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DEVELOPMENT OF HIGH EFFICIENCY, LOW COST ZnSiAs_2 SOLAR CELLS

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ABSTRACT

Several significant achievements are described in this third quarterly report. The first is the successful deposition of mirror-like, single phase, epitaxial ZnSiAs_2 layers on 100 Ge substrates using the organometallic growth approach. Secondly, the quality of the first layers have already exceeded that of the material grown with the original growth system. Carrier concentrations (holes) are approximately one order of magnitude lower. Thirdly, amorphous (glassy) deposits of zinc silicon arsenide, which heretofore have not been reported, have been grown. Both p- and n-type conductivities have been observed. Finally, several $\text{p-ZnSiAs}_2/\text{n-GaAs}$ structures have been grown which exhibit photovoltaic behavior. AMO conversion efficiencies of 1 to 3% have been measured.

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1.0 INTRODUCTION

The effort during the third quarter was directed primarily towards defining the conditions required to synthesize single phase, epitaxial ZnSiAs_2 using the RF induction heated, organometallic open tube vapor phase growth approach. In spite of some unexpected problems, the growth conditions were successfully identified and the system has routinely produced mirror-like, epitaxial ZnSiAs_2 on 100 Ge substrates for the last two weeks of the quarter.

The carrier concentrations measured in the first layers synthesized with this new technique were approximately one order of magnitude lower than those measured for the material grown with the original system. Furthermore, x-ray diffraction data has shown very clear improvements in the crystal quality.

An ohmic contact for p-ZnSiAs_2 has been identified which has facilitated the fabrication of several $\text{p-ZnSiAs}_2/\text{n-GaAs}$ structures which exhibit photovoltaic behavior. AMO conversion efficiencies of 1 to 3% have been measured. The results of spectral response measurements are described in more detail in this report in addition to voltage vs current characterizations.

Finally, amorphous (glassy) zinc silicon arsenide deposits were obtained quite unexpectedly during this research. While some glassy chalcopyrites have been reported before, this is believed to be the

first such report of a glassy zinc silicon arsenide. These deposits were obtained during the course of defining the ZnSiAs_2 growth conditions.

2.0 TECHNICAL DISCUSSION

2.1 General

This section describes the details of the experimental effort conducted and results obtained during the third quarter of this research. The discussion will begin with the modifications made in the growth system followed by a discussion of the results obtained from the initial set of growth experiments that led to the synthesis of identifiable ZnSiAs_2 but complicated by the presence of a persistent second phase, Zn_3As_2 . A radical departure from the traditional RF heated susceptor design which eliminated the two phase deposition and resulted in the growth of mirror-like, epitaxial, single phase ZnSiAs_2 is also described along with the improvements observed in the material quality.

The remainder of this section describes several other significant developments including the discovery of amorphous zinc silicon arsenide deposits, the fabrication of ohmic contacts, and the fabrication of p- ZnSiAs_2 /n-GaAs structures which exhibit photovoltaic behavior. I-V and spectral response data are included and discussed for these devices.

2.2 Growth System Modification

A Leeds and Northrup (L&N) Type 60 current acting type (CAT) controller with a L&N Speedomax H recorder was installed in order to

provide precise growth temperature control. A type K ungrounded thermocouple with a grounded Inconel sheath (1/8" OD) provides the temperature monitoring and process variable input to the L&N process controller. The 0 to 5 ma current output from the controller is fed into a current amplifier (gain of 400) which provides the necessary 0 to 2A drive to the saturable reactor in the LEPEL RF generator. Figure 1 shows a schematic of the system as it is now configured. The controller package routinely provides temperature stability and reproducibility of 0.2°C.

2.3 Zn Transport Rate

Operating data has shown that the DiMethyl Zinc (DMZn) transport rate is less than that expected based on equilibrium vapor pressure calculations. The DMZn is now maintained at 0°C (15° higher than originally calculated). An effective partial pressure of 82 torr was calculated from DMZn usage rate and bubbler flow rate data which is to be compared with a reported equilibrium vapor pressure of 125 torr at 0°C.

2.4 Two Phase Deposition Problem

The deposition conditions, used initially, attempted to reproduce those conditions that were used successfully in the earlier growth system. The RF susceptor design used initially was essentially that used in the horizontal tube continuous flow vapor phase systems used

Figure 1. Diagram of growth system used for organometallic growth of ZnSiAs_2 . Shown in reactor is a cross sectional sketch of a graphite susceptor typically used in this type of system.

to deposit Si from SiH_4 or GaAs from Tri-methyl gallium and AsH_3 (or other III-V compounds from appropriate materials). This design is of course the traditional rectangular graphite slab as shown in Figure 2.

The deposits obtained however were either pure Zn_3As_2 or multiphase deposits consisting of compounds containing Zn, Si, and As. Single phase, epitaxial ZnSiAs_2 was obtained one time but could not be easily reproduced. Typically, however, two phase deposits were obtained which were identified as Zn_3As_2 and ZnSiAs_2 using x-ray diffraction techniques and took on the appearance shown in Figure 3. The deposit shown was grown on a 111 Ge substrate. Figures 4a through 4d show a mapping of the distribution of the elements Zn, Si, and As obtained with a KEVEX (energy dispersive x-ray analytical attachment) used in conjunction with an ETEC scanning electron microscope (SEM).

The two phase depositions persisted through almost all reasonable variations in growth temperature, reactant flow rates, and reactant ratios.

2.5 Glassy Deposits

In addition to the two-phase deposits, mirror-like deposits were obtained that exhibited no discernible crystalline structure as determined with the x-ray diffraction technique. The deposits are amorphous as can be seen from the x-ray diffraction pattern shown in Figure 5. This sample was deposited on $\alpha\text{-Al}_2\text{O}_3$ substrates and was grown under Zn deficient conditions. The results of an electron microprobe quantitative analysis are also included in Figure 5.

Figure 2. Sketch of typical RF Induction heated graphite susceptor. Small wells were added to provide temperature calibration via correlation of melting and freezing points of known metals (or alloys) with the thermocouple readout.

Sample OM51B

Figure 3. SEM photomicrograph showing two-phase deposits of Zn_3As_2 . These were consistently obtained when using the traditional flat plate type RF heated graphite susceptor.

a. Photograph showing two-phase deposits

b. Zn map

Figure 4. SEM photograph (a) of a two-phase region shown magnified 1500 times. The photos in (b), (c), and (d) show the distribution of Zn, Si, and As respectively. These mappings were obtained via energy dispersive x-ray analysis techniques which display the relative concentrations of the indicated elements as a function of position.

c. Si map

d. As map

Figure 5. X-ray diffraction pattern showing amorphous zinc silicon arsenide deposit on α -Al₂O₃ substrate. Elemental composition determined with electron microprobe.

Similar results shown for another sample are shown in Figure 6 which shows the x-ray diffraction pattern obtained for glassy deposits obtained on a 111 Si substrate. The electron microprobe results are also shown but it is not certain how reliable the Si concentration is. Note however, that the Zn content is significantly higher than for the sample discussed in Figure 5. It is not known over what range of compositions that this glassy structure can be maintained. These deposits deserve additional study as they can be deposited on a variety of smooth, non-crystalline substrates and yet still exhibit a mirror-like, featureless growth habit.

2.6 Growth of Mirror-like, Single Phase, Epitaxial ZnSiAs₂

The two phase deposition problem discussed in section 2.4 persisted with the use of the traditional flat slab susceptor described earlier (see Figure 2). The glassy deposits, which tended to be Si rich, always occurred immediately downstream of the Zn₃As₂ or the two Zn₃As₂ - ZnSiAs₂ deposition region. Additionally, the occurrence of the heavy wall deposits (containing As and Zn) suggested a high degree of As and Zn transport away from the substrate surface and thus a hot wall susceptor design was evolved to reduce these losses. The hot wall susceptor (patent is being applied for) is shown in Figure 7.

The use of the hot wall susceptor resulted almost immediately in the synthesis of mirror-like, epitaxial, single phase deposits of p-ZnSiAs₂ (001 ZnSiAs₂ on 100 Ge substrates). X-ray diffraction data

Sample No. OM53D

Figure 6. X-ray diffraction pattern showing amorphous zinc silicon arsenide deposit on 111 Si substrate. Elemental compositions shown were determined with electron microprobe.

Deleted pending patent clearance

Figure 7. Sketch of new susceptor design that led to the successful growth of mirror-like, epitaxial ZnSiAs_2 using the organometallic growth technique.

COMPARISON OF EPITAXIAL 001 ZnSiAs₂ GROWN ON 100 GE SUBSTRATES. COPPER TARGET USED.

Fig. 8. X-ray diffraction patterns illustrating improvements in crystal quality obtained using organometallic system. The improvement is seen through the ability of the epitaxial layer to resolve the CuK _{α 1} and CuK _{α 2} x-ray lines. The deposits are (001) ZnSiAs₂ grown on 100 Ge substrates.

taken on these samples has shown that the layers are epitaxial and that the crystal quality has improved over the layers grown earlier. This is easily seen in Figure 8 which shows the typical 008 ZnSiAs_2 reflections for earlier material (Figure 8a, grown with the original growth technique) and the material grown with the hot wall susceptor (see Figure 8b). Evident in Figure 8b is the splitting of the $\text{CuK}\alpha$ doublet by the 008 ZnSiAs_2 reflection. This is generally typical of good single crystal substrate material and good epitaxial layers which were not seen for the ZnSiAs_2 layers grown earlier.

In addition to the improvement in crystal quality, an improvement (reduction) in carrier concentration was also observed in the newer material. Using the C-V technique (using Hg probe), hole concentrations as low as $9.3 \times 10^{17}/\text{cm}^3$ have been measured. Heavily doped n-Ge substrates (5×10^{18} electrons/ cm^3) were used and did not permit the use of the Hall Effect measurement technique. Layers have recently been grown on $\alpha\text{-Al}_2\text{O}_3$ substrates (1 $\bar{1}$ 02) and on high resistivity (100 to 300 $\Omega\text{-cm}$) n-type (111) Si substrates which should facilitate these measurements. However, the morphology did not appear to be quite as good as for the layers grown on Ge.

Growth rates for (001) ZnSiAs_2 on 100 Ge are in the 3 to 10 $\mu\text{m/hr}$ range depending on SiH_4 flow rate.

2.7 Ohmic Contacts

An acceptable ohmic contact has been demonstrated for p- ZnSiAs_2 . The contact is a four-layer metallization that has been used successfully

in wide bandgap III-V semiconductor alloys such as p-AlGaAs of which ZnSiAs₂ is an electrical analog. The structure is Mn/Ti/Pd/Ag which is then alloyed at 450°C for one minute under flowing N₂. The contacts are typically 15 mil diameter contacts deposited on 20 mil centers. A typical I-V curve obtained between two such contacts is shown in Figure 9.

2.8 p-ZnSiAs₂/n-GaAs Structures with Photovoltaic Behavior

p-ZnSiAs₂/n-GaAs structures were fabricated in order to provide the first insight into the optical behavior of ZnSiAs₂ material. The OM series samples represent ZnSiAs₂ with the organometallic system while the others represent ZnSiAs₂ grown with the earlier system. The intent is to examine the short wavelength portion of the spectral response curve to deduce the nature of optical absorption in the ZnSiAs₂ material. It is recognized that surface recombination, interface recombination, and bulk recombination effects can also influence the short wavelength portion of the spectral response and of course must be considered.

Three p-ZnSiAs₂/n-GaAs structures have been fabricated using 100 GaAs substrates doped with electron concentrations of $8 \times 10^{16}/\text{cm}^3$ and one grown on an n-type 100 GaAs substrate with electron concentration of $4.2 \times 10^{17}/\text{cm}^3$. All of these exhibited photovoltaic behavior. I-V curves (light and dark) were obtained and the basic solar cell performance parameters measured under AMO illumination.* The results of those measurements are listed in Table 1.

*A high pressure Schoeffel Xenon lamp, with Model LPS255HR 1000 watt power supply adjusted to give 135 mw/cm² illumination. (No filter was used to correct the IR end of the spectrum.)

Sample 158B .2 V/div horizontal
 10 ma/div vertical

Fig. 9 Current versus voltage characteristic as observed between two 15 mil dia Mn/Ti/Pd/Ag contacts on surface of ZnSiAs_2 . Contacts were alloyed at 450°C for one minute. The observed resistance is 18.2Ω which implies a maximum specific resistance of $2 \times 10^{-2} \Omega\text{-cm}^2$.

Table 1. Performance data for p-ZnSiAs₂/n-GaAs Structures*

Device	V _{oc} (v)	J _{sc} (ma/cm ²)	Fill Factor	Total ₂ Area (cm ²)	η(%)
137A-1	.8	8.81	.682	.00375	3.6
137B	.72	2.6	.75	.154	1.04
137C-6	.79	6.49	.658	.0462	2.5
OM73A-2	.86	3.79	.65	.0468	1.4

*Calculations are based on active area which is 44.2% of total area; not corrected for reflection loss.

The V-I curves for these devices are shown in Figures 10 through 13. Spectral response (relative) data was also taken for each of these devices and plotted. These curves are shown in Figures 14 through 17. The log₁₀ I vs V data indicates that the forward current is dominated by a recombination mechanism (n=2). The resulting curves are shown in Figures 18 through 20.

It is not clear whether a heterojunction exists or simply a diffused p-n junction in the GaAs resulting from the in-diffusion of Zn. In either case, the major contribution to the photovoltaic behavior is expected to be from the GaAs since it is the smaller bandgap material.

The purpose of this structure is to deduce some optical properties of the ZnSiAs₂ layer by examining the high energy portion of the spectral response curve. However, before any of the optical properties of the ZnSiAs₂ can be deduced from the high energy portion of the spectral response curves, it is important to know where the electrical junction is located. Once the location of the electrical junction is known, then the contribution of the GaAs to the high energy portion of the spectral response curve can be ascertained (assuming that the GaAs material parameters are known).

$$J_{sc}=8.81\text{ma}/\text{cm}^2$$

$$FF=.682$$

$$\eta=3.6\%$$

AMO illumination
(simulated)

vertical: .01ma/div

horizontal: .2v/div

Figure 10. V-I characteristics (dark and AMO illumination conditions) for sample No. 137A-1. Origin is located at center of grid.

$$J_{sc}=2.6\text{ma}/\text{cm}^2$$

$$FF=.75$$

$$\eta=1.04\%$$

AMO illumination
(simulated)

vertical: .2ma/div

horizontal: .2v/div

Figure 11. V-I characteristics (dark and AMO illumination conditions) for sample No. 137B. Origin is located at center of grid.

$$J_{sc}=6.49\text{ma}/\text{cm}^2$$

$$FF=.658$$

$$\eta=2.5\%$$

AMO illumination
(simulated)

vertical: .05ma/div

horizontal: .2v/div

Figure 12. V-I characteristics (dark and AMO illumination conditions)
for sample No. 137C-6. Origin is located at center of grid.

$$J_{sc}=3.79\text{ma}/\text{cm}^2$$

$$FF=.65$$

$$\eta=1.4\%$$

AMO illumination
(simulated)

vertical: .05ma/div

horizontal: .2v/div

Figure 13. V-I characteristics (dark and AMO illumination conditions)
for sample No. OM73A-2. Origin is located at center of grid.

Figure 14. Spectral response for p-ZnSiAs₂/n-GaAs
Structure No 137A-1

Figure 15. Spectral response for p-ZnSiAs₂/n-GaAs Structure No 137B

Figure 16. Spectral response for p-ZnSiAs₂/n-GaAs Structure No 137C-6

Figure 17. Spectral response for p-ZnSiAs₂/n-GaAs Structure No OM73A-2

Figure 18. Plot of $\log_{10} I$ versus voltage for p-ZnSiAs₂/n-GaAs structure no. 137A-1. (no illumination, room temperature)

Figure 19. Plot of $\log_{10} I$ versus voltage for p-ZnSiAs₂/n-GaAs structure no. 137C-6. (no illumination, room temperature)

Figure 20. Plot of $\log_{10} I$ versus voltage for p-ZnSiAs₂/n-GaAs structure no. OM73A-2. (no illumination, room temperature)

3.0 PLANNED EFFORT

The effort planned for the next quarter will be directed towards reducing the hole concentration below the $10^{17}/\text{cm}^3$ range so that n-type doping studies can be conducted. If n-type material can be successfully prepared, then ZnSiAs_2 p-n junction formation will be attempted.

Basal plane (0001) $\alpha\text{-Al}_2\text{O}_3$ will be used in order to facilitate Hall Effect measurements on the as-grown layers. Correlations between hole concentration and either the Si:As ratio or the Zn:Si ratio will be sought and the hole concentration will be minimized accordingly.

Additional effort will be directed toward locating the electrical junctions in the $\text{ZnSiAs}_2/\text{GaAs}$ structures using the Electron Beam Induced Current (EBIC) measurement technique in conjunction with the Scanning Electron Microscope.