



RESEARCH TRIANGLE INSTITUTE

DEVELOPMENT OF HIGH EFFICIENCY, LOW COST  $\text{ZnSiAs}_2$  SOLAR CELLS

RTI Project 41U-1803

Quarterly Technical Progress Report No. 1

for

U.S. Department of Energy

Contract No. DE-AC04-79ET23001

MASTED

April 9, 1979 to June 30, 1979

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## 1.0 INTRODUCTION

The purpose of this study is to continue an investigation of one of the chalcopyrite semiconductors ( $\text{ZnSiAs}_2$ ) in order to assess its suitability as a solar cell material. In work performed under ERDA Contract No. E(49-18)-2458,  $\text{ZnSiAs}_2$  had been synthesized using an open tube vapor phase epitaxial growth technique. Epitaxial layers of  $\text{ZnSiAs}_2$  had been deposited on Ge and GaAs substrates (both (001) and (112)  $\text{ZnSiAs}_2$  on (100) and (111) substrates, respectively).

Epitaxial deposits were routinely achieved while the surface appearance varied from mirror-like to a dull appearance which resulted from a relatively rough surface topography. Mirror-like finishes were clearly an achievable goal but required additional refinements in growth technique and substrate preparation before they could be routinely achieved.

At this time three critical goals have been identified that must be achieved before  $\text{ZnSiAs}_2$  can be realistically assessed.

1. Hole concentrations must be reduced from the current  $10^{18}$  to  $10^{19}/\text{cm}^3$  range to the  $10^{16}$  to  $10^{17}/\text{cm}^3$  range.
2. N-type  $\text{ZnSiAs}_2$  must be demonstrated.
3.  $\text{ZnSiAs}_2$  p-n junctions must be demonstrated.

The remainder of this report addresses the approach taken and the progress made toward achieving these goals as well as the planned effort for the next quarter.

## 2.0 TECHNICAL DISCUSSION

### Materials Growth Activity

The high carrier concentrations observed in the earlier p-ZnSiAs<sub>2</sub> were observed in growth on GaAs substrates. In particular, the Cr-doped (100) GaAs substrates that were used to facilitate Hall effect measurements resulted in autodoping of the ZnSiAs<sub>2</sub> layers with Ga. For this reason, the growth during this research was limited to Ge substrates, which provide the next best lattice match to ZnSiAs<sub>2</sub>. The Ge substrates used were n-type (undoped) with a resistivity of 10 to 40 Ω-cm.

ZnSiAs<sub>2</sub> was deposited using the original VPE system throughout the 650 to 670°C temperature range in order to determine the effect of temperature on morphology. While epitaxial deposits were achieved, the desired mirror-like finish was not consistently achieved for any one temperature throughout this range for the p-ZnSiAs<sub>2</sub>. It was noted, however, that more regular growth features were obtained in the 660 to 670°C range.

### n-ZnSiAs<sub>2</sub>

Deposits were obtained at the 670°C setting on two 100 Ge substrates. The second substrate (located approximately 1 inch downstream on the first substrate) had a mirror-like finish that was n-type and exhibited a 5.525 Å cubic lattice constant that is within 0.4 percent of the cubic ZnSiAs<sub>2</sub> lattice constant (5.542 Å reported by Stroud, Clark, and Springthorpe<sup>\*</sup>). This essentially reproduces the results that had been obtained earlier using this growth system under these growth conditions.

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\* Stroud, Clark, and Springthorpe, J. Cryst. Growth, 26 (1974), pp. 183-185.

### Electrical Evaluations

ZnSiAs<sub>2</sub>, deposited on quartz substrates for the purpose of electrical measurements, exhibited very high resistivity which was believed to be due to a large number of microcracks that resulted in completely isolated islands of ZnSiAs<sub>2</sub>. Secondly, In contacts that were successfully used on the epitaxial ZnSiAs<sub>2</sub> would not wet the layers deposited on quartz. Depositions on quartz substrates for the purpose of electrical evaluations were discontinued.

### Ion Implantation

Seven ZnSiAs<sub>2</sub> layers were implanted with 4 keV Se ions at a dose of  $5 \times 10^{13}$  ions/cm<sup>2</sup> and were subsequently coated with SiO<sub>2</sub>. The samples will be annealed and evaluated during the early part of the next report period. This work was performed courtesy of Dr. James Comas, Naval Research Laboratories, Washington, D.C.

### Organometallic Growth Approach

The original open tube vapor phase epitaxial growth system used to synthesize ZnSiAs<sub>2</sub> layers under the original contract and during the majority of this quarter has been converted to an RF induction heated organometallic system. This system will use an RF heated graphite susceptor to provide the required substrate temperature plus employ Zn(CH<sub>3</sub>)<sub>2</sub> (dimethyl zinc or DMZn) in lieu of elemental Zn plus the previously used SiH<sub>4</sub> and AsH<sub>3</sub>. The advantage of this system is that premature SiH<sub>4</sub> decomposition will be prevented, and extraneous wall deposits will be eliminated. The reactor has been fabricated and is a quartz tube with a single inlet reactant entry plus uses a water jacketed design to permit water cooling the reactor walls. This system is expected to improve Zn transport rate control as well as improve turn-around time by virtue of

the greatly reduced thermal mass and a back-flushed o-ring substrate loading port. Conversion to this system has been completed except for the loading port, whose delivery from the machine shop was delayed by one week.

### 3.0 PLANNED EFFORT

Planned effort for the next quarter includes determining growth conditions for the organometallic system and evaluating the deposited layers.

The ion implanted samples will be annealed and characterized to determine if the material was type converted and to look for p-n junction behavior. Additional samples will be submitted for continued ion implantation studies.

Emphasis during the upcoming period will be placed on measuring and reducing the carrier concentration of the p-ZnSiAs<sub>2</sub> layers using the new growth system. Synthesis and evaluation of the n-ZnSiAs<sub>2</sub> will be continued.

No problems are anticipated at this time that will impede this effort.