Design and Control Considerations for Scale-up of a CIGS Inline Co-evaporative Physical Vapor Deposition Process

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EXTENDED ABSTRACT

1. Introduction

$Cu(InGa)Se_2$ (CIGS) is quickly emerging as the most credible absorber material for economical large-scale manufacture of next-generation thin film solar cells. One of the most appealing advantages of CIGS-based solar cells is the potential to grow CIGS thin films on large-area flexible substrates in a roll-to-roll manufacturing technique leading to a high-throughput, low-cost, process. Rapid advances have been made in improving the efficiency of CIGS-thin-film-based solar cells (up to 19.2% [1]), but only at the laboratory scale for small-area substrates. Scale-up to large-area modules is proving to be much more difficult than expected [2], and most candidate commercial technologies remain at the pre-manufacturing development stage. Consistently producing

>15% efficiency CIGS-based solar-cells has remained a challenge even at the pilot stage. Various approaches for manufacturing flexible CIGS-based solar cell modules are listed in [3]. The highest efficiency CIGS-based flexible solar devices have been produced by sequential inline co-evaporative process. Alternative non-vacuum low-cost manufacturing techniques such as electrodeposition [4], chemical spray pyrolysis [5], and paste coating [6] are still at the laboratory stage and have so far failed to produce even 10% efficiency devices consistently.

The key quality variables that influence final solar cell efficiency are film thickness and composition, and their uniformity across the substrate width. The film composition is measured in terms of copper-ratio (CR) and gallium-ratio (GR) defined as follows:

$$CR = \frac{N_{Cu}}{N_{Ga} + N_{In}}$$
$$GR = \frac{N_{Ga}}{N_{Ga} + N_{In}} \quad (1)$$

where, N_{Cu}, N_{Ga}, and N_{In} are number of moles of copper, gallium and indium respectively. The film thickness variation (or non-uniformity) is given by:

$$T_{nu} = \frac{t_{\max} - t_{\min}}{2t_{\max}} \quad (2)$$

where, $t_{\max}$ and $t_{\min}$ are the maximum and minimum film thicknesses respectively. The overall operational objective for a successful commercial process is robust and tight control of the mean values of film thickness and composition as well as their uniformity across large-area substrate, for long deposition times. For example, thickness variation of more than ±10% around the mean value is unacceptable.

We discuss, in this paper, how successful scale-up involves problems in both design and control that must be considered simultaneously; and that unless the process is designed with explicit due consideration for the desired final film quality specifications, successful scale-up to achieve desired control and overall process performance will be difficult.

2. Co-evaporative thermal physical vapor deposition process

The particular manufacturing technique adopted at the University of Delaware's Institute of Energy Conversion (IEC) is the co-evaporative thermal physical vapor deposition (PVD) of CIGS thin-films onto a 6-inch flexible polyimide substrate using a roll-to-roll processing scheme (Fig. 1). The film is deposited by thermal evaporation from a series of linear elemental sources located sequentially in a vacuum deposition chamber. More specifically, controlled amounts of copper, gallium, and indium are delivered to the substrate, while selenium vapor, provided in excess using sparger pipes, is built into the film as determined by the stoichiometry. Ideally, the final film quality variables (measured by an X-ray fluorescence sensor located at the end of the deposition zone) should be controlled in a cascade manner by (i) an outer multivariable controller which manipulates the set-points for the elemental source effusion rates, and (ii) inner effusion rate regulatory controllers that achieve these desired set-points by manipulating power to each individual heating source. However, due to the unreliability and operational difficulties of direct effusion rate measurement techniques (such as atomic absorption spectroscopy), the desired effusion rates are achieved indirectly by controlling the individual source temperatures (provided by thermocouples placed at the bottom of each

source boat). The source temperatures required to achieve the desired effusion rates are determined using a simplified effusion model [7] that relates boat-temperature to effusion rate.

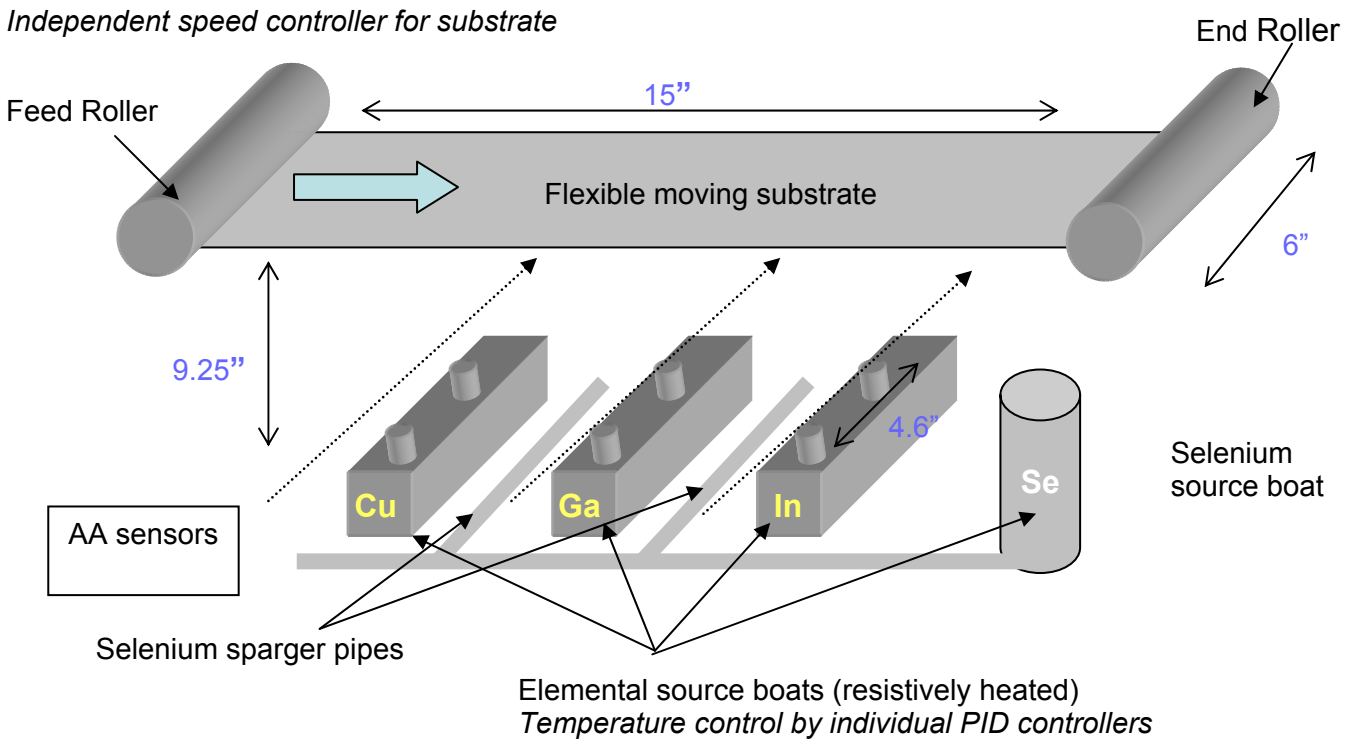

Figure 1: IEC co-evaporative inline PVD process

3. Scale-up issues

It has been customary to regard the scale-up of PVD processes strictly as a problem that can be handled exclusively by control, ignoring the possibility that pilot-scale process design assumptions, such as equal nozzle-effusion-rates in a multi-nozzle source boat, may no longer apply at the commercial scale. For the specific system under study, we have identified two primary issues (relatively insignificant for a pilot-scale

process) that *must* be resolved for a successful commercial-scale development: (i) melt-temperature gradients, and (ii) the reduction of melt-level with time.

3.1 Melt-temperature gradient

For the specific system under study, linear thermal boats with two nozzles each (as shown in Fig. 1) are used as sources for copper, gallium and indium. The heater assembly in the source-boat is asymmetric (see Fig. 2); the resulting melt-temperature profile will therefore be asymmetric. Since nozzle effusion rate essentially depends upon the melt-surface temperature directly underneath the nozzle, an asymmetric melt-temperature profile will result in a mismatch in the vapor flow rates through the two nozzles, and hence lead to film thickness non-uniformity. Holes drilled in the insulation for the current-leads reduce the effectiveness of the lead side insulation, thereby increasing the temperature gradient further.

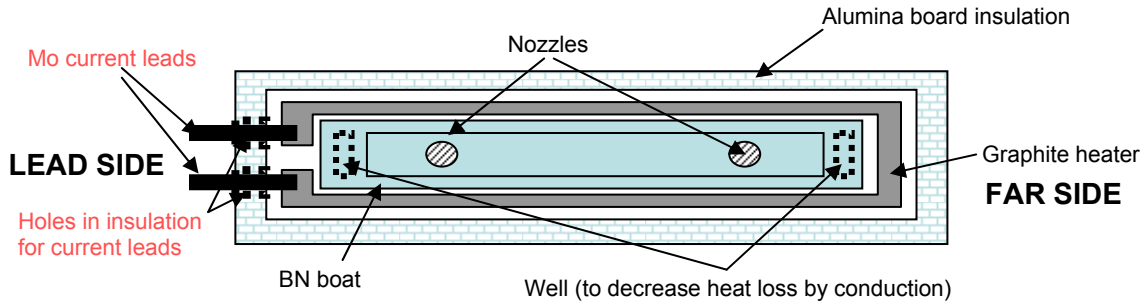

Figure 2: Asymmetric heater assembly

3.2 Melt level reduction with time

The melt level inside a source-boat will drop with time due to mass loss through the nozzles. For relatively small deposition times (< 2 hours) or lower flow rates, melt

level reduction may be neglected (Fig. 3). However, in a high-throughput commercial-scale process, in addition to higher vapor flow rates, deposition run-times are longer (>8 hours). Consequently, significant reduction in the melt-level occurs, affecting the melt-surface temperature as well as the nozzle flow rates and hence, the film thickness. Since it is difficult to prevent melt-level reduction by source-boat design modification (though designs with low melt cross-section area to melt-height ratio will have more pronounced melt-level drop than the others), the disturbance introduced in the process variables by the slow decrease in the melt-height should be rejected by process control. The development of a coupled heat and mass transfer model to describe how reduction in the melt level affects the vapor flow rates will be the topic of future publications.

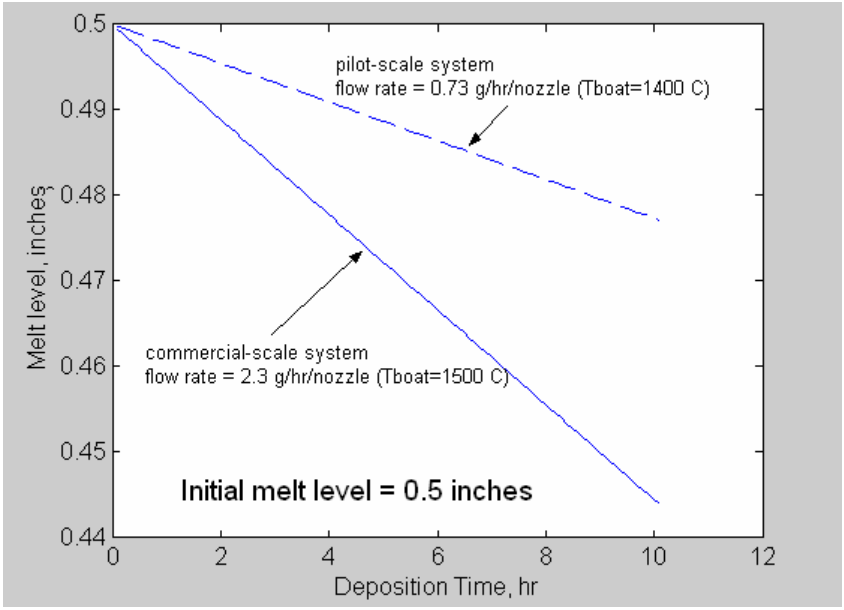

Figure 3: Melt level reduction with time (simulation)

Considering how these issues arise from elemental source design, and considering their impact on process controllability, we divide the scale-up issues into the following two components: (i) *The design issue* – where an elemental source is designed such that melt-temperature gradients are minimized, thereby reducing product quality variations,

and (ii) *The control issue* – where the mean values of the final film quality variables are robustly controlled such that the desired set-points are achieved while simultaneously rejecting the disturbances introduced by the melt-level reduction.

We focus mainly on the design issue in this paper. First, we discuss in detail how the two main issues mentioned above are related to the design and operation of the elemental sources, and how they influence the film quality control. Second, we present experimental results that quantify the temperature gradients in an elemental source-boat, and the effect of these gradients on film thickness uniformity under normal operating conditions. Finally, we present two design modifications that resolve the issue of thickness and composition non-uniformity over wider substrates.

4. Experimental Results

An independent vacuum bell-jar system was assembled to quantify temperature gradients within the source-boat, so that the normal operation of the pilot-scale inline process is not interrupted. Fig. 4 shows a schematic representation of the experimental system. A source-boat similar to the one currently in use in the pilot-scale system is placed inside the bell-jar. A 10-inch-by-1-inch glass substrate is located 9 inches directly above the source boat for copper film deposition to obtain the thickness profile along the substrate width. Since it is not possible to measure the temperature of the melt directly, thermocouples are placed as shown in Fig. 5 to measure the boat-end temperatures, thereby providing an indirect indication of the melt temperature gradient. The source-boat

bottom temperature is controlled using a digital PID controller implemented using the LabVIEW package.

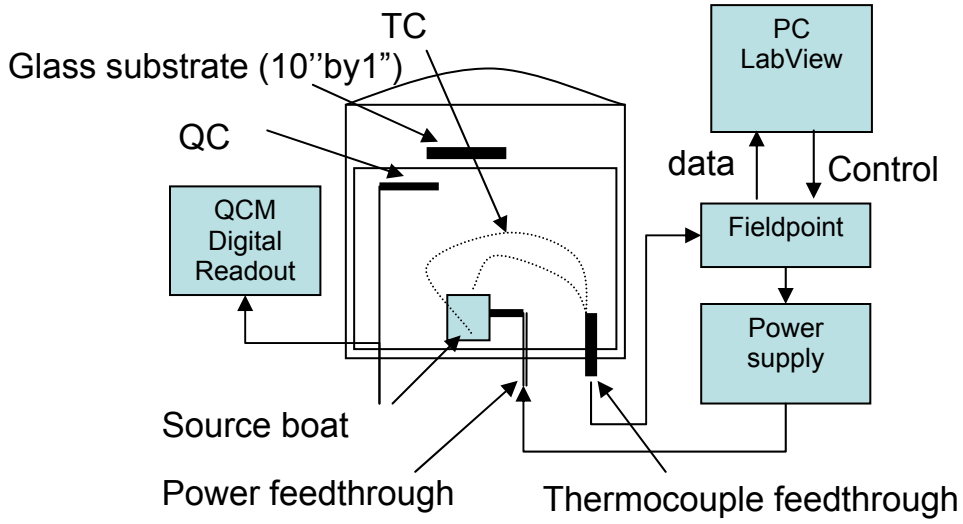

Figure 4: Experimental set-up

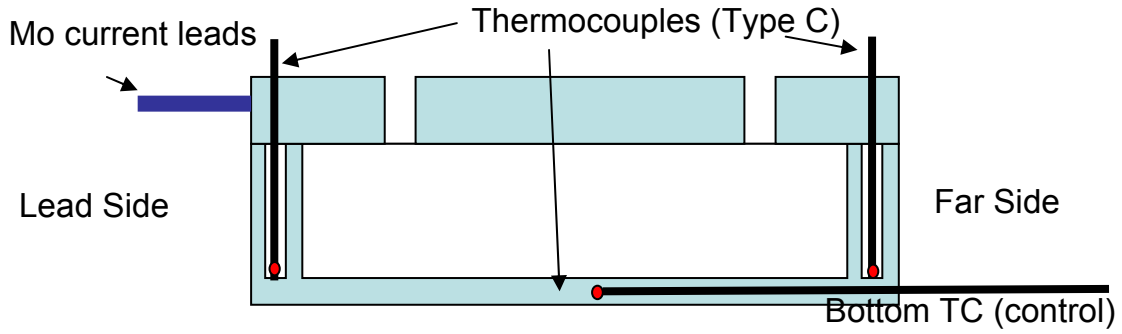

Figure 5: Thermocouple placement inside the source-boat.

Figs. 6 and 7 show the experimental results for temperature dynamics at the boat-ends for two separate runs (Run 1 and Run 2), while Figs. 8 and 9 show the respective film thickness profiles (negative co-ordinates are on the "Lead Side": see Fig. 5). As expected, the lead-side of the source-boat is cooler than the far-side.

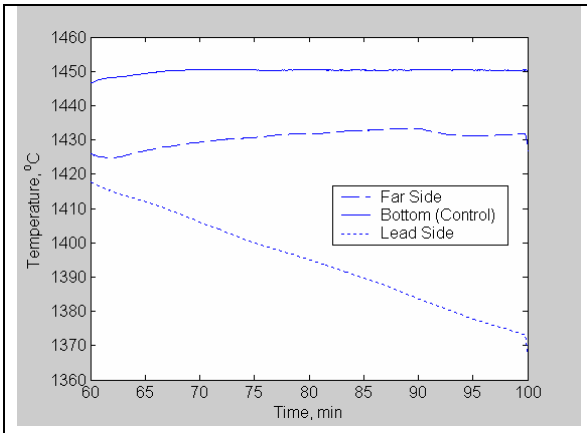

Figure 6: Temperature dynamics (Run 1)

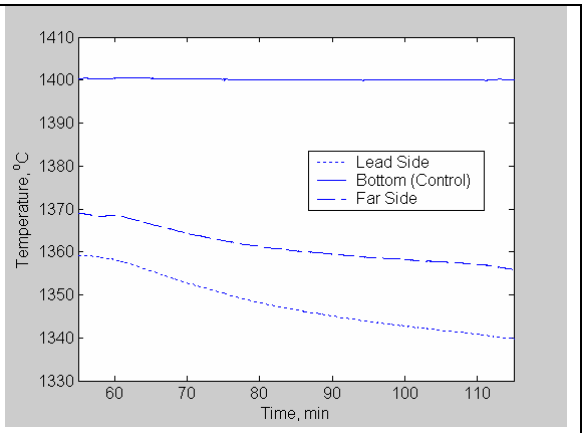

Figure 7: Temperature dynamics (Run 2)

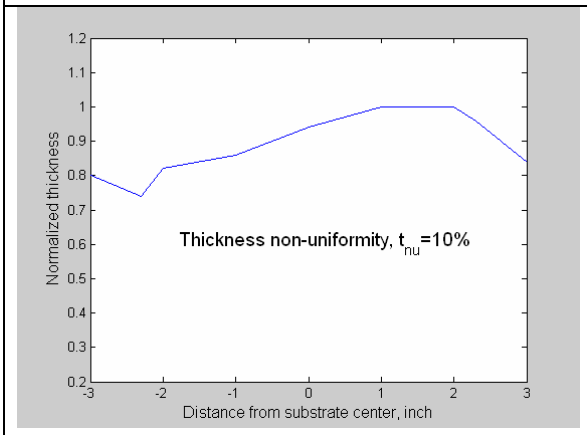

Figure 8: Thickness profile (Run 1)

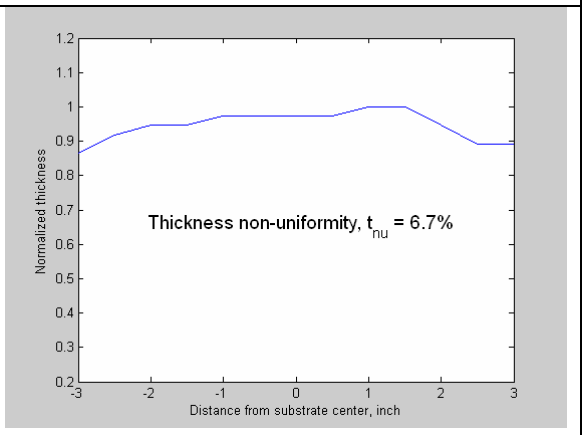

Figure 9: Thickness profile (Run 2)

The observed variation in the temperature dynamics for different experimental runs is mainly due to the changes in insulation properties (due to wear and tear, and deposited material). The temperature difference between the two ends of the boat ($\Delta T=T_{FS}-T_{LS}$) was observed to be between 20 °C to 50 °C. However, for relatively small 6"-wide substrates, this difference is not substantial enough to cause serious film thickness non-uniformity (the thickness uniformity for both Run 1 and Run 2 is less than 10%).

The following simple qualitative modeling of the heat fluxes at the boat-ends is sufficient to explain the observed temperature difference. The total heat loss at the lead side of the boat is given by:

$$\dot{Q}_L = \dot{q}_L^{rad} + \dot{q}_L^{cond} \tag{3}$$

where $\dot{q}_L^{rad}$ is the heat loss term due to radiation to the surroundings and $\dot{q}_L^{cond}$ is the conductive heat loss through the power leads. The total heat loss at the far side of the boat is given by:

$$\dot{Q}_F = \dot{q}_F^{rad} \tag{4}$$

where, $\dot{q}_F^{rad}$ is the radiative heat loss at the far side. Also, $\dot{q}_L^{rad} > \dot{q}_F^{rad}$ due to the presence of holes in the insulation (for the power leads) allowing direct radiative heat loss from the boat that is at a very high temperature. Clearly, $\dot{Q}_L$ is higher than $\dot{Q}_F$; this mismatch of heat losses at the boat ends is responsible for the temperature gradient in the source-boat.

An appropriate amount of extra insulation on the lead side may approximately balance $\dot{Q}_L$ and $\dot{Q}_F$. However, conductive-loss through the current leads and direct radiative heat-loss through the holes in the insulation cannot be completely eliminated. Moreover, insulation property changes due to material deposition and wear and tear, will make this a non-robust design. The results of one such attempt (Run 3) are shown in Figs. 10 and 11. The lead side temperature in this case is observed to be higher than the far side temperature, suggesting over-use of the insulation at the lead-side. However, the film thickness non-uniformity is, again, within the desired limits.

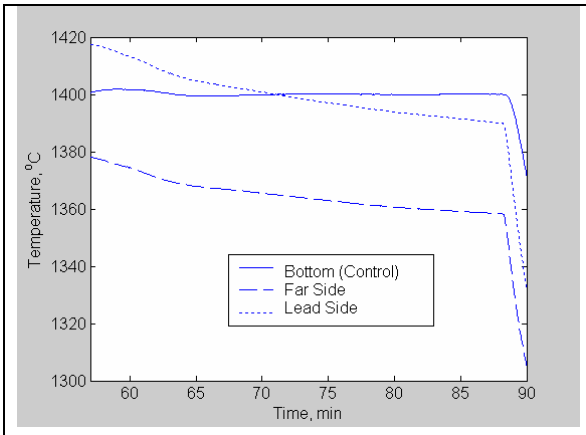

Figure 10: Temperature profiles (Run 3)

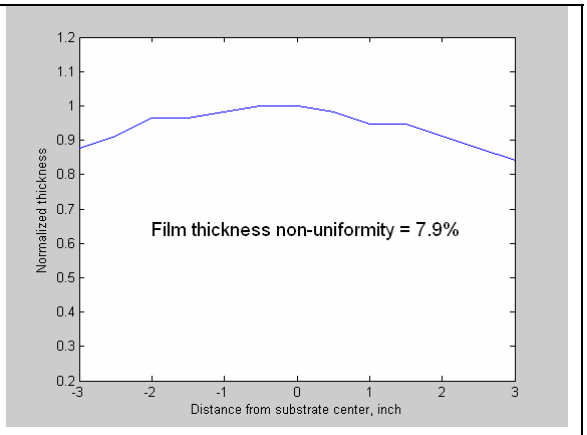

Figure 11: Film thickness profile (Run 3)

5. Effect of melt-temperature gradient on scaled-up process

For the pilot-scale (6”-wide substrate) system, the presence of an asymmetric melt-surface temperature profile was found to have no serious effect on the film thickness uniformity. In this section, we investigate via simulation whether this observation is valid in a scaled-up process. For co-evaporative inline PVD processes, the scale-up entails determination of optimum nozzle-to-nozzle distance, nozzle-to-substrate distance, and boat-to-boat distance such that the material utilization efficiency is maximized for a given substrate-width, and a film thickness non-uniformity constraint. For a commercial process with 12”-wide substrate and film thickness non-uniformity constraint of 8%, the optimum design parameters are listed in Table 1.

Table 1: Scaled-up process

Design Parameter	Parameter Value (inch)
Substrate width	12

Nozzle-to-nozzle distance Nozzle-to-substrate distance	8.6 8
Boat-to-boat distance	3.5

Results of simulations conducted to determine how the film thickness non-uniformity increases with melt-temperature difference underneath the nozzles are shown in Fig. 12.

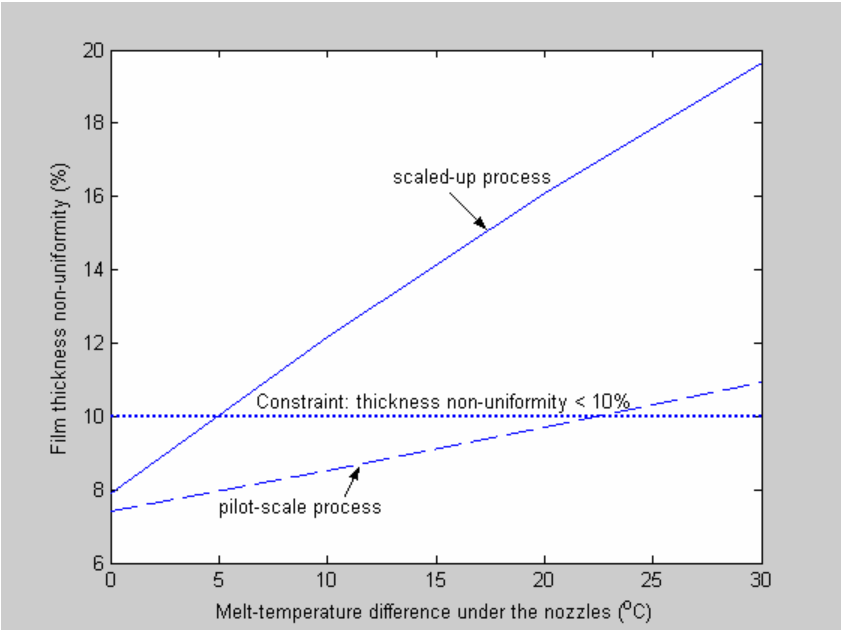

Figure 12: Variation of film thickness non-uniformity with melt-temperature difference under the two nozzles.

Observe from Fig. 12 that a temperature difference as low as 5 °C is enough to cause film thickness non-uniformity to exceed the acceptable limit of 10%. From the experimental results, we have observed that a temperature difference as high as 50 °C is present between the source-boat ends depending upon the insulation degradation. The

temperature difference is relatively lower between the melt-surfaces under the nozzles, but greater than 5 °C. Thus, to achieve the desired film thickness uniformity, a change in the elemental source-boat design is essential.

6. Proposed design modifications to achieve thickness uniformity

Maintaining film thickness within desired limits is not realizable unless equal vapor flow rates are maintained through the two nozzles. Since equal melt temperatures are required under each nozzle for equal nozzle flow rates, desired film thickness uniformity can only be achieved by an appropriate modification of the source-boat design. The goal of obtaining equal nozzle flow rates can be accomplished by two different approaches:

1. A source-boat design that produces a symmetric temperature profile inside the boat so that the melt-surface temperatures under each nozzle are equal.
2. A source-boat design that removes the dependence of vapor flow rates on melt-surface temperature under the nozzles.

6.1 Approach 1: symmetric heater assembly

A simple way to obtain symmetric melt temperature profile is to use a symmetric heater assembly (as shown in Fig. 13), thereby providing equal thermal energy to the two nozzles and also balancing the heat losses at the boat ends.

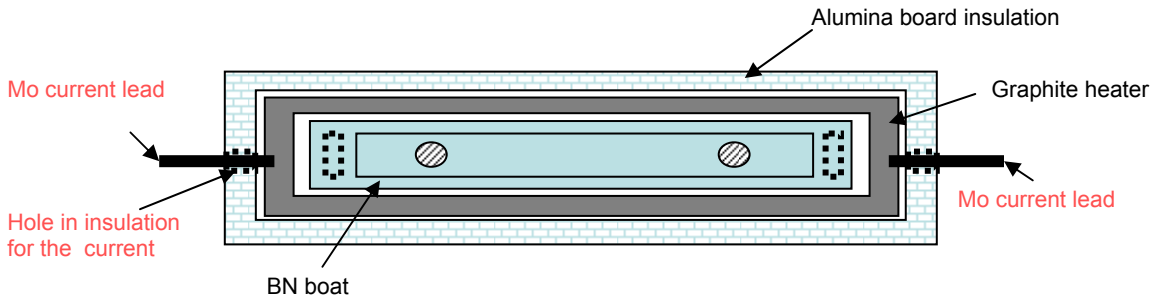

Figure 13: Symmetric heater assembly (Design 1).

This design modification achieves the desired equality of the nozzle flow rates since the melt temperature under each nozzle is equal.

6.2 Approach 2

There are two potential ways, as shown in Figs. 14 and 15, by which vapor flow rates can be made insensitive to the difference in the melt temperature under the nozzles.

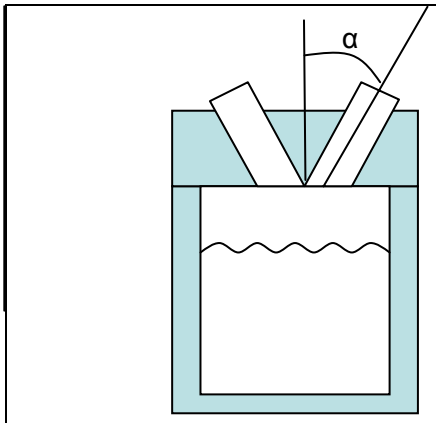

Figure 14: Cylindrical boat with tilted nozzles (Design 2)

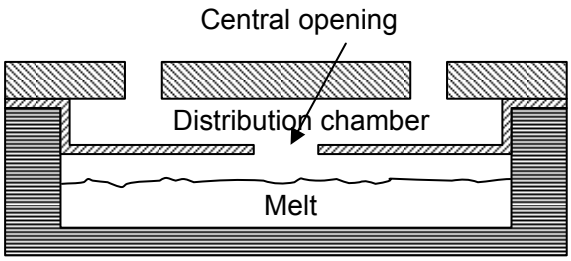

Figure 15: Linear boat with central opening (Design 3)

(1) A cylindrical source-boat with tilted nozzles (Design 2: shown in Fig. 14) such that the melt-side nozzle openings are close to each other: since both the nozzles "see" the same melt-surface, the two nozzle flow rates will be equal.

(2) A linear boat with a central opening (Design 3: shown in Fig. 15): the central opening equally distributes the vapor flow to the two nozzles, thereby achieving equal nozzle flow rates.

7. Design comparison

The proposed designs lead to equal nozzle effusion rates and hence desired film thickness uniformity, provided other design parameters (such as nozzle-to-substrate ratio and nozzle-to-nozzle distance) are chosen appropriately. Design 1, where only a symmetric heater assembly is required, is the simplest and involves minimum change in the system. Design 1 and Design 3 are identical in terms of film thickness uniformity and material utilization efficiency; however, Design 3 will have lower nozzle effusion rate than that of Design 1 because the vapor flow is restricted by the central opening.

Fig. 15 shows a comparison of Design 1 and Design 2 in terms of thickness non-uniformity (t_{nu}) and material utilization efficiency (m_{eff}). Observe that for a boat with tilted nozzles, both t_{nu} and m_{eff} are strong functions of the nozzle tilt angle. Also, note that m_{eff} of Design 2 is significantly lower than that of Design 1.

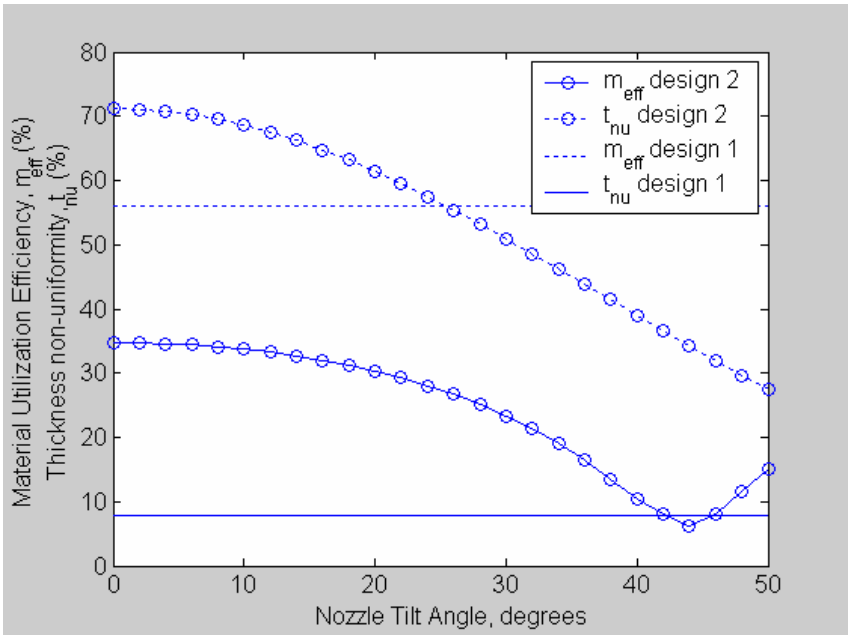

Figure 16: Comparison of Design 1 and Design 2.

From these arguments, it is clear that Design 1 is the better option both in terms of ease of implementation and material utilization efficiency. Future work involves conducting experiments with the modified source-boat to evaluate improvements in film thickness uniformity for wider substrates.

8. Conclusion

It is impossible to obtain desired film thickness uniformity in a co-evaporative PVD process with multi-nozzle linear thermal sources unless due consideration is given to the source-boat design. For the specific system under study, the assumption that melt temperature gradients do not adversely affect the film thickness uniformity is no longer applicable when the process is scaled-up to accommodate wider substrate. To achieve desired film properties, especially film thickness uniformity across the substrate, equal

nozzle effusion rates must be maintained in a multiple nozzle source-boat, which cannot be realized by the source-temperature control alone. Appropriate modifications in the source-boat design are essential to guarantee equal nozzle effusion rates. Three potential designs are proposed that will lead to equal nozzle flow rates and hence, film thickness uniformity. Once thickness uniformity across the substrate is assured, the desired thickness and composition set-points can be achieved in a cascade manner using an outer multivariable controller which manipulates the set-points for the elemental source effusion rates, taking into account the slow disturbances introduced into the process due to melt-level reduction, and an inner effusion rate regulatory controllers that achieve these desired set-points by manipulating power to each individual heating source.

9. References

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