

Annual Report  
**Liquid-Phase Deposition of  $\alpha$ -CIS Thin Layers**  
Phase I

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**Liquid-Phase Deposition of  $\alpha$ -CIS**

The goal of our project is to fabricate single-phase  $\alpha$ -CIS ( $\alpha$ -Cu-In-Se,  $\text{CuInSe}_2$ ) thin films for photovoltaic applications from a liquid phase (a Cu-In-Se melt). This approach of “liquid-phase deposition” (LPD) is based on the new phase diagram we have established for Cu-In-Se, the first complete equilibrium phase diagram of this system.<sup>1-3</sup> Fig. 1 shows the liquidus projection of the phase diagram - the surface indicating the temperature at which first solid material begins to form when cooling down from high temperatures at which the material is entirely liquid. The liquidus projection exhibits four composition fields in which the primary solid phase, i. e. the first solid material that forms on cooling down from an entirely liquid state, is  $\alpha$ -CIS. Remarkably, none of the four composition fields is anywhere near the (stoichiometric) composition  $\text{CuInSe}_2$  of  $\alpha$ -CIS.

On freezing a melt in contact with a substrate, the solid will nucleate on the substrate. Therefore, it should be possible to grow single-phase  $\alpha$ -CIS thin-films by (i) bringing a substrate in contact with a Cu-In-Se melt with a composition within one of the four relevant fields of Fig. 1, (ii) cooling it slowly to a temperature somewhat below the respective liquidus temperature, (iii) let a thin film form solidify on the substrate, and (iv) remove the remaining melt when the film has reached the desired thickness (Fig. 2).<sup>4</sup> The amount of melt needs to be chosen sufficiently large, such that the formation of the  $\alpha$ -CIS film, which incongruently depletes the melt

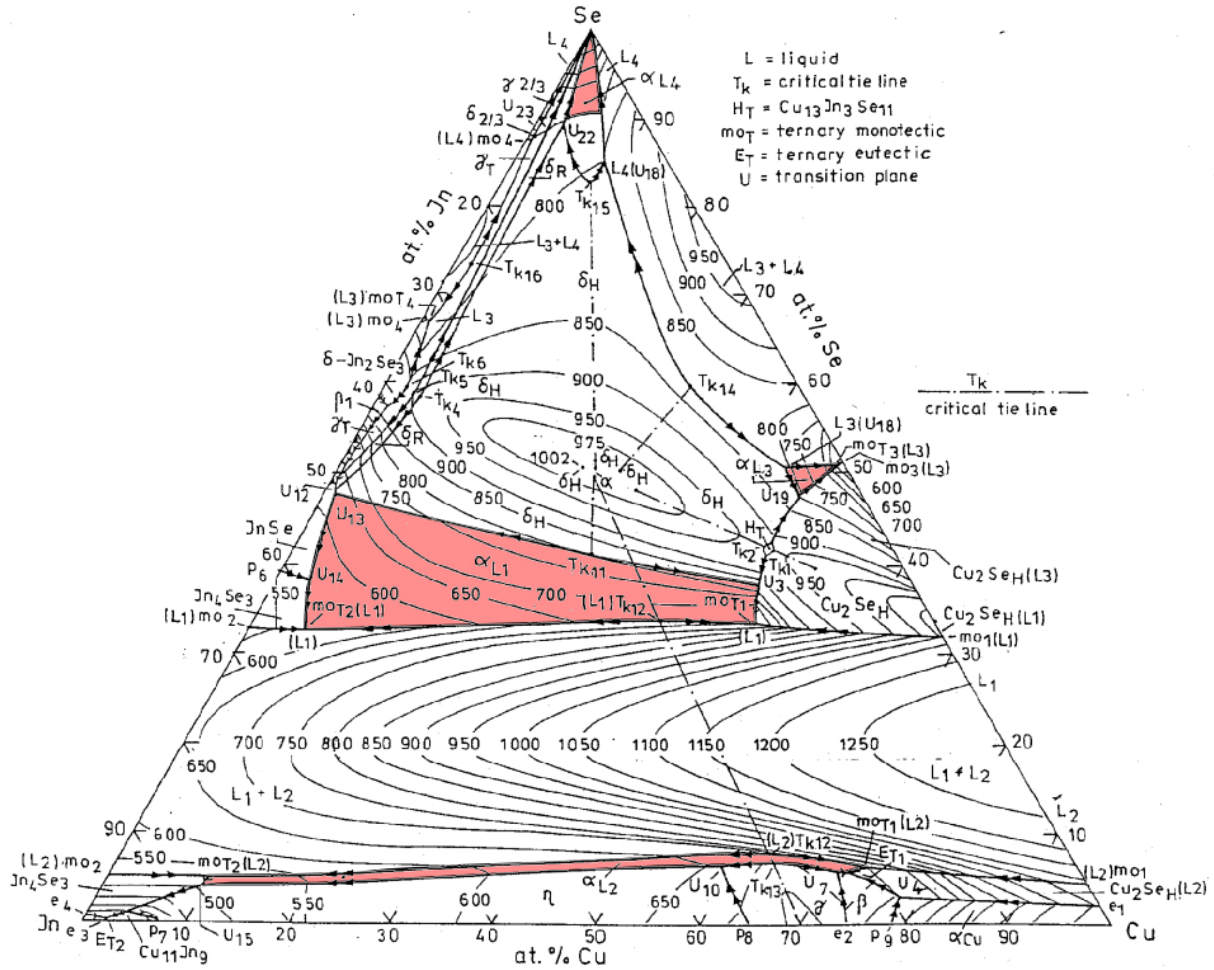


Figure 1: Liquidus projection of the Cu-In-Se phase diagram.

of Cu, In, and Se, does not significantly alter the melt composition. Subsequently, the system is cooled to room temperature.

Since the material freezing out from the melt will be single-phase  $\alpha$ -CIS and solidifies under near-equilibrium conditions (small supercooling, small driving force), we anticipate substantially lower concentrations of structural defects than in PVD layers. This includes all varieties of structural defects: point defects, dislocations, grain boundaries, and phase boundaries (defects - by definition - are *non*-equilibrium features). Indeed, the TEM image of Fig. 3, obtained from  $\alpha$ -CIS deposited on the inner wall of a fused silica tube during one of the DTA (differential thermal analysis) experiments that established the composition fields of primary solidification of  $\alpha$ -CIS in Fig. 1, reveals coarse-grained, pure  $\alpha$ -CIS with a very low concentration of extended structural defects.<sup>4</sup>

Based on the expected structural quality of the material, we anticipate substantial improvements in photovoltaic conversion efficiency. Moreover, the comparison between coarse-grained LPD and fine-grained PVD material will provide deeper insight into the effect of grain boundaries on photovoltaic conversion in  $\alpha$ -CIS, for which a new model was recently proposed.<sup>5</sup>

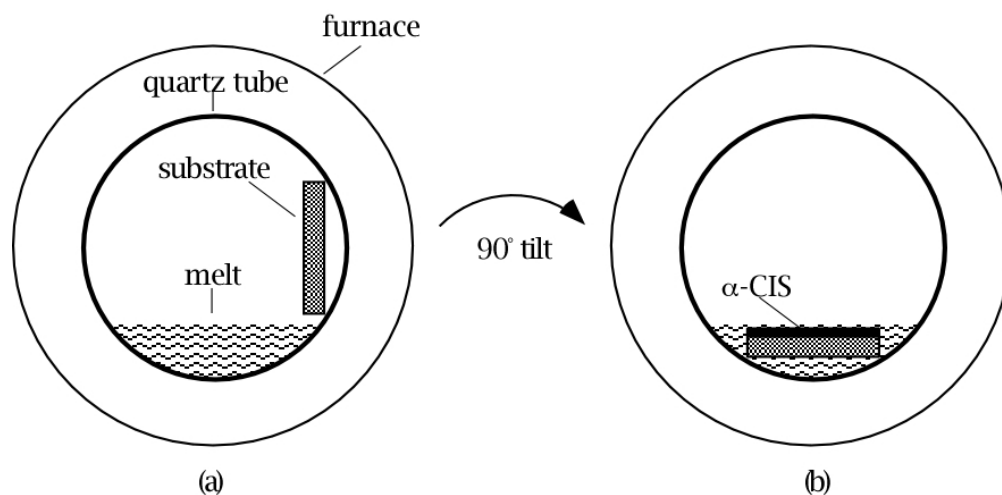


Figure 2: The concept of liquid-phase deposition (LPD). (a) Cu-In-Semelt with a composition in one of the shaded fields in Fig. 1. (b) Deposition of a thin  $\alpha$ -CIS film induced by slightly supercooling the melt in contact with a substrate.

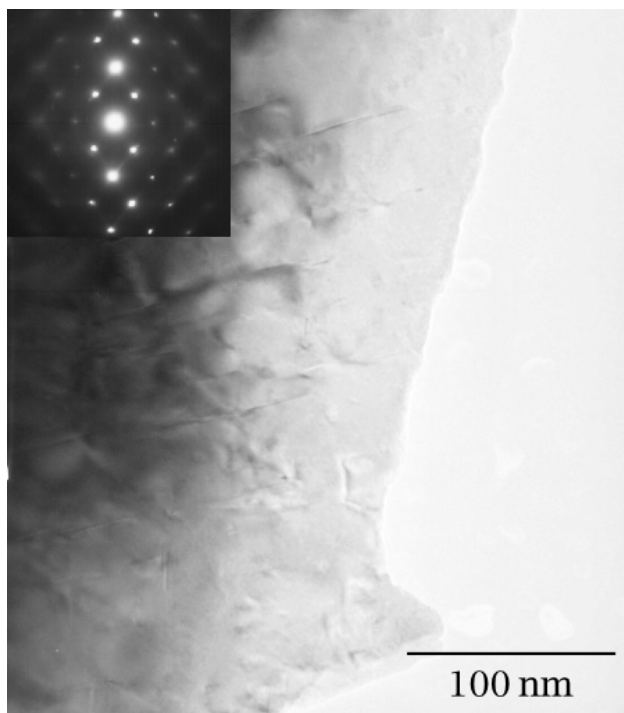


Figure 3: TEM image of  $\alpha$ -CIS produced during experiments we carried out to determine the new phase diagram. The diffraction pattern (inset) confirms that the region imaged here is a large grain of single-phase  $\alpha$ -CIS.

## Establishment of Infrastructure and Procedures

For the experimental work, we have engaged a highly qualified graduate student. Sufficient laboratory space for the experiments has been made available in the Department of Materials Science and Engineering at CWRU, as well as a furnace suitable for constructing the LPD reactor. At the beginning of our work, we have established the following important experimental techniques for preparing the actual liquid-phase deposition experiments:

1. *Encapsulation of the elemental starting materials in fused silica tubes.* We have installed a hydrogen gas tank and a gas torch sufficiently powerful for melting thick-walled fused silica tubes with a hydrogen flame. After cutting a section with a length of about 5 cm from a fused silica tube and cleaning the inner wall surface by chemical solvents, we close one end of the tube by melting it in the flame and then fill the tube with appropriate amounts of high-purity Cu, In, and Se. Subsequently, we evacuate the tube to a powerful rotary pump and flush it with high-purity argon under reduced pressure (800 mbar), which is known to reduce the vapor pressure of Se. Finally, we seal the ingot in the tube by closing the end connected to the pump.
2. *Fusing of starting material for liquid-phase deposition.* Two methods have been established for fusing the elemental ingots with sufficient control of the strongly exothermic fusing reaction. In the first method, we use inductive heating provided by a high-frequency generator. The second method is to provide the required heat directly with the gas torch. Compared to fusion in a tube or muffle furnace, these methods have the advantage that we can observe the reaction through the tube walls and quickly reduce the heat supply when the reaction tends to get out of control. In the beginning, we had the problem that the fused material showed a very strong tendency to stick to the inner wall of the fused silica tube. It seems that this problem can be overcome by using copper with a particularly low oxygen content and thorough cleaning of the inner wall tube prior to encapsulation. Nevertheless, several iterations of fusing and knocking off sticking parts of material from the inner walls of the fused silica tube are typically necessary before a shiny and integral piece of material is obtained that can serve for the liquid-phase deposition experiments.
3. *Installing a substrate in the reaction tube.* We have established a first, simple technique for installing a substrate for thin-film deposition in the fused silica tube containing the ingot: by heating the tube in the hydrogen flame from the outside, we attach a rectangular piece of fused silica to the inner wall such that its plane lies normal to the wall. In future experiments, we will then be able to tilt the Cu-In-Se melt over the substrate simply by rotating the fused silica tube. A problem with this preliminary method is that it can only be applied if the mismatch between the thermal expansion coefficients of the substrate material and fused silica is sufficiently small to keep the thermal stresses at the interface below a tolerable level.

We have designed, constructed, and installed a reactor suitable for LPD of  $\alpha$ -CIS thin films. The reactor is based on a three-zone furnace with hinges that enable us to open it and conveniently access the interior. We also have installed a good controller enabling us to adjust the temperature with a precision better than 1 K. The furnace contains a fused silica tube with a particularly

large diameter of 10 cm to give us sufficient flexibility for variations of the liquid-phase deposition experiments.

The primary tool for characterizing the phase composition, structure, and defects in the material we fabricate is TEM (transmission electron microscopy). Early in Phase I, therefore, we have trained the graduate student in conventional transmission electron microscopy (TEM), including electron diffraction (for phase identification). Meanwhile, the training has been completed with high-resolution and analytical TEM.

We have also trained the student in the corresponding procedures of TEM specimen preparation, which involves ion-beam milling with  $\text{Ar}^+$  ions as the final step. In first experiments with this method, segregation of In on the specimen surface were identified as a major obstacle for obtaining high-quality TEM specimens. However, this is a known problem, and meanwhile we have improved the specimen quality by fine-tuning the specimen preparation parameters based on information from the literature and photovoltaic partners. Exciting new opportunities for preparing high-quality cross-sectional TEM specimens will arise in the near future because the Department of Materials Science and Engineering is presently installing a FIB (focused ion beam system) in its Center for Surface Analysis of Materials.

## **Ingots for Liquid-Phase Deposition**

Ingots for LPD were prepared from all four relevant composition fields in Fig. 1. Their compositions are listed in Table 1. The second column indicates the nominal composition (as weighed), the third column the composition after fusion, as measured by XEDS (X-ray energy-dispersive spectrometry) in a scanning electron microscope, and the fourth column the composition in the resulting LPD-thin film, again as measured by XEDS in a scanning electron microscope.

We have recorded XRD (X-ray diffraction) patterns, and have verified compositions by XEDS for all ingots we have prepared so far. One of the ingots had a Cu:In:Se ratio close to 1:1:1 but has yielded layers with a Cu:In:Se ratio close to 1:1:2 (the stoichiometric composition of  $\alpha$ -CIS). This example confirms the significance of the ternary phase diagram and the basic hypothesis of our project, namely that  $\alpha$ -CIS can be precipitated from melts with compositions significantly *different* from 1:1:2. Not only does the stoichiometry of the deposited films correspond to the desired composition of  $\alpha$ -CIS – XRD patterns have also revealed the presence of chalcopyrite structure of  $\alpha$ -CIS.

## **Differential Thermal Analysis**

For adjusting a sufficiently small supercooling during LPD of  $\alpha$ -CIS layers, as it is required for fabricating material with a low concentration of structural defects, it is important to know the precise liquidus temperature for the respective composition of the ingot. While the liquidus projection in (Fig. 1) indicates the liquidus temperature for every relevant composition, experimental verification is important to interpolate between the isothermes and to accommodate

Table 1: Ingots of the Cu-In-Se alloys prepared and studied in Phase I

Ingot	Weighed (at%)	XEDS Ingot (at%)	XEDS Film (at%)
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

deviations between the nominal and the actual composition.

A suitable method for determining the liquidus temperature is DTA (differential thermal analysis). An apparatus for DTA method is available at Case Western Reserve University, however not for the relatively high liquidus temperatures of up to 1073 K we need to include in order to explore all four composition fields of Fig. 1. Moreover, we had special constraints concerning the specimen morphology arising from the need to keep the material encapsulated in a fused silica tube. For these reasons, we have established a contact with Dr. A. Sayir at the NASA Glenn Research Center in Cleveland. Dr. Sayir has a DTA apparatus appropriate for our temperature range that he made available.

Utilizing the DTA apparatus at the NASA Glenn Research Center, we determined the liquidus temperature of a suite of ingots by measuring the onset and outset temperatures of the first-order phase transformation of melting on the DTA plot; the liquidus temperature corresponds to the outset temperature during heating.

As an example, Fig. 4 shows the DTA plot for the ingot I1b of Table 1. The experimental liquidus temperature of 667 °C agrees well with the liquidus projection of Fig. 1. The small discrepancy originates from the fact that the composition lies slightly off the 700 °C isotherme.

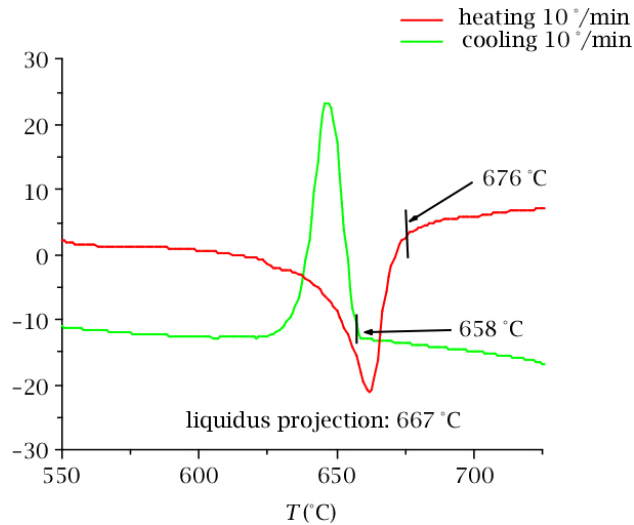


Figure 4: DTA (differential thermal analysis) of alloy I1b in Table 1.

## Wetting Behavior

Initially, attempts were made to deposit  $\alpha$ -CIS thin films onto fused silica and silicon substrates. However, it became soon apparent that the surface energies of these substrates were too low to promote sufficient wetting of the substrates by the molten ingot materials. Silicon can be used, but requires chemical or ion etching prior to the deposition of  $\alpha$ -CIS to “activate” the surface for wetting and subsequent layer growth to occur. To overcome this wetting issue we loaded fused silica substrates, etched with HF (hydrofluoric acid) and rinsed with dionized water, into a sputtering chamber and sputter-deposited a 1  $\mu\text{m}$  thick layer of Mo, followed by a layer of 100 nm of Cu. The sputtering chamber we utilized contained three separate cathodes, thereby allowing us to deposit the Cu film right after the Mo deposition occurred, without breaking vacuum in the chamber. The Cu layer served to passivate the Mo layer in that no oxide layer could form on the Mo. During liquid-phase deposition onto such substrates, the Cu layer diffuses into the ingot material, exposing a Mo surface with a surface energy high enough to promote uniform coverage of the substrate by the molten ingot material.

With the incorporation of these Cu-coated substrates, we were able to deposit films from all four composition fields suitable for primary precipitation of  $\alpha$ -CIS, as indicated in Fig. 1.

## Viscosity

In order to precipitate a thin layer of  $\alpha$ -CIS onto a substrate, a molten ingot with an appropriate composition needs to be slowly cooled down to or just below the liquidus temperature indicated by the ternary phase diagram. As expected from the usual exponential increase of the viscosity with decreasing temperature, we found that the viscosity of all ingots we tried so far greatly increases as they are cooled down to the corresponding respective liquidus temperature. After deposition of a thin layer on the substrate, therefore, it turned out to be difficult to tilt the

remaining melt off the surface of the deposited layer. Even when the substrates were turned upside down, the molten ingot did not easily release from the substrate. For this reason, the layers we have successfully deposited so far are quite thick: 10 to 15  $\mu\text{m}$ . For high-quality absorber layers, the thickness needs to be reduced.

Moreover, thick Cu-In-Se layers are difficult to prepare for TEM. Owing to the brittleness of the deposited material and the presence of stresses induced by thermal expansion mismatch, the layer-substrate adhesion of the thick Cu-In-Se layers we obtained is poor, rendering them very susceptible to destruction during the mechanical preparation required prior to the final thinning procedure. In order to obtain some first TEM specimens anyway, we have intentionally grown layers of exceedingly large thickness. For the same reasons that reduce the adhesion of the layer to the substrate, an exceedingly large layer thickness enables complete removal of layer from the substrate, which significantly facilitates the preparation of TEM specimens compared to the case of a thick Cu-In-Se layer adherent to a substrate of a different material.

## **Sliding Boat LPD Reactor**

### **Concept**

To circumvent the problems related to the unexpectedly high viscosity of Cu-In-Se melts, we have deviated from the original plan and constructed an entirely new, laboratory-scale reactor for depositing thinner films with better surface morphology.

In this new reactor, the molten material will reside in a “sliding boat” – a graphite well, which is slid over the *bottom* side of several stationary substrates. This approach provides much more control over the deposition process than it would be possible with the simple tilt mechanism we have been using so far. For this reason, the sliding boat setup is commonly utilized in liquid-phase epitaxy of III-IV and IV-IV semiconductors.

### **Sliding Boat**

The sliding boat is comprised of three main parts; track, substrate holder, and the reservoir, which are all shown together in Fig. 5. The outer portion or track of the boat simply provides a channel for the reservoir to slid back and forth in. The substrate holder fits nicely in the bottom of the track and below the reservoir. The construction material for the sliding is graphite. Graphite was chosen because it is available in high purity form, it is easily machined, and mostly because it is not wet by metals. The construction of the sliding boat is simple, but should prove to be effective for LPD of sufficiently thin  $\alpha$ -CIS films.





Figure 5: Sliding boat of the new sliding-boat reactor.

### Thermogravimetric Analysis

Several methods currently used for the deposition of  $\text{CuInSe}_2$  and  $\text{CuInS}_2$  require post-deposition annealing treatments in Se- or S-rich atmospheres to yield the desired chalcopyrite phase with the 1:1:2 stoichiometry. However, even when the deposited material has the correct stoichiometry, a chalcogenide-rich atmosphere is usually employed to maintain this composition. For the final construction of the sliding boat LPD reactor we had to determine at what pressures we need to operate in order to maintain the composition of the starting ingot as well as the composition of the deposited film. Therefore TGA (thermogravimetric analysis) was employed to measure the mass loss of various ingots as a function of temperature.

Figure 6 is a TGA plot of all the ingots made with compositions designated in Table 1.

Figure 6 reveals that there is *no* significant weight loss by vaporization of selenium from ingots with compositions in regions  $I_1$  (a, b, and c) and  $I_2$ . Significant weight loss is observed only from the selenium-rich regions designated  $I_3$  and  $I_4$ . Therefore, ingots with compositions in regions  $I_1$  and  $I_2$  should show no selenium loss during deposition and will not require the use of chalcogenide-rich atmospheres.

### Deposition Chamber

The use of an air-tight deposition chamber, shown in Fig. 7, will allow easier loading of samples, as samples will no longer have to be prepared within quartz ampoules by a hydrogen torch

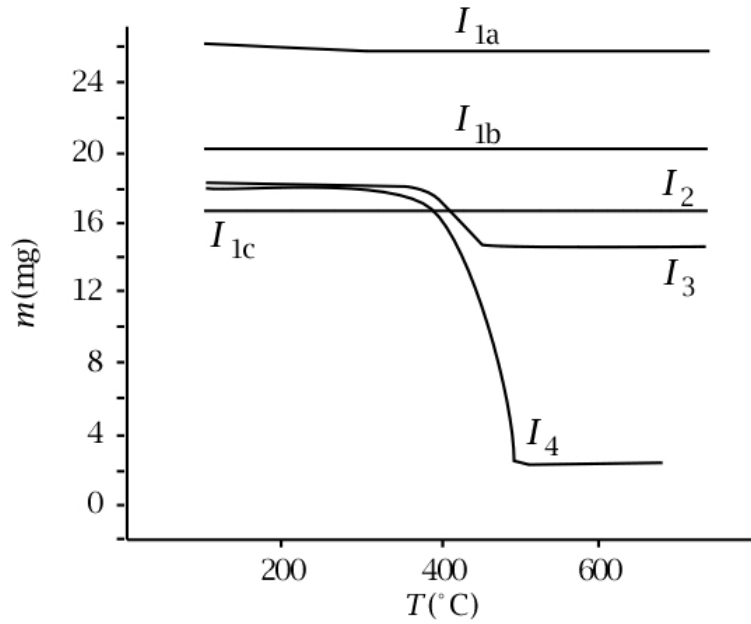


Figure 6: TGA plot of all the ingots made with compositions designated in Table 1.

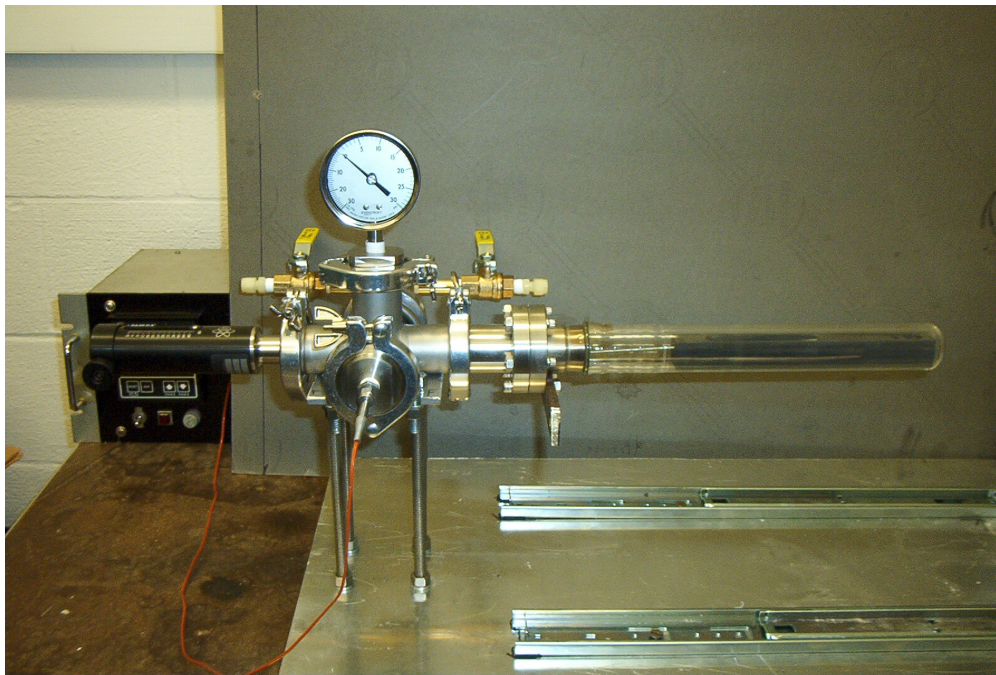


Figure 7: Deposition chamber of the new sliding-boat LPD reactor.

(although ingot materials will still be made by this method). The chamber is fitted with valves to allow pumping under vacuum as well as purging with high purity argon gas. Depositions will be carried out at slightly higher than atmospheric pressure, however prior to depositions the system will be under vacuum and heated to remove water and contaminants. Additionally, this type of chamber will allow the ability to utilize reacting gases to properly remove oxide

contaminants from the surface of the substrates prior to the actual deposition. Hydrogen is often used to remove surface oxides by converting the oxides to water. The removal of surface contaminants, mainly oxides, will increase the surface energy of the underlying substrates and will therefore promote better wetting behavior of the substrate by the molten ingot. At the far left of the deposition shown in Fig. 7, there is a linear manipulator vacuum feed-through purchased from MDC Vacuum Products Cooperation. This manipulator provides a convenient way to move the reservoir over the underlying substrates.

The TGA results shown before reveal that the selenium vapor pressure is not so significant from the ingot material made up from two of the selenium deficient compositional phase fields of the ternary equilibrium diagram. Despite the TGA results concerning the selenium vapor pressure, the LPD chamber is equipped with a pressure release valve in the event of overheating which could potentially result in the rupture of the furnace which would result in exposure to selenium vapor. Additionally, the gas removed from the pressure release valve will run through a cold trap to condense potentially dangerous selenium vapor.

The construction of the sliding-boat reactor was completed in the fourth quarter of Phase I. First tests have been performed, and we are confident that the new construction will enable us able to deposit thinner layers with better adhesion and to advance the quality of their microstructural characterization.

## Team Activities

The group at CWRU has actively participated in the National CIS Team Meetings with presentations explaining the ongoing project and recent results on the microstructure and phase equilibria in bulk Cu-In-Se “single crystals” and PVD-grown Cu-In-Se thin films obtained by TEM and XRD.

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