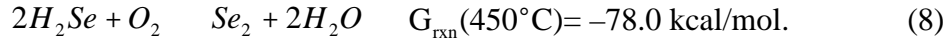
Experimentally, oxygen is introduced at the beginning of the process to prevent the agglomeration of liquid indium during the ramp up to reaction temperature and is present during the reaction at a ratio of  $O_2/(H_2S+H_2Se) = 0.01$ . Oxygen reacts in the gas phase with the hydride gases by the reaction,



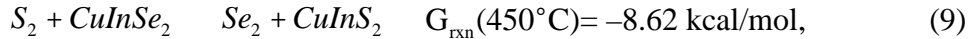
Since the dimer is more reactive than the other existing polymers,  $n$  is assumed to be 2 to estimate the maximum effect of  $O_2$ . The Gibbs free energy is calculated using values from Table 1 for the following reactions:



and



These reactions are strongly driven and it is assumed that all the  $O_2$  reacts with the hydride resulting in  $Se_2$  and  $S_2$  in the gas phase which reacts with the film by the reaction,



resulting in an equilibrium that favors the presence of  $CuInS_2$ . Using the same method as above for the calculation of the equilibrium constant,  $K$  is found to be 406. Figure 2 shows the predicted solid-vapor phase equilibrium for  $Se_2$  and  $S_2$ . However, the ratio  $O_2/(H_2S+H_2Se)$  is typically 0.01 and has a small effect on the steady state equilibrium in these experiments. Figure 3 shows the predicted and experimentally determined values for the fractional  $H_2S$  concentration in the gas phase compared to the fractional  $S$  concentration in the solid phase. The heavy solid line includes the contributions due to the hydride gases plus the presence of  $O_2$ . Contribution due to oxygen alone is represented by the dotted line. The data, represented by open boxes, match the model well over the range of interest. The presence of free  $S_2$  and  $Se_2$  results in a minimum sulfur

incorporation over the relative hydride concentration range, falling off to zero where the gas phase reaction with  $O_2$  becomes concentration limited at the low  $H_2S$  extreme. The experimental data also reflect these results.

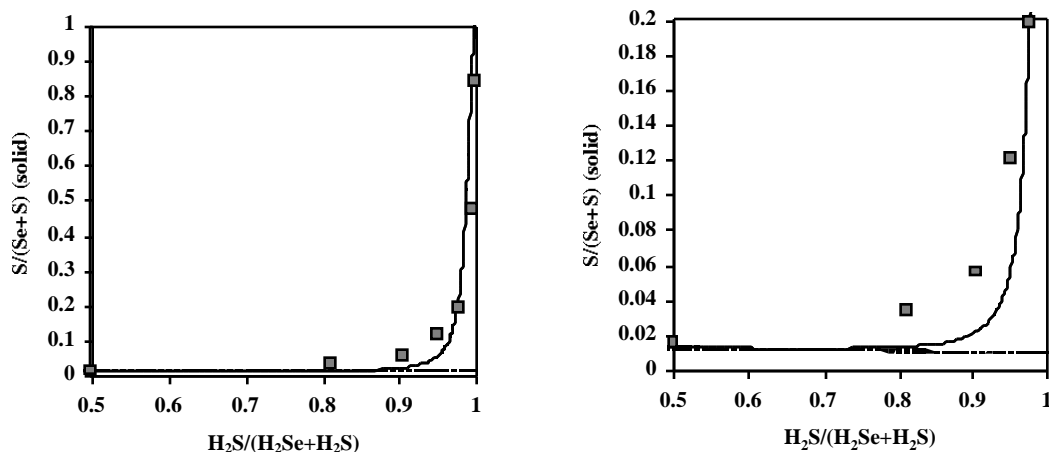


FIGURE 3. Steady state model for  $H_2Se + H_2S$  with  $0.01 O_2$ .

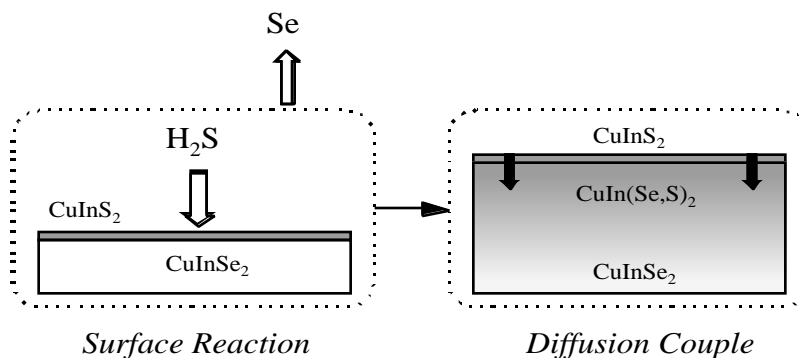


FIGURE 4. Proposed two-step diffusion process.

Based on the thermochemical analysis, films with graded composition (i.e., graded bandgap) can be formed by annealing  $CuInSe_2$  or  $CuInS_2$  films in a sulfur or selenium atmosphere, respectively. Preliminary data show that  $CuInS_2$  films annealed at  $450^\circ C$  in  $H_2Se$  completely convert to  $CuInSe_2$  after approximately 10 min. or more.  $CuInSe_2$  films annealed in  $H_2S$ , however, only partially convert after 120 min. at the same temperature. It is expected, based on the thermochemical analysis, that  $CuInSe_2$  films can be converted moderately fast to  $CuInS_2$  film in an elemental S atmosphere. Figure 4 depicts a proposed two-step process for the conversion of a  $CuInSe_2$  film. First, a surface reaction which is kinetically controlled occurs, forming a  $CuInS_2$  layer. This is followed by an interdiffusion process between the  $CuInS_2$  and  $CuInSe_2$  layers. Presently, experiments are under way to verify the proposed model.

## SUMMARY

A quantitative model for reaction of Cu-In films in a mixed  $H_2S-H_2Se$  flowing gas system has been developed and verified. The composition of  $CuIn(Se,S)_2$  film can be controlled

by the concentration  $H_2S+H_2Se$  and/or  $Se_2+S_2$ . Graded films can be made by annealing either  $CuInSe_2$  or  $CuInS_2$  films in a controlled Se and/or S containing atmosphere. Expanding this to include Ga in the films will provide a basis for engineering film compositions and bandgaps.

## ACKNOWLEDGMENTS

The authors would like to thank Brian McCandless for his help in carrying out this work, Kevin Hart and Tom Lampros for device fabrication, and T.W.F. Russell for useful discussions. This work was supported in part by NREL Subcontract No. XAK-7-17609-01 and EPRI Subcontract No. 8063-03.

## REFERENCES

1. Schock, H.W., and Shah, A., to be published in *Proc. 14th E.C. Photovoltaics Solar Energy Conf.*, 1997.
2. Mickelsen, R.A., and Chen, W.S., "Polycrystalline Thin-Film  $CuInSe_2$  Solar Cells," in *Proc. 16th IEEE Photovoltaic Specialists Conf.*, 1982, p. 781.
3. Shafarman, W.N., Klenk, R., and McCandless, B.E., *J. Appl. Phys.* **79**, 7324 (1996).
4. Phillips, J.E., and Shafarman, W.N., "Analysis of  $Cu(In,Ga)Se_2$  Solar Cells: Why Performance Decreases with Increasing Ga Content," to be presented at NCPV Program Review Meeting, Denver, CO, September 1998.
5. Orbey, N., Hichri, H., Birkmire, R.W., and Russell, T.W.F., *Progress in Photovoltaics* **5**, 237-247 (1997).
6. Marudachalam, M., Birkmire, R.W., Hichri, H., Schultz, J.M., Swartzlander, A., and Al-Jassim, M.M., *J. Appl. Phys.* **82**(6), 2896-2905 (1997).
7. Russell, T.W.F., "Technology Development Versus New Ideas Development by Universities," in AIP Conference Proceedings of *First Generation Photovoltaic Technologies: First NREL Conference*, 1997, pp. 93-99.
8. Verma, S., "A Chemical Reactor and Reaction Engineering Analysis of the Formation of Copper Indium Diselenide by Selenization," Ph.D. Thesis, University of Delaware, 1993.
9. Binsma, J.J.M., Giling, L.J., and Bloem, J., *J. Crystal Growth* **50**, 429-436 (1980).
10. Atkinson, B., B.S. Senior Project, University of Delaware, 1998.
11. Yamanaka, S., McCandless, B.E., and Birkmire, R.W., "Reaction Chemistry of  $CuInSe_2$  Formation by Selenization Using Elemental Se," *Proc. 22nd IEEE Photovoltaic Specialists Conference*, 1993, pp. 607-612.
12. Dzionk, C., Metzner, H., Hessler, S., and Mahnke, H.-E., *Thin Solid Films* **299**(1-2), 38-44 (1997).
13. Migge, H., and Grzanna, J., *J. Mater. Res.* **9**(1), 125-131 (1994).
14. Cahen, D., and Noufi, R., *J. Phys. Chem. Solids* **53**(8), 991-1005 (1992).
15. Knacke, O., Kubaschewski, O., and Hesselmann, K., *Thermochemical Properties of Inorganic Substances 2nd Ed.* **1-2**, New York: Springer-Verlag, 1991.