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STUDY OF II-IV-V_2 CHALCOPYRITE SEMICONDUCTORS FOR SOLAR CELL APPLICATIONS

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1.0 INTRODUCTION

This report describes the activities and results of the chalcopyrite materials synthesis effort during the third quarter of our work. Deposition of $ZnSiAs_2$ on 100 Ge and 111 Si substrates was continued with emphasis on identifying correlations between growth system settings and layer properties such as morphology, uniformity, growth rate, stoichiometry and crsytal structure.

2.0 ACTIVITY DURING THIRD QUARTER

Growth was performed throughout the temperature range 630°C to 670°C in 20°C increments. Each reactant transport rate was also varied by a factor of 2 with the growth temperature held constant.

A second reactor shown in Figure 1, was designed and installed to replace Reactor #1 which broke due to a build-up of deposits at the reactant inlet. The SiH_4 and AsH_3 inlet tubes were extended one inch further into the deposition region than the Zn tube inlet. An H_2 carrier gas is still introduced one inch upstream of the Zn tube inlet such that the upstream end of the deposition region is being continually swept with H_2 to prevent depositions from occurring ther. All three reactant inlets now extend well into a quartz liner which can easily be removed after each run. All deposits are thus confined to the liner wall and not to the main reactor walls.

Also shown in Figure 1 is the new Zn boat arrangement. A removable quartz "bucket" with a 7 gram capacity (Zn) is easily slid into a ring holder that is affixed to the end of a hollow push rod. A type K thermocouple located inside the hollow push rod is used to monitor the Zn source temperature. As before, Zn weight loss is measured after each run. When the furnace and the

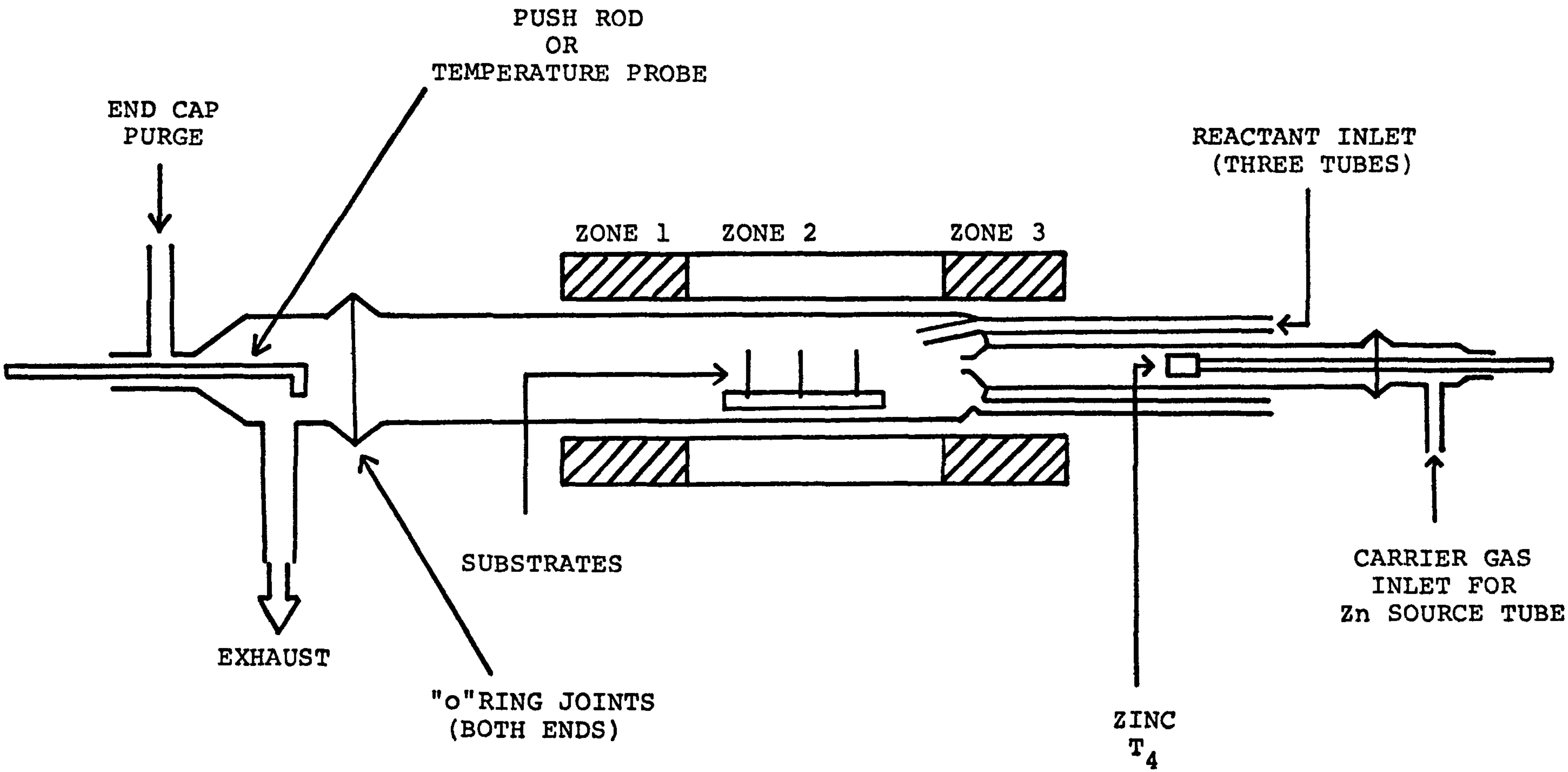

Figure 2. Reactor #2 used for deposition of $ZnSiAs_2$.

Zn source zone are at the proper temperatures, the run is then initiated by inserting the Zn boat via the push rod to it's proper location. In the time required for the Zn to reach its operating temperature, the SiH_4 and AsH_3 are phased in and the run is thus begun.

With the new reactor installed, emphasis was placed on verifying or redefining the growth conditions. Subsequent effort was then directed towards increasing the growth rate, extending the deposition region length and eliminating the Zn_3As_2 deposits on the first substrate. Finally, the conditions required for mirror-like epitaxial growth were pursued.

3.0 RESULTS

3.1 Operational

The new reactor is now confining the extraneous deposits to the removable liner, thus the buildup problem that led to the failure of the first reactor (after 44 runs) has been eliminated.

The $ZnSiAs_2$ deposition rate was increased by increasing the SiH_4 transport rate. However, a portion of the SiH_4 is still decomposing prematurely in the 4 x 6 mm inlet tube as it passes through the Zn source zone (ca 600°C). The higher SiH_4 flow rates being used let to complete blockage of the SiH_4 tube. HCl gas at ca 1000°C is now routed through this tube periodically to prevent complete blockage. Increased supplementary H_2 flow through this tube has reduced the pre-decomposition rate within this tube.

Zn transport control has been significantly inproved in two respects. First, transport of Zn can be initiated and terminated in more positive manner with a response time on the order of one to two minutes. Second, the Zn weight has been more consistent for identical settings of temperature and flow rate.

3.2 Deposits

The Zn_3As_2 deposits have been completely eliminated from the deposits on the first substrate encountered in the upstream portion of the reactor. This was a direct result of the increased SiH_4 transport. The deposition rate is now typically 2.5 µm/hr. in this region. Total $ZnSiAs_2$ deposition region length is in excess of eight inches with a surprisingly constant deposition rate over that length (less than 20% variation in thicknesses recorded).

The most significant result of the work during this quarter were the discovery of deposits which exhibited n-type conduction as indicated by thermal probe. X-ray diffraction data suggest a cubic structure and an electron microprobe analysis indicate an excess of Si. More complete analytical data is being obtained and will be presented during the next report period. These n-type deposits appeared concurrently with an increase in the deposition temperature from 650°C to 670°C (setting).

Deposits of p-$ZnSiAs_2$ (chalc. structure) on 111 or 100 Si have in general been polycrystalline and shown a tendancy to peel off while those on Ge have been adherent and have shown some evidence towards ordered growth. This indicates that we may have to grade from the Si to the $ZnSiAs_2$ by starting first with Si epitaxy and proceed step-wise to the $ZnSiAs_2$ composition. Since this will involve a higher temperature for the Si epi, the Ge substrates will be continued for the sake of obtaining adherent layers of $ZnSiAs_2$ for calculation purposes.

4.0 PLANNED ACTIVITY

The n-type deposits will be further characterized. Some SEM evaluations of selected layers will be performed to look for correlations of growth morphology to growth conditions.