

LIQUID PHASE DEPOSITION OF SINGLE-PHASE ALPHA-COPPER-INDIUM-DISELENIDE

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Introduction

The success of exploratory missions in outer space often depends on a highly efficient renewable energy supply, as provided by solar cells. Figure 1 shows a well-known example: The robotic vehicle “Rover,” constructed for NASA’s “Mars Pathfinder” mission. The solar cells for such applications not only need to have high conversion efficiency, but must possess a high *specific* power, thus a high power output per unit mass. Since future missions will demand for large aggregates of solar cells and space flights are expensive, the solar cells must furthermore be available at low costs (per unit power output) and – very important in outer space – have a long lifetime and a high resistance against structural damage introduced by irradiation with high-energy electrons and protons.

The photovoltaic materials that are presently available only partly fulfill all these requirements. Therefore, we propose to explore a new method for fabricating thin-films for cost-efficient solar cells with very high specific power, high irradiation resistance, and long lifetime, based on the α -phase of the Cu–In–Se system, “ α -CIS.”

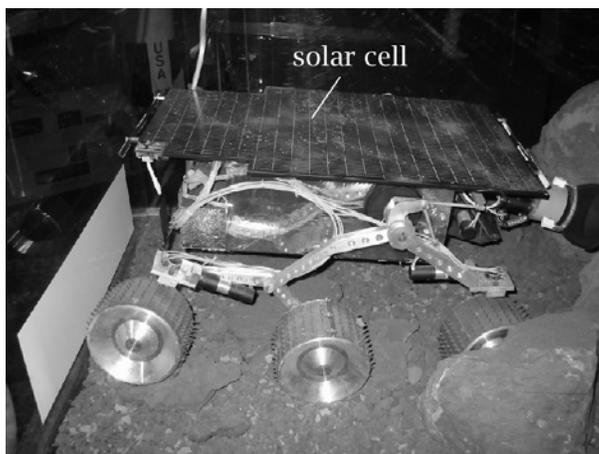


Fig. 1: The robotic vehicle “Rover,” which NASA sent to the surface of planet Mars (exhibit at NASA Glenn Research Center, Cleveland).

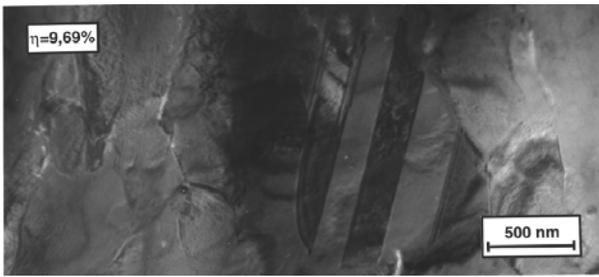


Fig. 2: Cross-sectional TEM image of a CIS film grown at 460 to 520 °C by PVD. Cu:In:Se ratio in the vapor: 1:1:2. Composition measured by XEDS: $\text{Cu}_{25.5}\text{In}_{24.8}\text{Se}_{49.8}$.

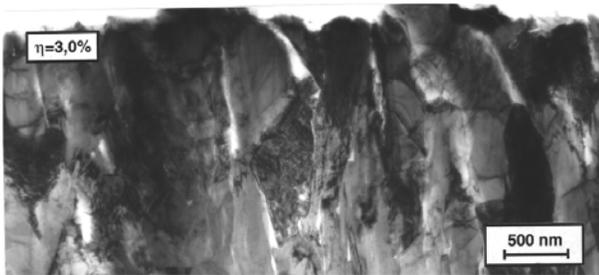


Fig. 3: Cross-sectional TEM image of a CIS film grown at 460 to 520 °C by PVD. Cu:In:Se ratio in the vapor: 1:3:5. Composition measured by XEDS: $\text{Cu}_{24.0}\text{In}_{25.9}\text{Se}_{50.2}$.

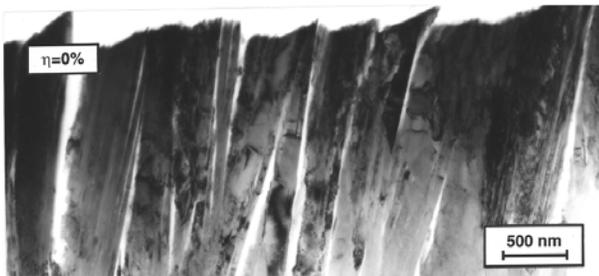


Fig. 4: Cross-sectional TEM image of a CIS film grown at 430 °C by PVD. Cu:In:Se ratio in the vapor: 1:2:3.5. Composition measured by XEDS: $\text{Cu}_{16.6}\text{In}_{32.2}\text{Se}_{51.2}$.

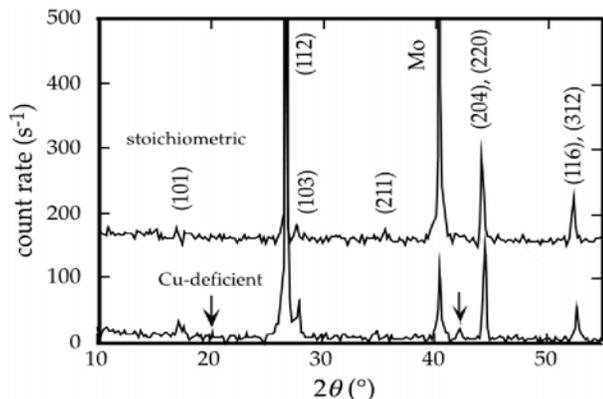


Fig. 5: X-ray scans of PVD-grown thin-films with stoichiometric (CuInSe_2) and with Cu-deficient composition.

The stoichiometric composition of α -CIS corresponds to CuInSe_2 . It has long been known that this compound possesses outstanding properties for thin-film solar cells. So far, however, one cannot fully exploit the advantages of this material, because it is not possible to make α -CIS layers with a sufficiently low concentration of structural and, consequently, electronic defects. In this paper, we describe a research program to overcome these limitations and to optimize the fabrication of α -CIS thin-films for solar cell applications in outer space.

Presently, the CIS films with the best photovoltaic performance are grown by physical vapor deposition (PVD). However, such films contain high concentrations of structural defects, which degrade their efficiency in photovoltaic devices: point defects, dislocations, large-angle grain boundaries, pores, anti-phase boundaries, cracks, or inclusions of other phases and, correspondingly, interphase interfaces [1].

Figures 2, 3, and 4 present cross-sectional TEM (transmission electron microscopy) bright-field images revealing these kinds of defects in CIS thin-films grown under a variety of different conditions by the group of H.-W. Schock at the Institut für Physikalische Elektronik, University of Stuttgart, Germany. The microcharacterization, including TEM, was carried out as part of the Ph.D. project of T. Haalboom at the Max-Planck-Institut für Metallforschung (*Materials Science*) in Stuttgart, Germany, under the supervision of F. Ernst.

As apparent from the micrographs, the microstructure sensitively depends on the processing conditions. For a Cu:In:Se ratio of 1:1:2 in the vapor, high temperatures (between 460 and 520 °C) lead to relatively large grains. Low temperatures (430 °C), in contrast, lead to the formation of extended, plate-like crystallites.

In addition to the defects mentioned before, thin-films grown with a Cu:In:Se ratio near 1:1:2 in the vapor always exhibit a high density of stacking faults and twin boundaries.

Another problem of PVD, apart from the high defect density in the films, is to control the chemical composition. Analysis of the films in Figs. 2, 3, and 4 by XEDS (X-ray energy-dispersive spectroscopy) revealed that the actual, local chemical composition of the thin-films may substantially differ from the nominal composition of the vapor (indicated in the figure captions). As demonstrated by the X-ray scans in Fig. 5, even slight deviations from the ideal composition CuInSe_2 lead to the formation of secondary phases. The two X-ray scans were obtained from stoichiometric and Cu-deficient CIS films. Both diffraction patterns exhibit reflections of the (desired) α - CuInSe_2 phase [2] and Mo-reflections of the substrate. Additional reflections at $2\theta =$

21.8° and 42.6°, however, indicate the presence of a second phase (defect phase β [3]) in the Cu-deficient material. Since the presence of second phases has a particularly adverse effect on the conversion efficiency [4], this material is not suitable for photovoltaic devices.

The present record of conversion efficiency with PVD α -CIS thin-films is at 18.8 % [5]. While this number is impressive, the theoretical conversion efficiency is still 30% higher (24%) [6]. Moreover, the efficiency of standard PVD material is way below 18%. There is no doubt that the high concentration of grain boundaries and phase boundaries encountered in PVD-grown material accounts for the major part of the discrepancy between actual and theoretical conversion efficiency [4]. Annealing can somewhat improve the structural properties, but usually of the film composition (particularly the Se content) and causes segregation [7-10].

The conversion efficiency of PVD-grown α -CIS thin-films is limited by structural defects, which form because these films grow far from thermodynamic equilibrium, under high driving forces, but with small atomic mobility. A promising approach for improving the structural quality of α -CIS, therefore, is by growing it from the melt, close to thermodynamic equilibrium.

CIS Growth from the Melt

Near-equilibrium growth from the melt will not only allow the fabrication of *single-phase*, pure α -CIS, but should also enable the growth of macroscopic α -CIS single crystals. Single crystals of α -CIS are valuable for studying the *intrinsic* properties of α -CIS, and to find out how much room there really is for improving the conversion efficiency of α -CIS thin-film solar cells by improving the structural quality of the material.

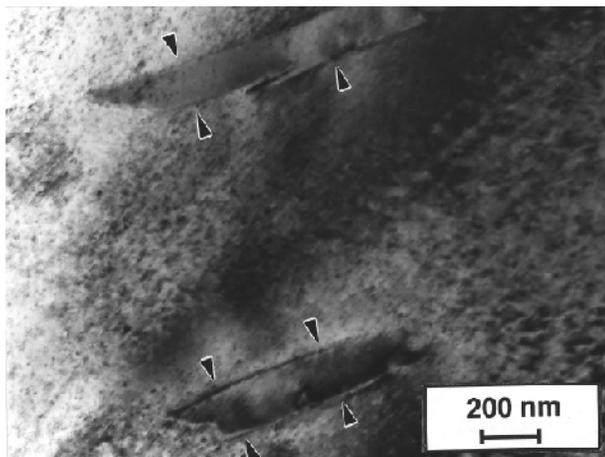


Fig. 6: TEM image revealing the presence of a second phase (“ β ”, arrowed regions) in a “single crystal” of $\text{Cu}_{23.6}\text{In}_{25.9}\text{Se}_{50.5}$.

Following this idea, C. R. Schwerdtfeger at the National Renewable Energy Laboratory (NREL) employed high-pressure, liquid-encapsulated directional solidification to grow (Cu-deficient) α -CIS single crystals and obtained apparently coarse-grained macroscopic crystals [11, 12]. However, no study of the microstructure of this material has been published. More recent attempts of M. Hornung to grow α -CIS single-crystals from the melt by the vertical gradient freeze method also failed [13]. SEM (scanning electron microscopy) and TEM studies on the largest grains of these “single crystals” revealed that they were never even single-phase α -CIS, but always contained a second phase (β) and an enormous density of α/β phase boundaries [14]. Fig. 6 presents an example from this material: a TEM image revealing particles of the β -phase in an α -CIS “single crystal”. Note that the β particles did not form because the solidified material had the incorrect composition. Careful analysis of chemical composition by XRF (X-ray fluorescence analysis) and ICP-OES (inductively-coupled plasma optical emission spectroscopy) confirmed that the composition of this material was

$\text{Cu}_{23.6}\text{In}_{25.9}\text{Se}_{50.5}$, thus sufficiently close to the stoichiometric composition of α -CIS for obtaining a single-phase material. The latest reports on α -CIS single crystals are by Cahen *et al.* [15], but again no detailed microstructural studies were published.

Cu–In–Se Phase Equilibria

To understand these drawbacks, we have recently investigated all phase equilibria of the entire Cu–In–Se system and determined the first complete and correct ternary phase diagram [16-18].

The new phase diagram, which constitutes one of the most complicated ternary phase diagrams known so far, explains why it is difficult (if not impossible) to grow single-phase α -CIS from a melt with the composition equal to or close to CuInSe_2 . Consider the $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ isopleth of Fig. 7, for which we have proven that it actually constitutes a *quasi*-binary vertical section of the Cu–In–Se phase diagram. On cooling a melt with the composition CuInSe_2 , the first solid phase is not α -CIS, but a high-temperature phase we denote as δ_{H} . On further cooling, α -CIS should then form from δ_{H} via a phase transformation. However, the melting point maximum of the δ_{H} phase field lies at a Cu content of 23.5%, thus considerably off (on the left hand side of α -CIS in Fig. 7) the 25.0% composition required for stoichiometric α -CIS (CuInSe_2). Therefore, if one tries to grow single-phase α -CIS by cooling down a melt with a composition in the vicinity of the stoichiometric composition CuInSe_2 , one first obtains the phase δ_{H} , which has the “incorrect” composition $\text{Cu}_{23.5}\text{In}_{26.0}\text{Se}_{50.5}$, surrounded by more Cu-rich material. On further cooling, this material cannot perfectly transform to α -CIS, owing to the limited kinetics. Instead, it will transform to $\alpha + \delta_{\text{R}}$. Consequently, one obtains a high density of phase boundaries.

Starting out from a composition not equal to but in the vicinity of CuInSe_2 does not yield single-phase material, either. As revealed in isothermal sections of the Cu–In–Se phase diagram [16-18], α -CIS establishes two-phase and three-phase equilibria with *nine* different phases! This variety of phase equilibria explains the difficulties other researchers have encountered when attempting to grow CuInSe_2 single crystals.

1.1 How to Solve the Problem

Figure 8, taken from [18], represents the most important data for our project: the projection of the *liquidus surface* of the Cu–In–Se phase diagram onto the composition triangle. (The liquidus surface separates liquid and solid phases in the ternary phase diagram. Figure 8 constitutes a topographical map of the liquidus surface, where contour lines indicate the temperature.) Figure 8 confirms in a more comprehensive (three-dimensional) way than the isopleth of Fig. 7 that a melt with the composition CuInSe_2 does *not* precipitate α -CIS, but the phase δ_{H} – and this is the reason why previous attempts to grow single-phase α -CIS from the melt have failed. On the other hand, the liquidus surface exhibits four different faces that *do* enable *direct*, “primary crystallization” of α -CIS from the melt (shaded regions in Fig. 8). However, the corresponding compositions are far away from the composition CuInSe_2 . This explains that direct precipitation of α -CIS from the melt was not discovered “accidentally.”

Summarizing, the new phase diagram explains the difficulties associated with growing single-phase α -CIS from a melt with the composition near CuInSe_2 , but also suggests melt compositions that do precipitate single-phase α -CIS *directly*, without causing any phase transformation such as $\delta_{\text{H}} \rightarrow \alpha$.

Liquid-Phase Deposition of α -CIS

According to Fig. 8, it should be possible to grow single-phase α -CIS thin-films by *liquid-phase deposition* (LPD) – by casting a melt with a composition within one of the shaded fields of Fig. 8 over a substrate, and cooling it slowly to a temperature somewhat below the liquidus temperature. According to Fig. 8, the melt will then *directly* precipitate a film of α -CIS onto the substrate, without further phase transformations. After the film has reached the desired thickness, the melt is removed from the substrate. Subsequently, the system is cooled to room temperature.

Since the material grown from the melt will be pure α -CIS and solidifies under near-equilibrium conditions, we anticipate substantially lower concentrations of structural defects than in PVD layers, and thus major advantages in photovoltaic efficiency (by definition, defects are non-equilibrium features). Indeed, the TEM image of Fig. 9, recently obtained from α -CIS material produced during the experiments carried out to determine the new phase diagram, reveals coarse-grained, pure α -CIS with a *much* lower concentration of defects than Figs. 2, 3, and 4.

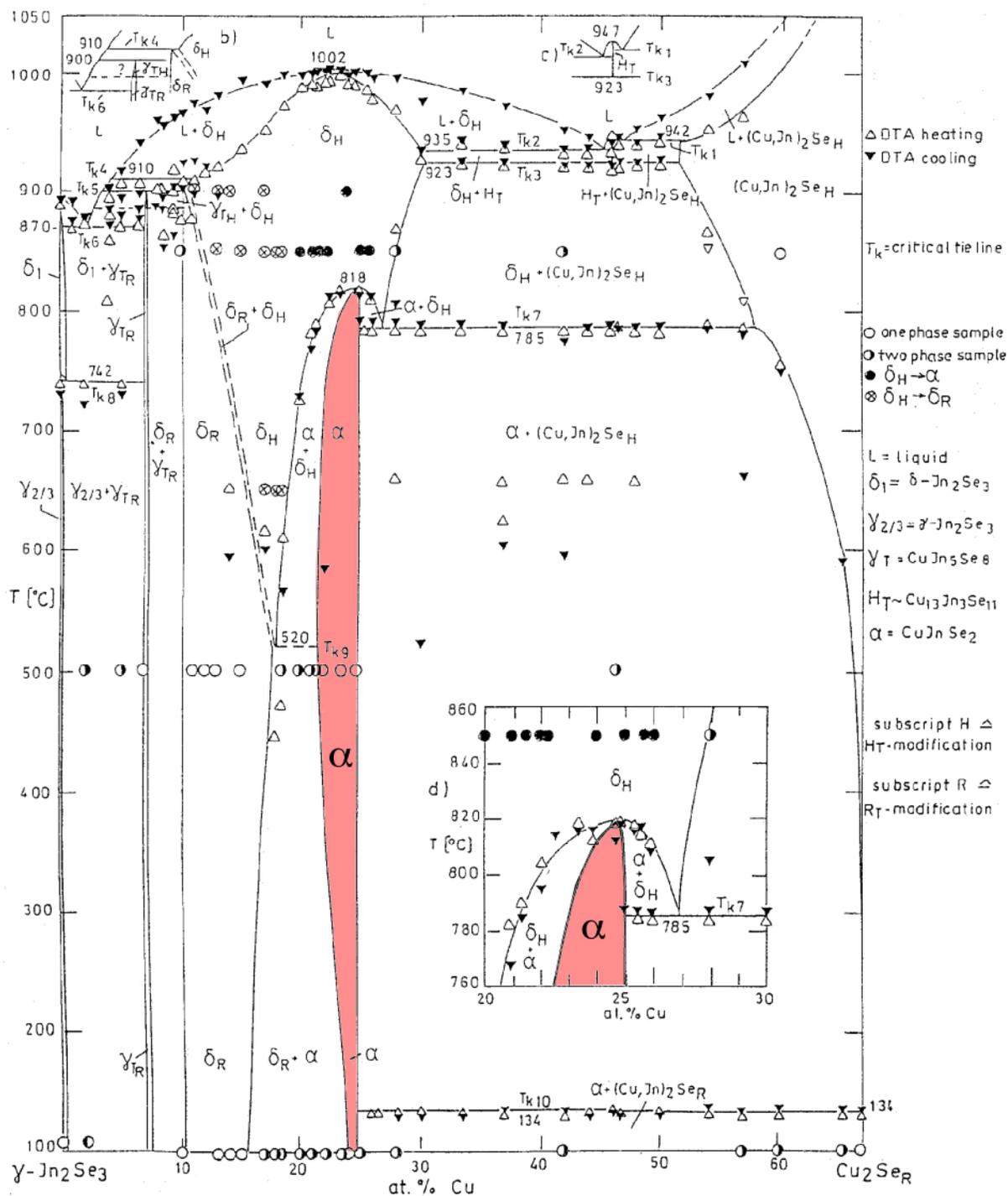


Fig. 7: The $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ isopleth, a *quasi-binary* vertical section of the new phase diagram.

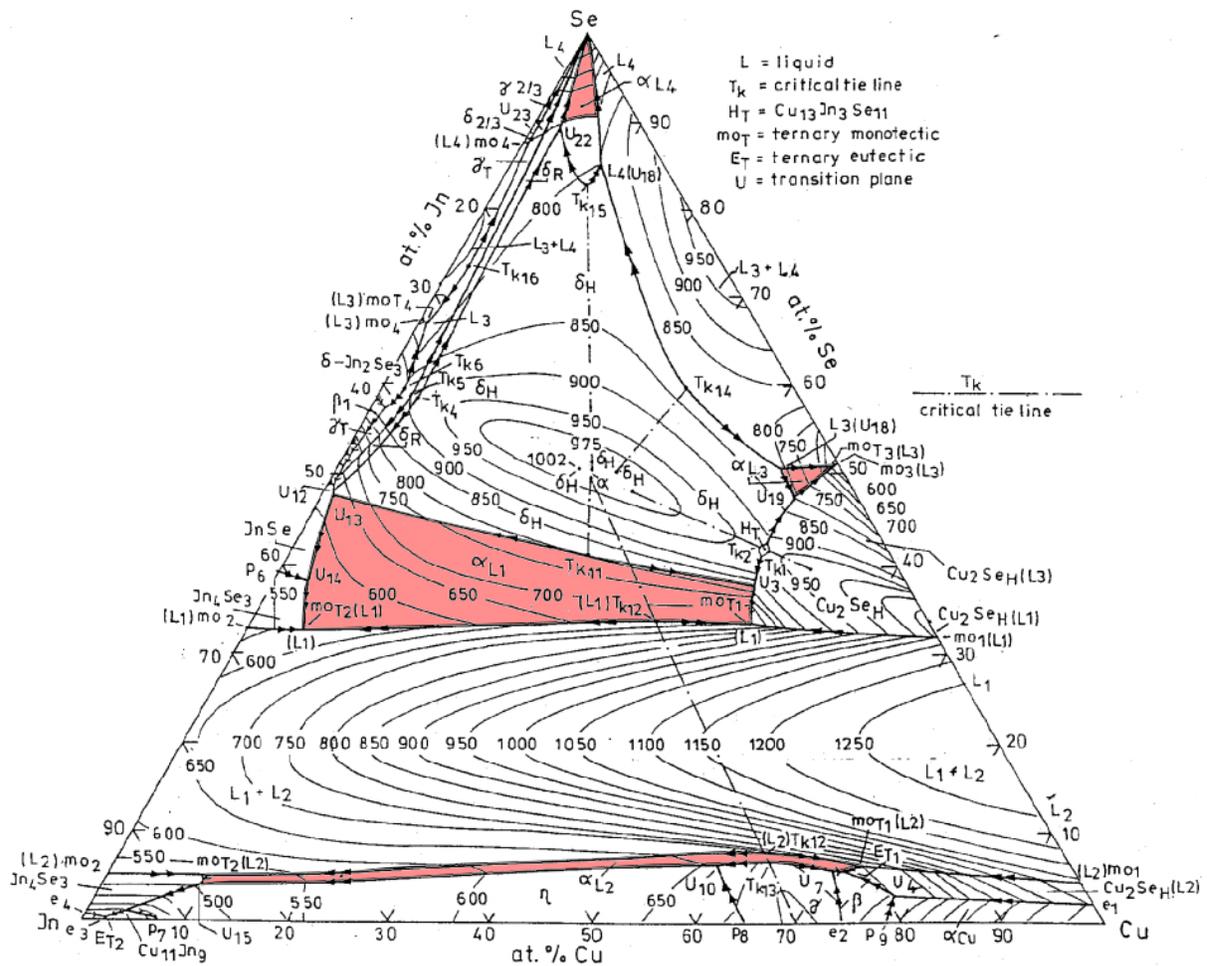


Fig. 8: Projection of the liquidus surface of the Cu–In–Se phase diagram onto the composition triangle. The four shaded areas indicate surfaces of primary crystallization of α -CIS – thus melt compositions from which α -CIS precipitates *directly*, with no further phase transformations.

Contrary to the typical PVD-grown material, moreover, LPD-grown α -CIS will be (nearly) *thermodynamically stable*. Since it is single-phase α -CIS, its lifetime in a solar cell will not be limited by ongoing diffusional phase transformations. Note that at low temperatures, the phase field of α -CIS, shaded in Fig. 7, becomes very narrow. A material outside of this narrow compositional range, as typically encountered in PVD-deposited thin-films, is not thermodynamically stable and will undergo diffusional phase transformations that may limit its lifetime in a solar cell. This issue is even more important in outer space than on the ground, because the cosmic radiation (vacancies by knock-on events) [19] and higher operating temperature owing to lack of heat convective heat release (no air) promote diffusion.

According to the isopleth in Fig. 10, it should be possible to precipitate α -CIS at temperatures below 400°C. This opens the perspective to deposit α -CIS thin-films onto temperature-resistant polymer films, enabling the fabrication of solar cells with very high-specific-power (power output per unit mass). Moreover, LPD will allow the fabrication of larger modules than PVD and can decrease the fabrication costs of α -CIS photovoltaic devices, because the deposition rate of LPD is much higher than for PVD, and LPD does not require UHV chambers, which are costly to set up and costly to maintain. Experiments of the Liquid-Phase Epitaxy Group at the Max-Planck-Institut für Festkörperforschung have shown that large ($\varnothing=4$ in) wafers can be efficiently coated by *centrifuging* the melt by rotating the substrate.

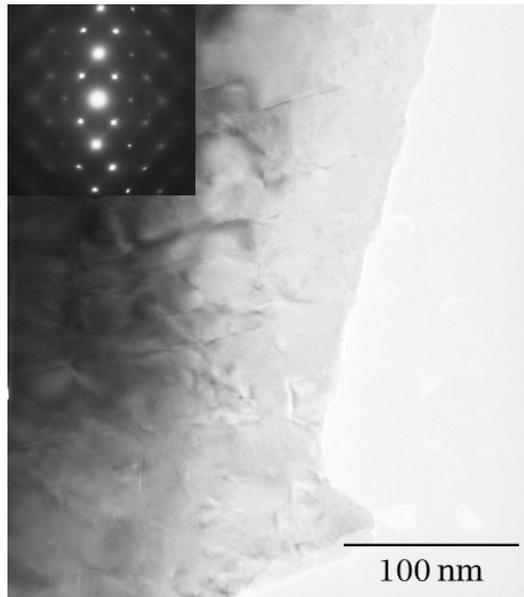


Fig. 9: TEM image of α -CIS produced during the experiments we carried out to determine the new phase diagram. The diffraction pattern (inset) confirms that the region imaged here is a large grain of single-phase α -CIS.

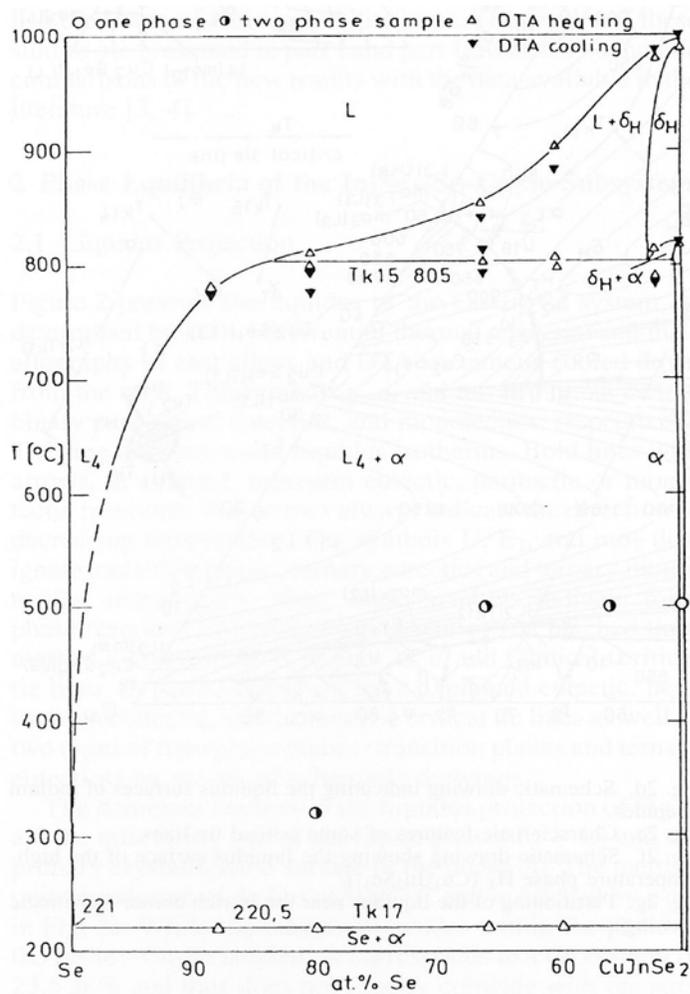


Fig. 10: Se-CuInSe₂ isopleth of the Cu-In-Se phase diagram [16-18].

Experimental

For the experimental technique of depositing a solid thin-film from a ternary liquid phase we will draw on the experience that has been gained with the deposition of $\text{Si}_x\text{Ge}_{1-x}$ thin-films from a Si–Ge–Bi melt in the Liquid-Phase Epitaxy Group at the Max-Planck-Institut für Festkörperforschung [20-22].

Fig. 11 presents a schematic cross-sectional view of a first, basic experimental setup we have installed for LPD of α -CIS. The experimental procedure is very similar to the one we have successfully applied for DTA (differential thermal analysis) in our study of phase equilibria of the Cu–In–Se system [16-18]. The material for the melt, a few grams of high-purity Cu, In, and Se, are encapsulated in a quartz tube. After evacuating the tube, it is flushed with Ar at 820 mbar. Encapsulating the material in quartz tubes allows us to observe the changes occurring during processing. In particular, by observing the diffusion zone at Cu stripes protruding from the Se or In melt we can carefully control the temperature. Owing to the large heat of formation and the high vapor pressure of Se, fusion of Cu–In–Se alloys normally causes excessive agitation of the components. The Ar-filling of the tubes, however, solves this problem [13].

After fusing the metal pellets, the newly formed solid solution is annealed in a muffle furnace for up to one hour at 950 °C. To improve the homogeneity of the temperature distribution during this treatment, the silica tube is embedded in a large body of heat-resistant steel. Subsequently, the tube is cooled in air and the ingot inspected. By mechanical agitation, we detach the newly formed material and any left-over of the ingot from the tube walls, put the tube back into the muffle furnace and melt it a second time. Depending on the composition, the melting point may vary between 950 and 1020 °C. After the fusing the ingot in an induction furnace, the ingot material is removed from the quartz tubes and broken up into

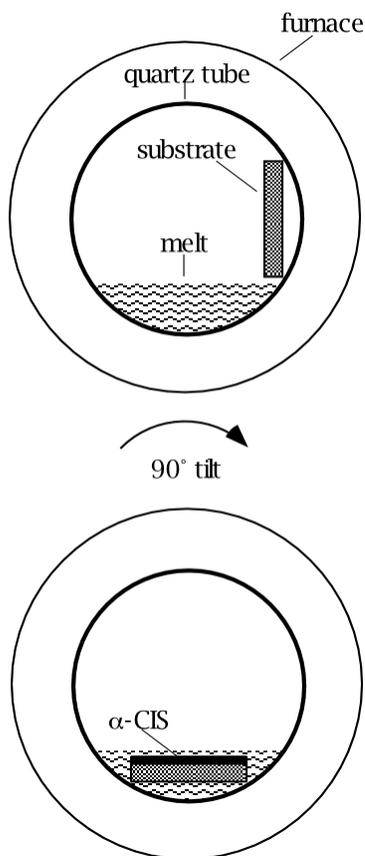


Fig. 11: Schematic cross-sectional view of the setup for liquid-phase deposition of α -CIS.

smaller sizes, each weighing approximately 250 mg. To confirm the homogeneity of the ingots, three separate pieces of the ingot taken from different regions of the ingot are prepared for XRD, DTA and XEDS analysis. By performing XEDS measurements the stoichiometry of the ingots are confirmed not only locally within the ingot but throughout. DTA confirms the liquidus projection, shown in Fig. 8, for any given composition.

A commercial tube furnace, equipped with a large-diameter (10 cm) quartz tube and a good temperature control (± 0.5 K), serves for the actual LPD experiments. After the liquidus temperature and the composition of the ingot are confirmed, a piece of ingot, •250 mg, is loaded (along with the substrate) into another quartz tube, where the actual LPD experiment takes place (Fig. 11b). By slowly heating the furnace to a temperature between 550 °C and 1020 °C (depending on the composition of the ingot), a homogeneous melt results. Then the quartz tube is tilted by 90°, such that the melt wets the substrate. By means of an electronic temperature control, we cool the melt to a well-defined temperature somewhat (ideally about 1°) below the temperature of the liquidus surface. Accordingly, the melt will begin to precipitate α -CIS.

In the presence of the substrate, nucleation of α -CIS does not begin homogeneously, in the melt, but heterogeneously, at the surface of the substrate. Subsequently, a closed layer of α -CIS grows and

covers the substrate. After the layer has grown to the desired thickness, the quartz tube is tilted back to the original position (Fig. 11b) and the system cooled down to room temperature.

If we choose the composition of the ingot in one of the four regions of the composition triangle where Fig. 8 indicates primary crystallization of α -CIS, the above procedure should produce a thin-film of single-phase α -CIS on the substrate.

First Results

Ingots were prepared from all primary phase fields represented on the liquidus projection of the Cu-In-Se system (shown in Fig. 8). Many initial attempts to produce thin-film α -CIS failed due to the inability of the melt to wet the substrate. For this reason, we used quartz substrates sputter-coated with 1 μm of Mo, followed by 100 nm of Cu. The intention was to increase the surface energy of the Mo layer. The Cu layer, deposited after the Mo layer without breaking vacuum to the chamber, served to inhibit surface contamination on the Mo. During the liquid-phase deposition process, the Cu layer diffused into the ingot material without altering the ingot composition to any significant extent, revealing a contaminant-free Mo layer. With the incorporation of these Cu coated substrates, we were able to deposit films from all four composition fields suitable for primary precipitation of α -CIS, as indicated in Fig. 8.

The liquidus projection of Fig. 8 gave us the temperature in which nucleation of α -CIS would occur. However, to confirm the exact liquidus temperature of the ingots that were fused together, DTA was employed. Fig. 12 shows the DTA plot for ingot designated I1b. From Fig. 12 the liquidus projection is found to be 667 °C. This is in good agreement with the projection given in Fig. 8. A small deviation results from making a composition up which lies slightly off one of the 700 °C contour lines.

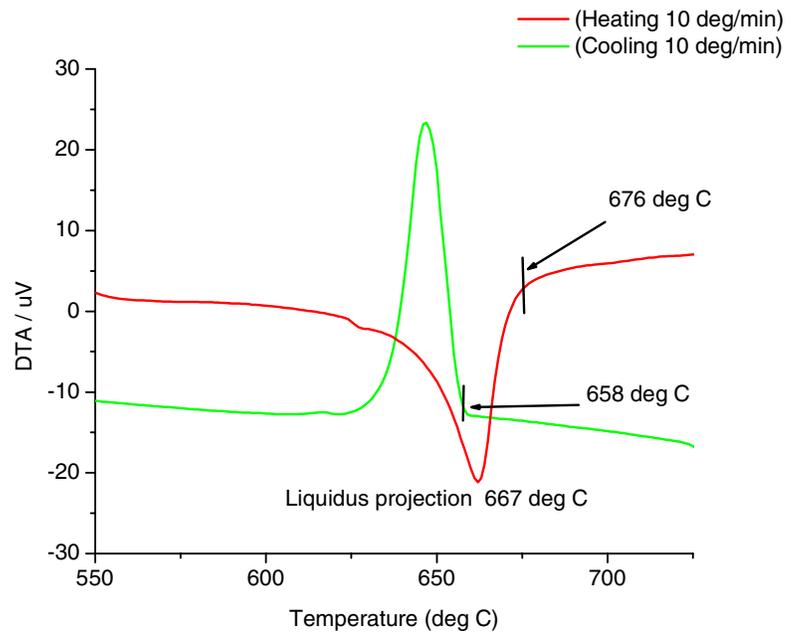


Fig. 12 DTA of ingot I1b revealing a liquidus projection of 667°C.

Films from all primary phase fields of the liquidus projection were deposited. Several of the deposited films simply exhibited the composition of the ingot material – especially those from the uppermost, Se-rich composition field. The fact that no change in composition was observed indicates that the precipitation of single-phase α -CIS was not successful with these particular fields. However, several deposited films contained compositions that did reflect considerable compositional changes, indicating the precipitation of a thermodynamically stable phase. A summary of compositions of the ingots made (measured by an analytical balance and confirmed by XEDS) and the films (also measured by XEDS) are given in Table 1. From Table 1, the ingot designated I1b initially had a composition corresponding to 1:1:1 Cu:In:Se and resulted in the deposition of a film with a stoichiometry of 1:1:2.

To verify that the stoichiometry of the film made from ingot I1b did correspond to the α -CIS phase, and not to a sum of several phases adding up to a 1:1:2 composition, XRD was utilized. Figure 13 is an XRD pattern from one of the films grown from the I1b ingot. The presence of a dominant peak at 26.6° confirms the presence of the (112) plane. This peak is the dominant peak within the spectrum as it is

Ingot	Ingot (weighed) Atomic %	Ingot Measured (EDS) Atomic %	Film Measured (EDS) Atomic %
I1a	Cu 12.0 In 47.5 Se 40.5	Cu 8.7 In 41.4 Se 49.9	Cu 4.19 In 52.69 Se 43.12
I1b	Cu 32.5 In 32.5 Se 35.0	-	Cu 24.76 In 27.10 Se 48.14
I1c	Cu 46.0 In 18.0 Se 36.0	-	Cu 59.50 In 15.58 Se 24.92
I2	Cu 55.0 In 38.5 Se 6.5	-	Cu 16.46 In 41.47 Se 42.08
I3	Cu 46.0 In 4.0 Se 50.0	Cu 45.40 In 2.66 Se 51.94	Cu 7.90 In 1.33 Se 90.77
I4	Cu 2.85 In 3.55 Se 93.6	Cu 4.46 In 2.81 Se 92.73	Cu 5.74 In 0.80 Se 93.46

Table 1 is a compilation of compositions, given in atomic percentages, for all ingots and films.

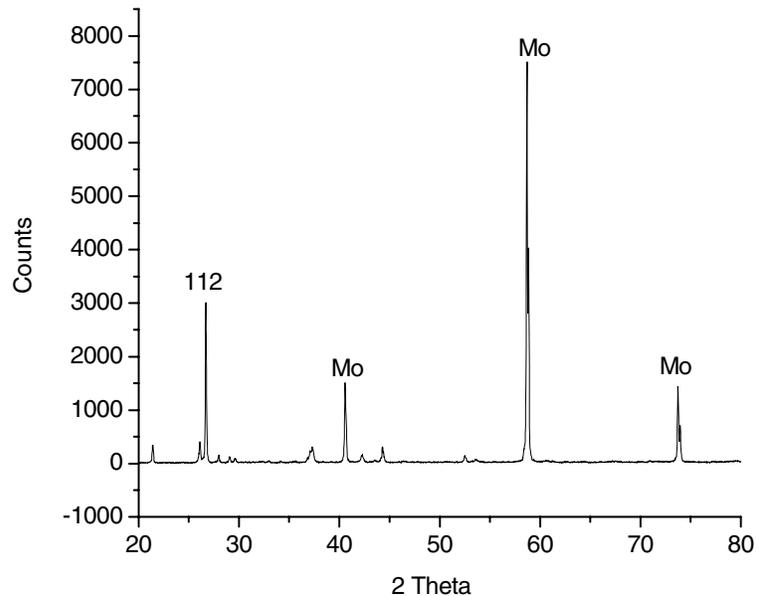


Fig. 13 XRD pattern of the LPD α -CIS from Ingot I1b.

one the two preferred growth planes of α -CIS along with the (220) plane (not predominately present).

Conclusion

Based on the results described in the previous section, we believe that it is possible to fabricate single-phase α -CuInSe₂ layers with high structural and electronic quality by liquid-phase deposition (LPD). Some experimental problems of this method have been identified, such as insufficient wetting of the substrate, high viscosity of the melt below the liquidus temperature, and the necessity of a very precise temperature control. However it seems that these problems can be overcome. As the experimental techniques are further developed, we hope that LPD will become an attractive method for fabricating high-quality α -CuInSe₂ thin films at low cost.

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