

EFFECT OF TEMPERATURE ON COPPER INDIUM SELENIZATION

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ABSTRACT

The reaction kinetics of copper indium diselenide formation is studied by measuring species composition as a function of time at 250°C and 325°C in a tubular CVD reactor. This extends our previous modeling and experimental study at 400°C. The initial copper indium alloy is analyzed at the reaction temperatures based on high temperature x-ray diffraction measurements. This modifies the understanding of the chemistry of the copper indium growth kinetics and a new set of model equations is presented. The specific reaction rate constants and activation energies for the chemical reactions are obtained enabling one to calculate the holding time for the reaction.

INTRODUCTION

Previously, a chemical reaction analysis of copper indium selenization at 400°C has been reported.¹ In that study, species concentration versus time experiments were carried out in a tubular CVD reactor by selenizing pre-sputtered Cu/In samples with H_2Se . A chemical reaction network for the mechanism of film formation was proposed, a mathematical model was developed and the specific reaction rate constants were estimated at 400°C. The present paper describes the continuation of that work to expand our understanding of the kinetics of copper indium selenization. Two main points addressed in this paper are:

- identification of the initial copper-indium alloy by obtaining x-ray diffraction patterns at high temperatures;
- estimation of activation energies for the specific rate constants.

Knowledge of the initial film composition prior to selenization is crucial in the analysis of film growth. At the reaction temperature used to make copper indium diselenide the phase diagram ² indicates that a copper indium layer consists of liquid indium with small amounts of dissolved copper and a copper indium alloy. The copper indium alloy is designated as $Cu_{11}In_9$ in the temperature range of 150-310°C and as phase at temperatures between 310-440°C. The phase is not clearly defined, and various researchers have proposed stoichiometric formulas of Cu_2In , Cu_7In_3 or $Cu_{2-x}In$.² The JCPDS (Joint Council for Powder Diffraction Studies) card files are available for the following Cu/In alloy species: $CuIn$ (35-1150), Cu_2In (42-1475), Cu_4In (42-1477), Cu_9In_4 (42-1476), $Cu_{11}In_9$ (41-883), $Cu_{16}In_9-A$ (26-523) and $Cu_{16}In_9-A'$ (26-522). The reported d-spacings of these Cu/In species are very close to each other with most of the major peaks overlapping. This is probably because these alloys have very similar copper to indium atomic ratios. In the selenization experiments, the species present are identified at room temperature by x-ray diffraction measurements and by comparing the measurement with JCPDS card files. Room temperature x-ray diffraction measurements accurately determine the presence of In_2Se , $InSe$ and $CuInSe_2$ species since they are at the same state at reaction temperature and room temperature where x-ray diffraction measurements are taken. The copper indium alloy, however, can transform into another phase upon cooling and the common identification of this phase as $Cu_{11}In_9$ may mislead one as to its description at higher temperatures. To gain a better understanding of the

copper indium alloy at the reaction temperatures, we have carried out experiments with copper indium samples using high temperature x-ray diffraction analysis.

To complete the kinetic analysis, we obtained additional time progressive data at 250°C and 325°C.³ The same experimental procedure was followed as in our earlier work.¹ In addition, the knowledge of rate constants at three temperatures enables us to obtain the activation energies and the frequency factors, information essential for the design, operation and control of commercial scale reactors.

EXPERIMENTAL

The experimental apparatus consisting of a quartz reactor (50.8 mm in diameter and 750 mm long) with a heating jacket, a gas handling system and a waste treatment system for H_2Se effluent has been described previously.^{1,4,5} *Cu-In* layers were sputtered from elemental targets in a DC Magnetron Sputtering system (Kurt-Lesker) on a 25x25 mm² molybdenum coated sodalime glass. About 2500 Å of copper and 6150 Å of indium was deposited to have a *Cu:In* molar ratio of about 0.9. The reactor was first evacuated to pressures less than 3×10^{-9} bar to remove contaminants, then filled with argon to atmospheric pressure. After the temperature and gas flow rates were stabilized *Cu-In* bilayers were inserted in the reaction zone and reacted for times from 1 to 120 minutes. At the end of the desired reaction time, the selenized substrates were pulled out of the heated zone and allowed to cool in an inert argon atmosphere. Experiments were carried

out at 250°C and 325°C in a H_2Se/Ar mixture with H_2Se molar composition of 0.35% at a gas velocity of 76 cm/min. The selenized samples were analyzed by x-ray diffraction for identifying the species and obtaining their mole fraction. The peak intensity is directly proportional to the volume fraction of the species for a homogeneous sample showing no preferential orientation. This relation is applied using single phase thin film standards to determine the volume fraction of individual species in the reacted samples. Thin films of Cu , In , Cu/In alloy, In_2Se and $CuInSe_2$ were analyzed by XRD to establish quantitative standards. The texture of the standard films was compared with that of reacted films to ensure the validity of the analysis. For all films analyzed there were no detectable differences between the orientation of standards and reacted films. The amounts of elemental Cu , In and Se and, hence, the total mass of the growing film were determined by atomic absorption spectroscopy. The methods of analysis are given in detail elsewhere.^{1,5}

To identify the copper indium alloy at the reaction temperatures, experiments were carried out in the research laboratories of the DuPont Company using a Rigaku bi-plane high temperature x-ray diffractometer with Cu/In samples having a molar ratio of 0.9. The samples were heated to 150°C, 170°C, 200°C, 350°C, 375°C, 400°C and 425°C and then cooled back down to room temperature. X-ray diffraction patterns were obtained at each temperature. The experiments were carried out in a reducing atmosphere of hydrogen to minimize oxide formation. The detailed analysis of this data will be presented elsewhere.⁶

RESULTS

The species identified in the Cu/In selenization at 250°C and 325°C are summarized in Table 1. The main species were: In_2Se , $InSe$, $CuInSe_2$ and Cu_xIn_y (Cu/In alloy). This is consistent with our previous observation at 400°C.^{1,5} At 400°C the reaction to form $CuInSe_2$ proceeds much faster and is completed in about 30 minutes. At 250°C and 350°C the reaction is still proceeding at 120 and 90 minutes, respectively. The slow rate of reaction at lower temperatures is advantageous in terms of identifying species, especially at short times.

At 250°C, the Cu/In alloy gives the major XRD peak up to reaction times of 120 minutes and $CuInSe_2$ appears in small quantities after 25 minutes. At 325°C the rate of depletion of the Cu/In alloy is much faster than that at 250°C, although it is still present in films selenized for 90 minutes. $CuInSe_2$ starts to form at around 10 minutes of selenization.

The mass growth rate of the film is presented in Figure 1. The amounts of the individual identified species are shown in Figures 2, 3 and 4. The data are smoothed considering the slight variations in the initial amount of the sputtered *Cu-In* bilayers.

Since the Cu/In alloy is the only species that may change its state upon cooling to room temperature, x-ray diffraction patterns obtained at high temperatures were analyzed.

The high temperature diffraction spectra of the Cu/In layers were corrected for shifts in d-spacing due to expansion at the elevated temperatures and then compared with the JCPDS card files for species identification.⁶ The diffraction pattern at 400°C is given in Figure 5. The results indicate that it is not possible to identify a single *Cu/In* species at the elevated temperatures of interest, since a variety of species coexist. We, thus, use Cu_xIn_y to represent the *Cu/In* alloy with a x:y ratio ranging from 1 to 2 and study two limiting cases, the reaction of *CuIn* and *Cu₂In*, to represent the film growth mechanism. The intermediate cases will fall in between.

REACTION ANALYSIS

The reaction pathway leading to the formation of *CuInSe₂* proposed previously^{1,7} includes $Cu_{1/2}In_0$ in the chemistry and is presented in Table 2. The modified chemical equations using the limiting cases of *CuIn* and *Cu₂In* are also given in Table 2. All other equations in the reaction network remain the same. The material balance equations for the *i*th species is¹:

$$\frac{dn_i}{dt} = r_d(i) - r_r(i) + r_{rxn}(i)V_f \quad (1)$$

where n_i is the number of moles of species *i*, $r_d(i)$ is the rate of delivery of species *i* to the film (mol/min), $r_r(i)$ is the rate of removal of species *i* (mol/min), $r_{rxn}(i)$ is the rate of reaction of the *i*th species (mol/min.cc), *t* is time of reaction and V_f is the film volume(cm³).

For the species In , In_2Se , $InSe$, Cu_xIn_y , Cu_2Se and $CuInSe_2$, Equation 1 reduces to:

$$\frac{d([i] V_f)}{dt} = r_{rxn} (i) V_f \quad (2)$$

since $n_i = [i]V_f$ and the rate of delivery and removal terms are zero. The reaction rate expressions shown in these model equations assume that the rate is proportional to the rate constant, k_i and the pertinent reactant species concentration. Since the selenization experiments are carried out under such conditions that the selenium species concentration can be assumed to remain constant, a modified set of rate constants defined as k' ($=k[Se]$) are used in the model equations. This simplifies the solution of the model equations since they are uncoupled from the selenium species balance equation. The model is described in detail elsewhere.^{1,4,7}

The mass balance equations for the new chemical equation set containing the two limiting cases of $CuIn$ and Cu_2In are given in Table 3. We have also included the equations for the previous chemical reaction set with $Cu_{11}In_9$ in this table for comparison. The differential component mass balance equations are the same for In , $InSe$, $CuInSe_2$ and the copper indium alloy. The balance equations that are affected by the change in the proposed chemistry are those for In_2Se and Cu_2Se . The parameters in these balance equations depend on the value of x and y in the original Cu/In alloy, Cu_xIn_y , as follows:

$$\frac{d\left([In_2Se]V_f\right)}{dt} = \left(k_2[Se][In] - k_3[Se][In_2Se] + y k_A[Se][Cu_2In]\right)V_f \quad (3)$$

$$\frac{d\left([Cu_2Se]V_f\right)}{dt} = \left(x k_A[Se][Cu_2In] - k_7[Se][InSe][Cu_2Se]\right)V_f \quad (4)$$

The mass balance equations shown in Table 3 are solved simultaneously to obtain the set of rate constants which best describe the experimental composition-time data. The initial values for the Cu/In alloy and *In* are estimated neglecting the amount of free copper dissolved in liquid indium and assuming that all the copper deposited is incorporated in the Cu_xIn_y species. The values of the rate constants were optimized with the simplex optimization algorithm¹ to get the best fit for all species compositions. The previous data at 400°C is also reworked using the new chemistry. The values of the rate constants at three temperatures are given in Table 4. Indium is not observed in any of the selenized samples because it reacts very fast with selenium to form In_2Se . Therefore, it was not possible to determine the value of k_2 accurately as a function of temperature. The model equations are not sensitive to its value. At 400°C the values of k_3 and k_7 are the same as those reported previously, because the only change in the new reaction set is that of the Cu/In alloy. The value of k_A previously reported to be 0.2 min⁻¹ is within the range 0.16-0.4 min⁻¹ obtained with the new set. Figures 2-4 show a comparison of the model predictions using the optimized rate constants and experimental data.

The temperature dependence of a specific reaction rate constant k_p is represented by the Arrhenius equation.

$$k_i = k_{i0} \exp(-E_{ai}/RT) \quad (5)$$

In Equation 5, k_{i0} is the frequency factor, E_{ai} is the activation energy and R is the gas constant. The activation energy is determined experimentally by carrying out the reaction at several different temperatures. When the natural logarithm of the Arrhenius relation is taken, it can be seen that a plot of $\ln k_i$ versus $1/T$ should be a straight line whose slope is proportional to the activation energy. Once this information is obtained the value of the rate constant at any temperature can be estimated.

The Arrhenius plots for the rate constants k_3 and k_7 and k_A are given in Figure 6. The results obtained by using $CuIn$ (dashed line) and Cu_2In (solid line) are both presented in Figure 6. The ensuing values of activation energies are reported in Table 4.

CONCLUSIONS

Cu-In bilayers are reacted at 250°C and 325°C with H_2Se in a tubular CVD reactor. The species involved in the film growth are identified and their compositions are determined as a function of time. The reaction rate constants are estimated for 250°C and 325°C and at 400°C, using the previously obtained data at this temperature. Activation energies are estimated enabling one to calculate reaction rate constants at any desired temperature.

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FIGURE CAPTIONS

Figure 1. Mass growth rate of the film at 250°C, 325°C and 400 °C.

Figure 2. Number of moles of In₂Se versus time: Comparison between model predictions and experimental data (solid lines: model predictions with Cu₂In, dashed lines: model predictions with CuIn; scattered points: experimental data)
a) 250°C b) 325°C c)400 °C

Figure 3. Number of moles of InSe versus time: Comparison between model predictions and experimental data (solid lines: model predictions with Cu₂In, dashed lines: model predictions with CuIn; scattered points: experimental data)
a) 250°C b) 325°C c)400 °C

Figure 4. Number of moles of species versus time: Comparison between model predictions and experimental data (solid lines: model predictions with Cu₂In, dashed lines: model predictions with CuIn; scattered points: experimental data)
a) CuIn b)Cu₂In c)Cu₂Se d)CuInSe₂

Figure 5. X-ray diffraction pattern of Cu/In at 400°C: **1:** Cu₁₁In₉ and Cu₁₆In₉-A; **2:** In₂O₃; **3:** Cu₁₁In₉; **4:** Cu₁₆In₉-A and Cu₉In₄; **5:** Cu₁₆In₉-A' and Cu₉In₄; **6:** Cu₁₆In₉-A and Cu₁₆In₉-A'; **7:** Mo; **8:** Cu₁₆In₉-A', Cu₁₆In₉-A, Cu₂In and Cu₉In₄; **9:** Cu₁₆In₉-A and Cu₄In

Figure 6. Arrhenius plot: rate constant as a function of temperature (solid lines: results using Cu_2In , dashed lines: results using CuIn)

Table 1. Species Observed in Copper-Indium Bilayer Selenization- Summary of XRD Results

a. T= 250 ° C

Time (min)	Metals	Binary Selenides	Ternary Selenides
5	Cu_xIn_y	In_2Se	
10	Cu_xIn_y	$In_2Se, InSe$	
25	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
30	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
45	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
60	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
90	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
120	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$

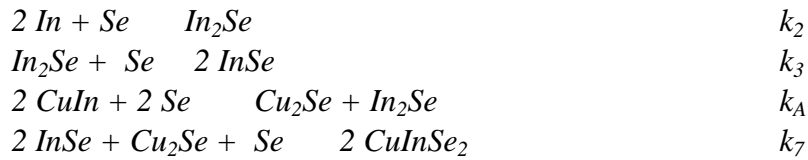
b. T= 325° C

Time (min)	Metals	Binary Selenides	Ternary Selenides

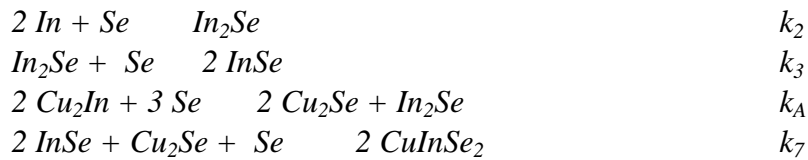
2	Cu_xIn_y	$In_2Se, InSe$	
5	Cu_xIn_y	$In_2Se, InSe$	
10	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
20	Cu_xIn_y	$In_2Se, InSe$	$CuInSe_2$
30	Cu_xIn_y	$InSe$	$CuInSe_2$
45	Cu_xIn_y	$InSe$	$CuInSe_2$
65	Cu_xIn_y	$InSe$	$CuInSe_2$
90	Cu_xIn_y	$InSe$	$CuInSe_2$

Table 2. Reaction Pathways For $CuInSe_2$ Formation

New Reaction Set with $CuIn$



New Reaction Set with Cu_2In



Previously Proposed Reaction Set with $Cu_{11}In_9$

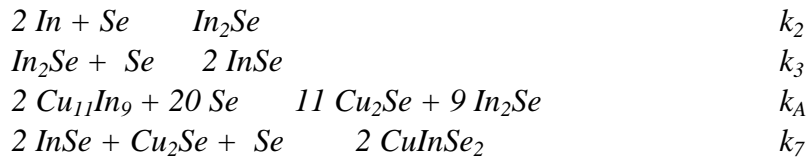


Table 3. Reaction Analysis Model Equations

with Cu₂In as the Cu/In Alloy

$$\frac{d([In]V_f)}{dt} = -2k_2 [Se][In] V_f = -2k'_2 [In] V_f$$

$$\frac{d([In_2Se]V_f)}{dt} = (k_2 [Se] [In] - k_3 [Se] [In_2Se] + k_A [Se] [Cu_2In]) V_f = (k'_2 [In] - k'_3 [In_2Se] + k'_A [Cu_2In]) V_f$$

$$\frac{d([InSe]V_f)}{dt} = (2k_3 [Se] [In_2Se] - 2k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k'_3 [In_2Se] - 2k'_7 [InSe] [Cu_2Se]) V_f$$

$$\frac{d([Cu_2In]V_f)}{dt} = -2k_A [Se] [Cu_2In] V_f = -2k'_A [Cu_2In] V_f$$

$$\frac{d([CuInSe_2]V_f)}{dt} = (2k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k'_7 [InSe] [Cu_2Se]) V_f$$

$$\frac{d([Cu_2Se]V_f)}{dt} = (2k_A [Se] [Cu_2In] - k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k'_A [Cu_2In] - k'_7 [InSe] [Cu_2Se]) V_f$$

with CuIn as the Cu/In Alloy

$$\frac{d([In]V_f)}{dt} = -2k_2 [Se][In] V_f = -2k'_2 [In] V_f$$

$$\frac{d([In_2Se]V_f)}{dt} = (k_2 [Se] [In] - k_3 [Se] [In_2Se] + k_A [Se] [CuIn]) V_f = (k'_2 [In] - k'_3 [In_2Se] + k'_A [CuIn]) V_f$$

$$\frac{d([InSe]V_f)}{dt} = (2k_3 [Se] [In_2Se] - 2k_7 [Se] [InSe] [Cu_2Se]) V_f = (2k'_3 [In_2Se] - 2k'_7 [InSe] [Cu_2Se]) V_f$$

$$\frac{d([\text{CuIn}] V_f)}{dt} = -2k_A [\text{Se}] [\text{CuIn}] V_f = -2k'_A [\text{CuIn}] V_f$$

$$\frac{d([\text{CuInSe}_2] V_f)}{dt} = (2k_7 [\text{Se}] [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f = (2k'_7 [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f$$

$$\frac{d([\text{Cu}_2\text{Se}] V_f)}{dt} = (k_A [\text{Se}] [\text{CuIn}] - k_7 [\text{Se}] [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f = (k'_A [\text{CuIn}] - k'_7 [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f$$

with $\text{Cu}_{11}\text{In}_9$ as the Cu/In Alloy

$$\frac{d([\text{In}] V_f)}{dt} = -2k_2 [\text{Se}] [\text{In}] V_f = -2k'_2 [\text{In}] V_f$$

$$\frac{d([\text{In}_2\text{Se}] V_f)}{dt} = (k_2 [\text{Se}] [\text{In}] - k_3 [\text{Se}] [\text{In}_2\text{Se}] + 9k_A [\text{Se}] [\text{Cu}_{11}\text{In}_9]) V_f = (k'_2 [\text{In}] - k'_3 [\text{In}_2\text{Se}] + 9k'_A [\text{Cu}_{11}\text{In}_9]) V_f$$

$$\frac{d([\text{InSe}] V_f)}{dt} = (2k_3 [\text{Se}] [\text{In}_2\text{Se}] - 2k_7 [\text{Se}] [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f = (2k'_3 [\text{In}_2\text{Se}] - 2k'_7 [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f$$

$$\frac{d([\text{Cu}_{11}\text{In}_9] V_f)}{dt} = -2k_A [\text{Se}] [\text{Cu}_{11}\text{In}_9] V_f = -2k'_A [\text{Cu}_{11}\text{In}_9] V_f$$

$$\frac{d([\text{CuInSe}_2] V_f)}{dt} = (2k_7 [\text{Se}] [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f = (2k'_7 [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f$$

$$\frac{d([\text{Cu}_2\text{Se}] V_f)}{dt} = (11k_A [\text{Se}] [\text{Cu}_{11}\text{In}_9] - k_7 [\text{Se}] [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f = (11k'_A [\text{Cu}_{11}\text{In}_9] - k'_7 [\text{InSe}] [\text{Cu}_2\text{Se}]) V_f$$

