CuInSe₂ phase formation during Cu₂Se/In₂Se₃ interdiffusion reaction

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Diffusion couples based upon Cu₂Se/In₂Se₃ pairings have been examined in order to identify the kinetics of intermediate phase development and the associated phase equilibria. For the diffusion couples annealed at 550 °C for 1.5 h, all phases included in the Cu₂Se–In₂Se₃ pseudobinary phase diagram section developed including the CuInSe₂ (CIS) phase. Also, the In₆Se₇ phase formed for annealing times in excess of 1.5 h at 550 °C, indicating a modification of the diffusion pathway outside the pseudobinary phase diagram section. The growth of the CIS phase formed by reactive diffusion follows parabolic kinetics ($x^2=kt$) with the k value of 3.3×10^{-8} cm²/s. CIS phase precipitates with a dendritic morphology are also produced within the Cu₂Se side of the diffusion couple far from the initial interface, indicating that In is the fast component during interdiffusion. Based upon electron diffraction analysis and simulation of electron diffraction patterns, the dendritic shaped CIS precipitate structure was uniquely determined to be the metastable zinc blende type rather than the stable chalcopyrite-type structure. The structure and orientation relationship between the metastable CIS phase and the Cu₂Se matrix satisfy the conditions established for the development of a solid state dendritic morphology. © 2000 American Institute of Physics. [S0021-8979(00)06508-7]

I. INTRODUCTION

The CuInSe₂ (CIS) phase has been studied for photovoltaic applications due to a favorable band gap and relatively high absorption coefficient, which contribute to an attractive efficiency for solar cell operation.^{1,2} In the manufacturing process for photovoltaic thin film devices the CIS phase is produced by a reactive phase formation involving several steps. In addition, several thin film processing models for CIS synthesis, CIS crystal growth during solidification and phase equilibria information for the ternary Cu–In–Se system have been reported.^{3–6} For the Cu–In–Se ternary system, the Cu₂Se and In₂Se₃ phases have been suggested to represent a pseudobinary system including the intermediate CIS phase.^{6,7} The portrayal of the reactions involving Cu₂Se and In₂Se₃ to develop CIS is often represented in terms of a pseudobinary section. Of course, a true pseudobinary section would also satisfy the constraint that all tie lines representing equilibrium between coexisting phases would remain in the plane of the section. However, when several of the previous versions of the section that are shown in Fig. 1(a) are examined, it is evident that there is significant disagreement concerning the phase equilibria over major portions of the composition range. Indeed, some of the reported phase equilibria violate the phase rule. Although the direct application of bulk phase equilibria to thin film processing conditions must be done with care, the information presented in Fig. 1(a) is inconsistent and cannot be used to guide the analysis of processing. In an attempt to resolve the phase equilibria, a recent tentative assessment has been reported and is shown in Fig. 1(b).⁸ For the composition range of the CIS phase the work

of Boehnke⁴ has been accepted with the β phase as a defect chalcopyrite structure and the γ phase as a layered structure. While there are still gaps in phase equilibria information for certain composition ranges, the overall representation in Fig. 1(b) is self-consistent. At the same time, it is also evident that additional experimental data are necessary for a more complete assessment.

In applying the relationships given in Fig. 1(b) to the interpretation of reactive phase formation it is important to consider also the evolution of the diffusion path. In a binary system the diffusion path follows the connection between the end members along the tie lines between adjacent phases. In a pseudobinary section of a ternary system the diffusion path is not constrained to follow the tie lines in the plane. In a ternary system the diffusion path will usually depart from the straight line connecting path between the initial end members and in fact will cross this line at least once in order to satisfy mass balance. Under local equilibrium conditions the diffusion path will follow tie lines in two phase regions, but usually this path will not coincide with the pseudobinary section unless all components exhibit equal diffusivities. Moreover, due to transient kinetic conditions all of the phases encountered by the diffusion path may not form initially, but can develop at steady state. The diffusion path is invariant for steady state conditions in an infinite system, but can change with time in a finite system as the end members are modified by interdiffusion. While the pseudobinary behavior has been invoked in the analysis of CIS synthesis reactions during thin film processing, a clear determination of the diffusion path during reaction has not been defined in prior work. The identification of the diffusion pathway between Cu₂Se and In₂Se₃ during interdiffusion reaction together with the phase evolution and solubility behavior are

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(a)

(b)

FIG. 1. (a) Pseudobinary phase diagram of the Cu_2Se and In_2Se_3 system, (b) evaluated Cu_2Se – In_2Se_3 pseudobinary phase diagram (see Ref. 8).

important in determining the rate limiting factors in the processing of CIS and represent the objectives of the current work.

II. EXPERIMENT

Each of the Cu_2Se and In_2Se_3 ingots was prepared and sectioned by a diamond saw to yield slices with a nominal thickness of 3 mm. The sectioned pieces were coupled with clamps made of Invar to minimize thermal expansion during isothermal heat treatment. After isothermal annealing, the samples were mounted in epoxy and were cut perpendicular to the interface. Then, the reaction couples were polished with magnesia powders followed by $0.3\ \mu\text{m}$ alumina powders. The prepared reaction couples were investigated by scanning electron microscopy [(SEM)(JEOL 60)] and electron probe microanalysis [(EPMA)(CAMECA-SX50)].

The microstructures that were developed during the annealing of the reaction couples were observed by SEM. The component composition values were determined by EPMA. In the EPMA analysis the Cu_2Se phase was used as a standard for obtaining the Cu concentration, and the In_2Se_3 phase was used as a standard for attaining the concentration of In and Se. The reference crystals of lithium fluoride (LiF), thallium acid phthalate (TAP), and pentaerythritol (PET) were employed to analyze the elements Cu, Se, and In, respectively. The EPMA analysis was carried out without peak interference at an acceleration voltage of 15 kV and a beam current of 20 nA. In order to obtain crystallographic information, the Cu_2Se powders were also analyzed by using x-ray diffraction. The Cu_2Se powders were attached to the sample holder with double stick tape. A Philips computer-controlled diffractometer system was used in a reflection mode with Cu $K\alpha$ radiation at 40 kV and 25 mA. Typically, a step size of 0.05° (2θ angle) was used with a data collection time of 10 s per step.

The samples for transmission electron microscopy (TEM) observation were cut from the Cu_2Se part of the diffusion couple and thinned using an ion-milling method. The TEM investigation was carried out on a Philips CM200/ST microscope equipped with an energy dispersive x-ray (EDX) analysis system.

III. RESULTS AND DISCUSSION

A. The development of intermediate phases

A backscattered electron (BSE) image of the $\text{In}_2\text{Se}_3/\text{Cu}_2\text{Se}$ diffusion couple annealed for 1.5 h at 550°C is shown in Fig. 2(a) and the enlargement of the selected area of Fig. 2(a) is shown in Fig. 2(b) (secondary electron image) together with a schematic illustration to highlight different layers. EPMA line scanning results for the above reaction couple are given in Fig. 2(c). It should be noted that the composition axis of the pseudobinary phase diagram given in Fig. 1 is represented by mole % of In_2Se_3 , which does not indicate clearly the individual component concentration

FIG. 2. (a) BSE image of $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 550 °C for 1.5 h, (b) the enlargement of the selected area of (a); secondary electron image and the schematic illustration of the different diffusion layers, (c) EPMA line scanning of the $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ diffusion couple.

variation. In order to identify the corresponding component composition variation with respect to the mole % of In_2Se_3 , the calculated reference bar is indicated below the phase diagram. The reaction pathway was obtained as $\text{Cu}_2\text{Se}/\text{CIS}/\beta/\gamma/\text{In}_2\text{Se}_3$, in which three intermediate phases were developed. As identified by the contrast difference in Figs. 2(a) and 2(b), the EPMA line scan indicates a region

FIG. 3. BSE image of $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 550 °C for 8 h.

between the β phase and the In_2Se_3 end where the composition changes smoothly, until there is a drop in Cu concentration at 45 μm in Fig. 2(c). The observed composition profile is consistent with the most recent phase equilibria assessment in Fig. 1(b) indicating a narrow ($\beta + \gamma$) two-phase region. A decrease in the Cu concentration with distance indicates that Cu atoms move from the Cu_2Se phase to the In_2Se_3 phase. Similarly, increases in the In and Se concentration with distance indicate that In and Se atoms move from the In_2Se_3 phase to the Cu_2Se phase. When the reaction couple was annealed at 550 °C for 8.0 h (Fig. 3), the CIS and β phases were again developed clearly, and the In_6Se_7 phase was observed as a precipitate in the β and γ phase region. The thickness of the CIS phase increased from about 14 to 40 μm when the annealing time increased from 1.5 to 8 h at 550 °C. The growth of CIS phase followed diffusional growth kinetics ($k = x^2/t$) and the estimated kinetic parameter, k was $3.3 \times 10^{-8} \text{ cm}^2/\text{s}$. It should be noted that while the CIS phase layer grows under parabolic diffusion kinetics, the thickness of the β phase did not change with increasing annealing time. While it may be related to the precipitation of the In_6Se_7 phase in the β and γ phases and the change of the diffusion path, the origin of this growth behavior is not clear.

In order to examine the trajectory of the diffusion pathway, the EPMA line scanning results for the $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed for 1.5 h at 550 °C are plotted in Fig. 4. The estimated concentration ranges of the CIS, β and γ phases are shown in the shaded area. It is noted that the diffusion pathway did not follow the connecting line between Cu_2Se and In_2Se_3 (pseudobinary system). The diffusion pathway of $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couples annealed for 3.0 and 8.0 h at the same temperature was observed as $\text{Cu}_2\text{Se}/\text{CIS}/\beta(\text{In}_6\text{Se}_7)/\gamma/\text{In}_2\text{Se}_3$. Again, the diffusion pathway did not follow the pseudobinary system. It should be noted that all of the intermediate phases on the pseudobinary system are developed as well as the In_6Se_7 phase which mainly precipitates in the β phase layer region during the interdiffusion annealing (>3 h).

B. The development of CIS phase in the Cu_2Se phase

When the reaction couple is annealed at 550 °C, the CIS phase is observed not only as a diffusion layer, but also as

FIG. 4. The schematic isothermal phase diagram of In–Se–Cu at 550 °C [dotted curves indicate the diffusion pathway based upon EPMA line scans (circled points)] for the $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 550 °C for (a) 1.5 and (b) 3 h.

precipitates within the Cu_2Se side [Fig. 5(a)]. The concentration profiles of EPMA line scanning [Fig. 5(b)] confirmed that the precipitates are placed in the composition range of CIS phase, which is in equilibrium with Cu_2Se . It is noted that in the Cu_2Se phase the solubility of In is low (<2 at. %). In order to examine whether the development of the CIS precipitates is related to the interdiffusion reaction or is related to a change in solid solubility with temperature which yields precipitation during slow cooling, a diffusion couple was rapidly quenched after annealing at 550 °C for 1.5 h. The rapidly quenched diffusion couple developed a microstructure with CIS precipitates that is very similar to that in the furnace cooled sample [see Fig. 5(a)]. This indicates that the development of dendritic CIS precipitation occurs during interdiffusion and also suggests that the low solubility of In in Cu_2Se does not have a strong temperature dependence.

The BSE image of the Cu_2Se side (the same reaction couple) annealed at 650 °C for 1.5 h is shown in Fig. 6. The dendritic shape CIS phase precipitates in the Cu_2Se are clearly evident. The precipitates are uniformly but sparsely distributed in the Cu_2Se phase and show a reduced amount near the $\text{Cu}_2\text{Se}/\text{CIS}$ layer interface (right side of Fig. 6). The observation of a precipitation reaction within the Cu_2Se side of the diffusion couples clearly indicates that the diffusion reaction leading to the formation of the CIS phase proceeds along a virtual pathway involving the development of a supersaturation.⁹ Moreover, both the extent of the reaction and the dendritic morphology of the CIS precipitates raise some intriguing issues regarding the reaction kinetics.

The development of CIS phase precipitates throughout the Cu_2Se end of the diffusion couple indicates extremely fast In diffusion through the Cu_2Se phase. A rough estima-

FIG. 5. (a) BSE image of a CIS precipitate in the Cu_2Se side of a $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 550 °C for 1.5 h, (b) EPMA line scanning of the dendritic shape CIS phase developed in the Cu_2Se phase.

tion from the placement of the dendritic CIS phase can be obtained by employing, $x \cong (Dt)^{0.5}$, where D is diffusion coefficient, x is diffusion distance, and t is time. Taking the diffusion distance as about 1.5 mm and the annealing time as 1.5 h (from Fig. 6), the diffusion coefficient of indium in Cu_2Se is estimated as $4.2 \times 10^{-6} \text{ cm}^2/\text{s}$. The estimated diffu-

FIG. 6. BSE image of the Cu_2Se side of the $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 650 °C for 1.5 h. Note the development of CIS phase as dendritic precipitates within the Cu_2Se side.

sivity is quite high and approaching values normally considered for diffusion in liquids. However, there was no indication of liquid phase formation during the diffusion reaction.

The present observation of rapid atomic transport of In through Cu_2Se is also in agreement with other indications reported in the literature.^{2,10} This characteristic is considered in the analysis of phase synthesis during thin film processing to yield the CIS product.² However, the consequence of the rapid transport in modifying the reaction diffusion pathway has not been considered in the process models. The penetration of In through the Cu_2Se side of the bulk diffusion couple in 90 min at 550 °C clearly signifies that for thin film processing, the influence of a finite diffusion geometry is a major factor. One key point is that the diffusion pathway during CIS phase synthesis in thin films will vary with reaction time in a finite system.

In phases such as Cu_2Se that are characterized by covalent and ionic bonding the diffusivity is known to be sensitive to departures from exact stoichiometry which can generate significant point defect concentrations that will promote rapid atomic transport. Further a recent structural analysis of Cu_2Se reveals certain atomic configurations within the lattice that can act as channels to support the fast ionic transport of Cu.¹¹ This suggests a possible mechanism for the rapid diffusion behavior of In to follow the path of Cu along the vacancy sites. For example, the diffusion behavior in the CIS and Cu_2Se phases has been monitored with electrochemical cell experiments.^{12–15} At the room temperature, the order of the Cu chemical diffusion values in CIS and Cu_2Se have been reported to depend on composition and cover the range from about 10^{-6} to 10^{-10} cm^2/s and from about 10^{-6} to 10^{-8} cm^2/s , respectively. The composition dependence of chemical diffusion coefficient indicates that Cu vacancies play an important role for the ionic migration, in which the main diffusion mechanism has been concluded to be vacancy diffusion through copper sites.^{12,13} Since the Cu vacancy site can be an effective diffusion path for the In^{3+} ionic diffusion, it is assumed that In would diffuse in Cu_2Se at the same rate as Cu diffuses in the Cu_2Se phase. Based upon the analysis and data developed by Tinter and Wiehöfer¹³ the diffusivity of In in Cu_2Se at 650 °C is estimated to be about 5×10^{-7} cm^2/s which is generally consistent with the diffusion behavior observed during the precipitation of CIS within Cu_2Se .

The dendritic shape CIS phase development in the Cu_2Se phase appears to occur both within grains and at grain boundaries as shown in Fig. 7. Although the development of a dendritic morphology for solid state precipitates is not common, there have been several well documented examples.^{16–19} In analyzing the formation of dendritic CIS precipitates it is useful to consider the general requirements that have been identified by Doherty²⁰ as the following:

- (1) The precipitate-matrix interfacial energy should be relatively isotropic so that the formation of a shape perturbation does not induce an excessive increment of the interfacial energy. This condition is normally satisfied by a cube on cube orientation relationship between phases of the same structure.

FIG. 7. The optical micrographs of CIS precipitates in the Cu_2Se ($\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ reaction couple annealed at 550 °C for 3.0 h); (a) CIS precipitate developed at the grain boundary (marked “P1”), (b) CIS precipitate developed within the Cu_2Se grain (marked “P2”).

- (2) Diffusivity within the growing particle must be low, so that the shape perturbation can develop with minimal diffusional smoothing.
- (3) The lattice mismatch must be low. This results in a low interfacial diffusivity.
- (4) The precipitate nucleation density must be low so that the dendritic precipitate can develop before the overlap of diffusion fields from adjacent precipitates.

For the current case, conditions (2) and (4) are satisfied, since the number density of the dendritic CIS phase is low and the diffusion analysis indicates that for Cu, $D_{\text{CIS}}/D_{\text{Cu}_2\text{Se}} \approx 10^{-2} - 10^{-3}$. In order to examine the remaining conditions (1) and (3), it is necessary to consider the structural information concerning the CIS phases and find the orientation relationship between dendritic CIS precipitate and the Cu_2Se matrix.

C. Structure identification of the Cu_2Se and CIS phases

In order to understand the In diffusion behavior during the annealing process and the formation of the dendritic precipitate, the microstructures of the Cu_2Se matrix and the CIS precipitate were investigated. The Cu_2Se phase has many polytypes including tetragonal and face-centered-cubic (fcc)-type structures. The x-ray diffraction (XRD) spectrum of the Cu_2Se matrix is shown in Fig. 8. It is identical with that

FIG. 8. X-ray diffraction pattern of the Cu_2Se powder.

obtained by Sakuma *et al.*,¹¹ except for the appearance of two extra peaks near $2\theta \approx 13^\circ$ and $2\theta \approx 40^\circ$ which can be indexed as $1/2\{111\}$ and $3/2\{111\}$, respectively, suggesting a superstructure of the (111) plane in the Cu_2Se matrix. The notable feature for the XRD spectrum, both in the present work and that in the work of Sakuma *et al.*,¹¹ is that the diffraction factor for the $\{200\}$ plane is nearly zero, whereas this diffraction peak always appears in the other fcc structures for the $\alpha\text{-Cu}_2\text{Se}$ phase. Therefore, it is concluded that the basic structure of the $\alpha\text{-Cu}_2\text{Se}$ matrix is the same as the atomic structure determined in the literature¹³ with the space group $Fm\bar{3}m$ as shown in Fig. 9(a), where the Se anions at $4a$ (000) sites are not illustrated. The copper cations take the $32f(xxx)$ site with $x=0.297$ (denoted as $32f_I$) and $x=0.471$ (denoted as $32f_{II}$), respectively. The average occupancy for the copper ion is 22% at the $32f_I$ site and 3% at the $32f_{II}$ site. Based upon an estimation of the interstitial space in the Cu_2Se structure and the indium ion size, the possibility of the indium interstitial diffusion has been ruled out. However, considering the very low occupancy of the Cu ions in the lattice and the double periodicity of (111) plane of the Cu_2Se structure (refer to Fig. 8), it is reasonable to suppose an ordering distribution of vacancies at $32f$ sites in (111) plane. A two-dimensional projection of the Cu_2Se lattice to a (110) plane is shown in Fig. 9(b). The $(1\bar{1}1)$ planes are perpendicular to the plane of the paper and indicated by bold lines. The $32f$ sites circled with a dashed line are supposed to have a much lower occupancy than average. The ordering of the lower-occupancy plane may account for the double periodicity of (111) plane and provide the In ions with a rapid transport path for substitutional diffusion.

As for the structure of the CIS phase, the most stable structure is chalcopyrite type at one atmosphere regardless of synthesis method.^{21–25} Under high pressure it may transform to a NaCl-type structure with higher coordination.²⁶ On release of the pressure, a metastable zinc blende-type structure may be produced as an intermediate phase before the stable chalcopyrite structure is restored at ambient pressure. An

FIG. 9. (a) The atomic structure of Cu_2Se with the space group of $Fm\bar{3}m$, (b) two-dimensional projection of the Cu_2Se lattice to a (110) plane.

electron diffraction technique was used to obtain structural information for the CIS phase formed within the Cu_2Se matrix during solid state diffusion. The CIS precipitate phase was found to have a zinc blende (fcc) structure. At the same time, the similarities between the zinc blende- and chalcopyrite-type structures suggest that the slow diffusion of In and Cu in the CIS phase compared to Cu_2Se would also apply for the metastable structure.

A high-resolution TEM (HRTEM) image from a region near the precipitate–matrix interface is given in Fig. 10. The semicoherent interfacial structure and microstrain contrast near the interface is evident. The common diffraction pattern from the CIS phase and the Cu_2Se matrix is shown in Fig. 11(a). The indexing for the two sets of the electron diffraction patterns (EDPs) is shown in Fig. 11(b). The lattice parameters for these two phases are similar and the orientation relationship between them can be denoted as

$$\langle 011 \rangle_{\text{CIS}} // \langle 011 \rangle_{\text{Cu}_2\text{Se}}, \{200\}_{\text{CIS}} // \{200\}_{\text{Cu}_2\text{Se}},$$

i.e., they have the same crystallographic orientation and similar unit cell size. The lattice parameter for the CIS phase is slightly larger than that for the Cu_2Se matrix.

The establishment of the structure of the CIS precipitates as a zinc blende type that allows for the observation of a cube-on-cube orientation relationship and a coherent precipitate–matrix interface also signifies that all of the cri-

FIG. 10. [011]-zone HRTEM image for the CIS phase and the Cu_2Se matrix. A semicoherent interface and microstrain contrast near the interface can be identified.

teria necessary to develop a dendritic morphology during solid state precipitation have been satisfied, but with a metastable phase formation reaction. The kinetic selection that favors the metastable zinc blende structure for the precipitate over the stable chalcopyrite structure can also be understood from the component composition profiles associated with the diffusion pathway. Even though the atomic transport of In through the Cu_2Se phase is very rapid, the solubility of indium in Cu_2Se is low based upon the EPMA measurements. This suggests that the relative supersaturation of indium in Cu_2Se that is available as the driving free energy for nucleation of the CIS phase is small. For the most part, the kinetic phase selection during nucleation is governed by the work to develop a nucleus which can be expressed by $\Delta G^* = A\sigma^3/\Delta G_v^2$, where A is a geometric factor, σ is the precipitate–matrix interfacial energy, and ΔG_v is the driving free energy which is related to the supersaturation, S (e.g., $\Delta G_v = kT \ln S$, where k is the Boltzmann constant and T is temperature). The overall nucleation rate is proportional to $\exp[-\Delta G^*/kT]$ so that for a low S only product phases with a low value for σ will be selected in the nucleation competition. Thus, precipitate structures that provide for coherent interfaces and low σ such as the zinc blende structure are favored by an overwhelming margin. Moreover, the low value for S will also yield a relatively low nucleation product phase density which will allow for significant precipitate growth under a dendritic morphology before diffusion field impingement between neighboring precipitates.

IV. SUMMARY

The clear identification of the diffusion pathway on Cu–In–Se system is important for analyzing the formation kinetics of CIS (CuInSe_2) phase. The product phases obtained from $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$ diffusion couples annealed at 550 °C for 1.5 h were observed as CIS, β and γ phase. Based upon the concentration profiles, it is evident that the diffusion pathway does not follow the Cu_2Se – In_2Se_3 pseudobinary isoplethal section. The fluxes of components exhibited maximum values in the CIS phase. For the same reaction

(a)

(b)

FIG. 11. (a) A common diffraction patterns (both are [011]-zone) from the CIS phase and the Cu_2Se matrix; (b) schematic to illustrate the indexing of the two diffraction sets from the two phases.

couple annealed at 550 °C for 3 and 8 h, the In_6Se_7 phase was also developed inside β phase. In the Cu_2Se phase, the dendritic shape CIS phase formed within the Cu_2Se grains and at the Cu_2Se grain boundaries, indicating that In is the fast component in diffusion through Cu_2Se , following ionic lattice diffusion through the Cu vacancy sites of Cu_2Se the phase. The transient path is also indicated by the rapid transport of In in Cu_2Se which yields precipitation of the CIS product within the Cu_2Se side of the bulk diffusion couple. The changing diffusion pathway also signifies that the interdiffusion reaction proceeds in a finite system which will be important in thin film processing. A metastable zinc blende-type structure (fcc) of the CIS phase was developed in a fcc Cu_2Se matrix by a solid state precipitation reaction. The orientation relationship and the similar structure between these two phases as well as their relative diffusion and nucleation behavior account for the development of the CIS dendritic morphology within the Cu_2Se matrix.

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- ¹A. Rockett and R. W. Birkmire, J. Appl. Phys. **70**, R81 (1991).
- ²R. Klenk, T. Walter, H.-W. Schock, and D. Cahen, Adv. Mater. **5**, 114 (1993).
- ³K. Lu, J. H. Perepezko, K. A. Lindahl, and B. Lanning, Philos. Mag. Lett. **76**, 299 (1997).
- ⁴U.-C. Boehnke and G. Kuhn, J. Mater. Sci. **22**, 1635 (1987).
- ⁵J. von Bardeleben, J. Appl. Phys. **56**, 321 (1984).
- ⁶J. Parkers, R. D. Tomlinson, and M. J. Hamshire, J. Cryst. Growth **20**, 315 (1973).
- ⁷K. J. Bachmann, H. Goslowsky, and S. Feichter, J. Cryst. Growth **89**, 160 (1988).
- ⁸C. H. Chang, A. Davydov, B. J. Stamberry, and T. J. Anderson, Proceedings of the 25th IEEE PVSC, 1996 (unpublished), p. 849.
- ⁹J. S. Kirkaldy and D. J. Young, *Diffusion in the Condensed State* (The Institute of Metals, London, 1987).
- ¹⁰E. Buhks, Sol. Energy Mater. **13**, 213 (1986).
- ¹¹T. Sakuma, K. Suguyama, E. Matsubara, and Y. Waseda, Mater. Trans., JIM **30**, 365 (1989).
- ¹²G. Dagan, T. F. Ciszek, and D. Cahen, J. Phys. Chem. **96**, 11 009 (1992).
- ¹³U. Tinter and H.-D. Wiehöfer, Solid State Ionics **9&10**, 1213 (1983).
- ¹⁴I. Lyubomirsky, M. K. Rabinal, and D. Cahen, J. Appl. Phys. **81**, 6684 (1997).
- ¹⁵I. Lubomirsky, K. Gartsman, and D. Cahen, J. Appl. Phys. **83**, 4678 (1998).
- ¹⁶R. A. Rick, A. J. Porter, and R. C. Ecob, Acta Metall. **31**, 41 (1983).
- ¹⁷S. R. Summerfelt and C. B. Carter, Acta Metall. Mater. **40**, 1051 (1992).
- ¹⁸M. F. Henry, Y. S. Yoo, D. Y. Yoon, and J. Choi, Metall. Trans. A **24**, 1733 (1993).
- ¹⁹J. H. Perepezko, Microstructure stability in Intermetallic Compounds, Vol. 1, *Principles*, edited by J. H. Westbrook and R. L. Fleischer (Wiley, New York, 1994), Chap. 36, p. 849.
- ²⁰R. D. Doherty, Met. Sci. **16**, 1 (1982).
- ²¹Y. Kuwahara, H. Oyanagi, H. Yamaguchi, M. Aono, S. Shirakata, and S. Isoomura, J. Appl. Phys. **76**, 7864 (1994).
- ²²E. Tzvetkova, N. Stratieva, M. Ganchev, I. Tomov, K. Ivanova, and K. Kochev, Thin Solid Films **311**, 101 (1997).
- ²³L. Margulis, G. Hodes, A. Jakubowicz, and D. Cahen, J. Appl. Phys. **66**, 3554 (1989).
- ²⁴J. M. Merino, J. L. Martín de Vidales, S. Mahanty, R. Díaz, and F. Rueda, J. Appl. Phys. **80**, 5610 (1996).
- ²⁵A. Jayaraman, P. D. Dernier, H. M. Kasper, and R. G. Maines, High Temp.-High Press. **9**, 97 (1977).
- ²⁶K. J. Range, G. Engert, and A. Weiss, Solid State Commun. **7**, 1749 (1969).