

COPPER INDIUM ALLOY TRANSFORMATIONS

Nese Orbey^a, Glover A. Jones^{b,*}, Robert W. Birkmire^a and T. W. Fraser Russell^a

a) Institute of Energy Conversion, University of Delaware, Newark, DE, 19716

b) DuPont Company, Central Research and Development, Experimental Station, Building 228/320D, Wilmington, DE 19880-0228. (DuPont Company Contribution Number: 7722)

*Corresponding author

ABSTRACT

Phase transformations of copper indium alloy thin films are analyzed by hot stage X-ray diffraction over the temperature range from 30°C to 425°C in controlled ambient. Thin films of *Cu/In* with a molar ratio of approximately 0.9 were used. *In situ* experiments were carried out in a reducing hydrogen atmosphere to minimize oxide formation. The as-deposited *Cu/In* alloy transformed at 150°C to form $Cu_{11}In_9$. Ramping the temperature to the upper limit of 425°C revealed an additional transformation at 350°C to form $Cu_{16}In_9$.

INTRODUCTION

Copper indium alloys have established technological importance in thin film solar cell manufacturing and as solders for interconnections in the electronics industry. In solar cells, they are used as precursors for the growth of $CuInSe_2$ films. Thin films of $CuInSe_2$ and alloys with Ga and S have been fabricated on laboratory scale solar cells with efficiencies over 18 %, ¹ thus providing a promising set of materials for high efficiency solar cells for inexpensive electric power generation. The $CuInSe_2$ thin films used for these high efficiency solar cells have been made by the reaction of Cu/In metal precursors in a Se -containing atmosphere, selenization, or by multi-source elemental evaporation of Cu , In and Se onto heated substrates at 400°C - 500°C. The challenge is to scale up the laboratory cell processing to commercial-scale module manufacturing. For the selenization process, this necessitates understanding the reaction kinetics and the role Cu/In precursors play during selenization at the reaction temperatures. ² Therefore, to understand Cu/In film growth, the study of alloy phase transformations in thin films is required at these reaction temperatures. Since Cu/In phase transitions appear to occur rapidly, an effective means of capturing growth mechanisms is provided by high temperature X-ray diffraction instrumentation designed to accommodate special reducing or oxidizing atmospheres in the temperature interval 20°C - 1500°C. Other intermediate species requiring days or weeks to equilibrate can be detected reliably by room temperature XRD measurements where phases are routinely examined over time as a complement to the more rigorous high temperature *in situ* XRD studies. ³⁻⁵

Among recent review articles, Subramanian and Laughlin³ present the most extensive assessment of *Cu/In* phase diagrams. According to their phase diagram, there are two phases at the atomic composition of interest, 52.6% *In* and 47.4% *Cu*: 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°C -310°C and as $Cu_{11}In_9$ phase at temperatures between 310°C - 440 °C. The $Cu_{11}In_9$ phase is not clearly defined, and various researchers have proposed stoichiometric formulas of Cu_2In , Cu_7In_4 or $Cu_{2-x}In$.^{3,5,6} Bolcavage *et al.*⁵ reexamined several portions of the *Cu/In* phase diagram and found that the phase $Cu_{11}In_9$ was stable at low temperatures rather than decomposing at 157°C. They also claim that Cu_2In exists at temperatures between 305°C -389°C while Cu_7In_4 exists at lower temperatures. The data used in these studies were taken from samples allowed to equilibrate for long periods of time, which were then crushed; diffraction patterns were obtained on powder specimens at room temperature.

Phase behavior of thin films of *Cu/In* alloys at 200°C were addressed by Albin, *et al.*⁴ They report the presence of $Cu_{11}In_9$, $CuIn$ and an “undetermined phase” by comparing room temperature X-ray data with JCPDS (Joint Council for Powder Diffraction Studies) card files. However, the samples in that study were not quenched and were allowed to cool in an uncontrolled environment which might affect the results. Various compositions of *Cu/In* were studied, ranging from approximately 11% to 60% *In*. The same phases were obtained, although the phase diagram^{3,5} indicates changes in this composition range.

At room temperature and at the composition of interest, the phases present are Cu , In , $CuIn$ and $CuIn_2$ (Keppner phase).^{7,8} JCPDS 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). Indexing of $CuIn_2$ was facilitated by the data of Keppner et al.⁸ In most cases, the reported d-spacings of these Cu/In species are very close to each other with most of the major peaks overlapping. In the present study, performed at a single Cu/In composition, crystalline phase transformations were determined *in situ* for Cu/In bilayers heated in a manner similar to the actual solar cell fabrication.

\

EXPERIMENTAL

The copper-indium thin film samples were prepared the same way as required for the fabrication of solar cells.² $Cu-In$ layers were sputtered, at room temperature, from elemental targets in a DC magnetron sputtering system onto 2.5 x 2.5 cm² Mo coated soda lime glass substrate. The thickness of the molybdenum coating was 1500 nm. Approximately 250 nm of copper was deposited on this layer followed by deposition of 615 nm of indium, to give a $Cu:In$ molar ratio of about 0.9. The samples were then cut into 1.5 x 2.5 cm² sections to fit the sample holder in the X-ray diffraction system.

X-ray diffraction patterns were acquired using automated theta-two theta X-ray diffractometers^{9,10} equipped with a 500 cc reactor for *in situ* investigations of thin film properties in the temperature interval of 20°C to 1000°C. Data was acquired over the 2 θ range from 10 to 70 degrees, in steps of 0.03 degrees with counting times of 15 to 20

seconds using copper K- radiation at 40 keV and 40 mA and spectrally purified using a graphite monochromator.

Each sample was mounted on a slab of Inconel 600 measuring 2.5 x 2.5 x 0.238 cm, having a thermal well 0.159 cm in diameter and 0.127 cm deep, to accommodate a *Pt/PtRh13* thermocouple. The measurements were conducted in a controlled environment with an automated temperature and gas flow protocol using a controlled ramp and thermal increments of 25°C, and in a He-H₂ gas mixture. Before each scan, the reactor was evacuated to approximately 10 mT overnight, followed by hydrogen back-fill, and then gradual equilibration with helium until a steady state of 40% H₂ and 60% He was reached. XRD patterns were taken at temperatures from 29°C to 425°C. For data taken at the different temperatures, Mo was used as an internal standard for determination of alloy inter-planar spacings.

RESULTS AND DISCUSSION

The diffraction data obtained *in situ* at different temperatures are presented in Figure 1 as intensity in arbitrary units versus the Bragg angle (2θ). The experimental data were taken over the two theta range of 10-70 degrees; however, only the data over the range 30°C - 54°C are presented in Figure 1 to enhance the range at which most of the peaks were observed. The most intense peak in all the spectra is the *Mo* peak at $2\theta = 40.52$ (d-spacing = 0.2225 nm) which was used as an internal standard. The peaks at $2\theta \sim 34.8^\circ$, 37° , and 39.6° appearing in all spectra are instrumental, and only peaks with counts

greater than 5 were considered in the analysis. X-ray patterns made up by other peaks were then compared with JCPDS card files for *Cu/In* alloys phase identification: *CuIn* (35-1150), *Cu₂In* (42-1475), *Cu₄In* (42-1477), *Cu₉In₄* (42-1476), *Cu₁₁In₉* (41-883), *Cu₁₆In₉-A* (26-523), *Cu₁₆In₉-A'* (26-522) and *Cu₄In* (42-1477).

At 29°C, the starting crystalline phases were *Cu* at $2\theta = 43.3$ (d-spacing: 0.20869 nm), *CuIn* at $2\theta = 34.5$ and 38.5 (d-spacing: 0.2596 nm and 0.23305 nm) and the Keppner phase,⁸ *CuIn₂* at $2\theta = 33.3$ (d-spacing: 0.26867 nm). These assignments are in agreement with generally accepted observations reported in the literature.^{7,8} Figure 1a shows that as the substrate is heated to 150°C, peaks prevalent at 29°C disappear and two new peaks emerge at $2\theta = 41.23$ (0.2188 nm) and $2\theta = 42.07$ (0.2146 nm), indicating a phase transition. Subsequent scans at 170°C and 200°C reveal no additional phase transitions, which is in accord with the phase diagram.^{3,5} The experimental data at 200°C are given in full detail in Table 1 where d-spacings and corresponding peak intensities are listed along with the d-spacings and relative intensities of the various *Cu/In* alloys as reported in the JCPDS database. According to the phase diagram,³ in the temperature range of 153°C - 310°C, the copper indium alloy is *Cu₁₁In₉*. Our data are in agreement in that the spectra obtained between 150°C to 200°C are the same and that all peaks matched the *Cu₁₁In₉* peaks reported in the JCPDS data base. Table 1 also indicates matches with other *Cu/In* alloy species. However, above the melting point of In, the equilibrium phases are liquid In with dissolved Cu and solid Cu-In alloy. It is speculated that the system is near

equilibrium and based on phase rule, and the Cu-In alloy consists of a single phase which is most likely $Cu_{11}In_9$.

Table 2 and Figure 1b show that subsequent heating to 350°C results in another phase transition as the peak at $2\theta = 41.23^\circ$ disappears and the peak at $2\theta = 42.07^\circ$ shifts to $2\theta = 41.94^\circ$. The onset of additional peaks at $2\theta = 30.59^\circ$, $2\theta = 35.46^\circ$ and $2\theta = 39.68^\circ$ are most likely due to the formation of In_2O_3 . However, while the $2\theta = 30.59^\circ$ peak belongs exclusively to In_2O_3 , the other two peaks are also characteristic peaks of various Cu/In alloys as shown in Table 2.

It is difficult to identify a single Cu/In alloy species in the temperature range of 350°C to 400°C. The phase diagram^{3,5} indicates a transition above 310°C, and uncertainties are reported about the / phase with proposed stoichiometric formulas of Cu_2In , Cu_7In_4 or $Cu_{2-x}In$.^{3,5,6} The major peaks for the high temperature Cu/In phases are very closely spaced with most major peaks overlapping. In the tables the possible Cu-In crystalline phases are ordered according to increasing Cu/In molar ratio. As the temperature increases above 310°C, the phase diagram indicates that the mole fraction of the In-rich liquid phase relative to the solid Cu-In phase increases by more than a factor of two, and the mole fraction of Cu in the solid phase increases. Thus, if the system remains near equilibrium, the $Cu_{11}In_9$ can be expected to transform to $Cu_{16}In_9$, the alloy with phase with the next higher Cu/In molar ratio.

Figure 1c shows XRD patterns for temperatures from 375°C down to 150°C where the $Cu_{16}In_9$ transforms back to the $Cu_{11}In_9$. This observation, more than any other, convinces us that no other transformations occur between these temperatures.

CONCLUSION

X-ray diffraction data of reacted copper and indium films at a Cu/In ratio of 0.9 in hydrogen, in the temperature interval 30°C to 425°C, are presented. The data indicate two prominent transitions within the limits of temperature: first, $Cu_{11}In_9$ is formed at around 150°C and remains stable at that temperature over the data collection cycle of 1 hour; and second, the next transition occurs at 310°C and produces an apparently stable phase of $Cu_{16}In_9$, which is consistent with the phase diagram. These results provide a foundation for analyzing the reaction kinetics of formation of $CuInSe_2$ films used for solar cells, which were grown by the selenization process.

ACKNOWLEDGMENTS

We gratefully acknowledge technical discussions with Brian McCandless and Erten Eser of the Institute of Energy Conversion and the special contributions of the DuPont Company Corporate Center for Analytical Research for the use of its facilities in the examination of Cu/In alloy transformations. The DuPont Company contribution number for this work is 7722. This work has been supported in part by the Defense Advanced Research Projects Agency Agreement No: MDA972-95-3-0036.

FIGURE CAPTION

Figure 1. X-ray diffraction scans: a) 29°C - 200°C; b) 200°C - 400°C; c) 375°C - 150°C.

TABLE CAPTIONS

Table 1. X-ray diffraction data at 200°C: Numbers in () are the relative intensity of the XRD peaks.

Table 2. X-ray diffraction data at 350°C: Numbers in () are the relative intensity of the XRD peaks.

REFERENCES

- 1) M.A. Contreras, B. Egaas, K. Ramanathan, J.Ul. Hiltner, A. Swartzlander, F. Hasoon and R. Noufi, *Prog. In Photovoltaics*, Short Communication, July-August (1999).
- 2) N. Orbey, H. Hichri, R.W. Birkmire and T. W. F. Russell, "Effect of Temperature on Copper Indium Selenization," *Progress in Photovoltaics*, **5**, 237 (1997).
- 3) P. R. Subramanian and D. E. Laughlin, "The *Cu-In* (Copper-Indium) System," *Bulletin of Alloy Phase Diagrams*, **10**, 5, 554 (1989).
- 4) D.S. Albin, G.D. Moonet, J. Carapella, A. Duda, J. Tuttle, R. Matson and R. Noufi, "The Phase Behavior of Evaporated Copper and Indium Precursors for Selenization," *Solar Cells*, **30**, 41 (1990).
- 5) A. Bolcavage, S. W. Chen, C. R. Kao, Y. A. Chang and A. D. Romig, "Phase Equilibria of the *Cu-In* System I: Experimental Investigation," *Journal of Phase Equilibria*, **14**, 14 (1993).
- 6) G. C. Che and M. Ellner, "Powder Crystal Data for the High Temperature Phases *Cu₄In*, *Cu₉In₄(h)* and *Cu₂In (h)*," *Powder Diffraction*, **7**, 107 (1992).
- 7) J. S. Chen, E. Kolawa and M.-A. Nicolet, "*Cu/In* Deposited at Room Temperature: Morphology, Phases and Reaction," *Solar Cells*, **30**, 451 (1991).
- 8) W. Keppner, R. Wesche, T. Klas, J. Voigt and G. Schatz, "Studies of Compound Formation at Cu-In, Ag-In and Au-In Interfaces with Perturbed - Angular Correlations," *Thin Solid Films*, **143**, 201 (1986).
- 9) D.R. Corbin, L. Abrams, G. A. Jones, M. L. Smith, C. R. Dybowski, J. A. Hriljac and J. B. Parise, "Entrapment and Controlled Release of Xenon in Cd⁺² Exchanged

Zeolite Rho,” *Journal of the Chemical Society, Chemical Communications*, **12**, 1027 (1993).

- 10) Z. K. Zenkatesan, S. L. Suib, D.R. Corbin, S. Schwarz and G. A. Jones, “Encapsulation Studies of Hydrogen on Cd Exchanged Zeolite Rho at Atmospheric Pressure”, *Catalysis Today*, **31**, 199 (1996).

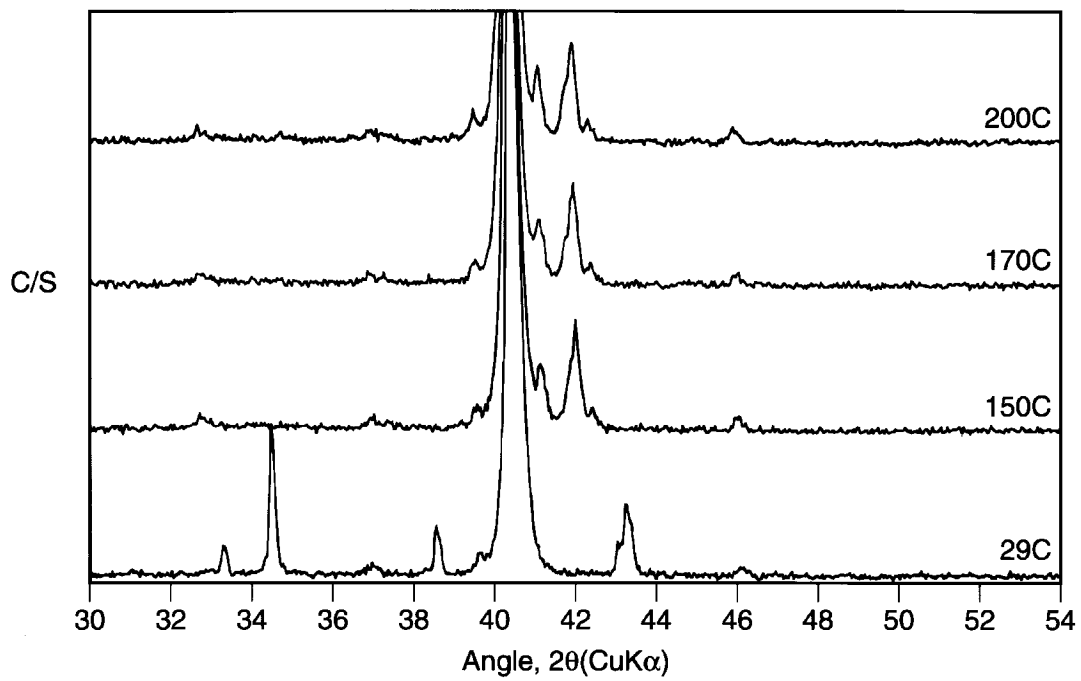


Fig. 1a

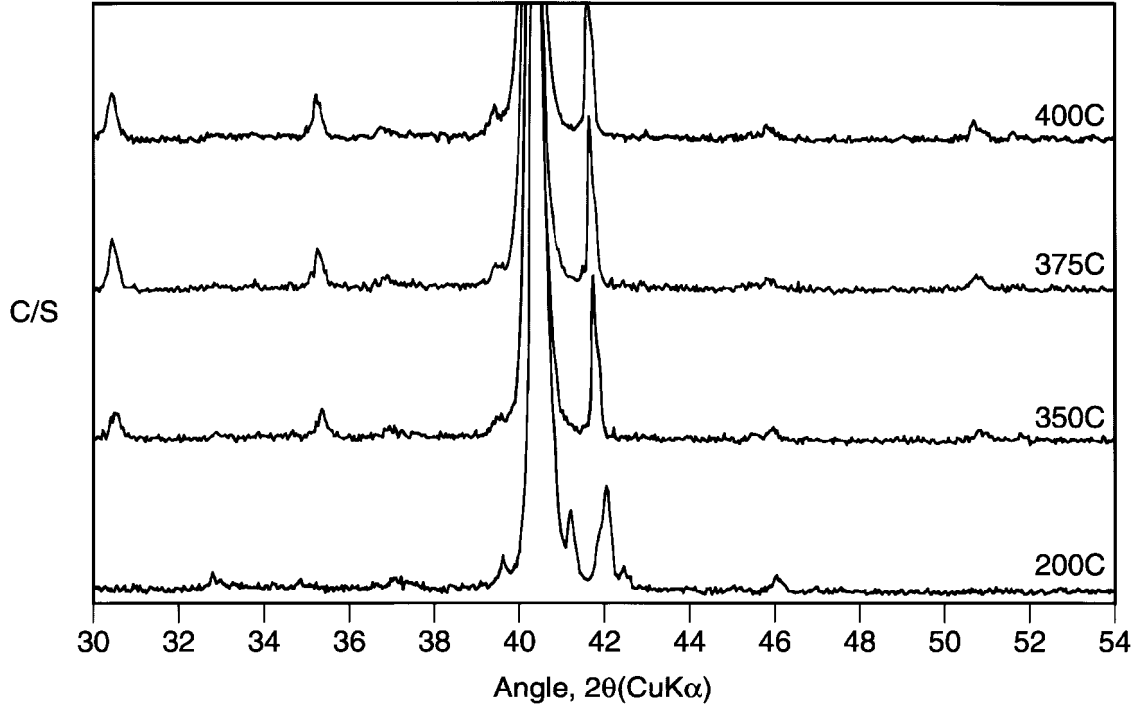


Fig 1b

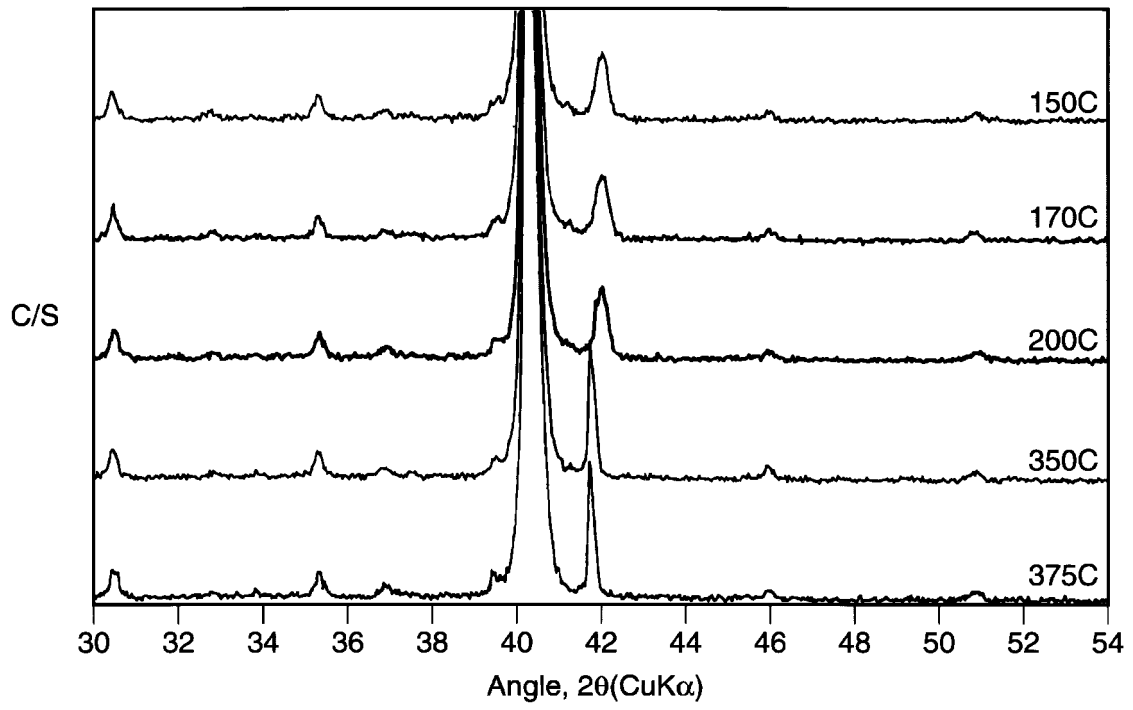


Fig. 1c

Table 1. X-ray diffraction data at 200°C.

<i>Experimental</i>			JCPDS Card Files				
2 (Å)	d (Å)	I (Cts)	Cu₁₁In₉ [1.22]* 41-0883	Cu₁₆In₉-A [1.77]* 26-0523	Cu₁₆In₉-A' [1.77]* 26-0522	Cu₂In [2.0]* 42-1475	Cu₉In₄ [2.25]* 42-1476
29.26	3.0507	12	3.052 (80)	3.05 (70)	3.03 (100)	3.0347 (50)	3.0355 (75)
32.78	2.7304	8	2.716 (80)				
41.23	2.1882	35	2.177 (100)	2.184 (75)	2.186 (80)		
42.07	2.1464	46	2.145 (100)	2.140 (100)	2.155 (80)	2.1416 (100)	2.1435 (100)
42.42	2.1299	11	2.136 (100)		2.139 (80)		
45.04	2.0118	7	2.047 (10)	2.046 (100)			

* Cu/In ratio of the alloy

Table 2. X-ray diffraction data at 350°C.

<i>Experimental</i>			JCPDS Card Files					
2 (Å)	D (Å)	I (Cts)	Cu₁₁In₉ [1.22]* 41-0883	Cu₁₆In₉-A [1.77]* 26-0523	Cu₁₆In₉-A' [1.77]* 26-0522	Cu₂In [2.0]* 42-1475	Cu₉In₄ [2.25]* 42-1476	In₂O₃ 06-0416
29.31	3.04498	11	3.052 (80)	3.05 (70)	3.03 (100)	3.0347 (50)	3.0355 (75)	
30.59	2.9206	12						2.921 (100)
35.46	2.5303	14		2.530 (40)				2.529 (30)
41.94	2.153	68	2.145 (100)	2.140 (100)	2.155 (80)	2.1416 (100)	2.1435 (100)	
51.05	1.788	6	1.788 (20)	1.785 (40)			1.7860 (15)	1.778 (35)
60.81	1.5225	6	1.525 (60)		1.524 (40)	1.5155 (50)		1.525 (30)

* Cu/In ratio of the alloy