IMPROVED SEMICONDUCTORS FOR PHOTOVOLTAIC CELLS

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C00/2460-8
Quarterly Report, No. 8
April 1, 1978 to June 30, 1978
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1. SUMMARY

During this quarter, the main thrust of work has been the development of a Zn$_3$P$_2$ based, Schottky barrier solar cell with 5% AM1 conversion efficiency. Transparent metal film (TMF) devices, fabricated by sputter depositing magnesium, were evaluated. Sputter deposition was necessary to prepare air stable films with reproducible electrical and optical properties. The highest conversion efficiency achieved (no A-R) is 1.72%. An alternative, Schottky barrier grid device was devised to avoid the difficulties encountered with transparent metal films. Using relatively thick (2000 Å) magnesium films and line spacing on the order of twice the nominal $L_n$, a total area conversion efficiency of 6.08% was measured. Correcting for grid blockage yields an active area efficiency of 7.6%.

The diffusion length of minority carriers had been measured for a large number of single crystal devices using a spectral response technique as well as a newly developed laser scanning method. Good agreement between methods is obtained. Diffusion lengths as long as 9 μm have been found.

An extensive study of metal semiconductor contacts to Zn$_3$P$_2$ has been made. A simple Schottky model based on metal and semiconductor work functions does not explain the barrier height dependence. A model recently advanced by Brillson, which correlates barrier height with the enthalpy of the reaction taking place at the metal semiconductor interface is in excellent agreement with the data.

Thin films of Zn$_3$P$_2$ have been prepared by the close space transport method using muscovite mica as the substrate. The dependence of growth rate on temperature is that expected for an energy activated process. The activation energy deduced is in good agreement with the enthalpy of vaporization of Zn$_3$P$_2$. The grain size of the resulting films is of the order of 5-10 μm for 10 μm thick films. The electrical resistivity of thin Zn$_3$P$_2$ films is in excellent
agreement with that of single crystals annealed at the same vapor composition, and is two orders of magnitude less than films prepared by thermal vacuum evaporation.

11. DEVICE STUDIES

A. Introduction

The major goal of work conducted during this quarter was the development of a high efficiency (>5%) Zn₃P₂, Schottky barrier photovoltaic device. Two types of devices were prepared: (1) transparent metal film (TMF) devices and (2) Schottky barrier grid (SBG) devices.

As discussed in the previous quarterly report, attempts to prepare transparent aluminum film devices by vacuum evaporation yielded generally poor results. The electrical and optical properties of vacuum deposited films were not reproducible and a substantial dependence of these properties on the substrate employed and evaporation rate was noted. In contrast, sputter deposition yielded aluminum films with internally self consistent and reproducible properties. All devices prepared during this quarter were sputter deposited. Due to the limited progress shown by work on TMF devices during the previous quarter an alternative thick metal film, Schottky barrier grid device was also studied.

B. TMF Devices

TMF devices were prepared on nominally 200-cm, 10¹⁶ cm⁻³ chemically polished crystals using the microelectronic pattern mask described in previous reports. This device structure yielded a total area of 4.5 x 10⁻³ cm², not including contact pad area. Sputter deposited transparent magnesium films, prepared on glass showed reproducible electrical and optical properties which are in good agreement with values calculated from bulk properties. (Figure 1). It was
Figure 1 a): Sheet resistance of rf sputter deposited magnesium films.

b): Transmission and reflection of rf sputter deposited metal films on glass.
not possible to prepare thin 200 Å magnesium films by evaporation which were stable in air for even a short time. Sputter deposited films were relatively air stable, showing changes in resistivity only after several days exposure to air. In order to eliminate oxidation of the magnesium films deposited on Zn$_3$P$_2$, 5000 Å of SiO$_2$ was sputter deposited without breaking vacuum over the active area of the device.

Figure 2 shows the light (ELH-AM1-100 mw/cm$^2$) and dark current voltage characteristics of the best transparent (d=150 Å) magnesium device. The total area AM1 efficiency of this device is 1.72% (Voc. = .365V, $J_{sc} = 10.0$ mA/cm$^2$, FF = .47). Since the actual transmission of the magnesium TMF structure is calculated to be nominally 50%, the maximum corrected current density is 20 mA/cm$^2$. Corrected for transmission, the maximum observed efficiency is increased from 1.72% to 3.4%. The current density and open circuit voltage were fairly uniform ($J_{sc} = 8.91 \pm 3.3$ mA) across the wafer.

Fit of the light and dark diode current voltage dependence to

$$J = J_o (\exp - \frac{\phi_b}{kT} \exp - \frac{qV}{nkT}) - J_L$$

With $J_o = 120T$ A/cm$^2$ shows an effective barrier height of 0.7 eV in good agreement with value of barrier height obtained by internal photoelectric emission. Diode factors of 2.5 suggest current flow of the diode is dominated by generation-recombination within the depletion region. Under illumination, the effective barrier height is lowered to 0.64 eV, resulting in a lower open circuit voltage than expected from translating the dark curve by $J_L$.

C. Schottky Barrier Grid Devices

Stripe geometry devices were fabricated during this quarter as an alternative to TMF devices. Progress towards a successful TMF device was limited to the development of technology for preparing reproducible, transparent films. A stripe geometry was chosen because (a) the long (6 μm) minority carrier diffusion length
ZP113W7-C5
4000Å SiO$_2$/150Å Mg

VOC = .365 V.
JSC = 10.0 mA/cm$^2$
F.F. = .47
EFF = 1.72%

Fig. 2: Light and dark current voltage characteristic of transparent magnesium (150Å) film device.
in Zn$_3$P$_2$ allows the use of line spacings with adequate light transmission, and b) stable, thick metal films can be utilized. Magnesium was used as the barrier metal in all devices.

Figure 3 shows a schematic drawing of the device geometry used in this study. It consists of two large contact pads separated by a grid pattern. The line spacing of grids was 12 µm or twice the nominal diffusion length of 6 µm. The actual line width and separation of devices varied from sample to sample. The actual dimensions of completed devices were measured with the aid of a microscope.

Devices were prepared on chemically polished, 20Ω-cm, crystal wafers. Magnesium was thermally evaporated over the entire surface to a thickness of about 2000 Å. The evaporation rate was critical and held to about 100 Å/sec. to overwhelm the rate of O$_2$ impingement (∼5 Å/sec) at the deposition pressure. Higher rates gave a non-specular surface which was undesirable for photolithography. Ohmic contact was made to the back of the wafer with vacuum deposited silver ∼5000 Å thick. Samples were coated with ∼0.5 µm Kodak 747 micro-resist, prebaked, exposed developed and postbaked. The resulting image was etched using a solution of 10.0 ml of 30% H$_2$O$_2$ and 25 grams disodium EDTA diluted to 1 liter with deionized water, and adjusted to a pH of 10 with NaOH.

SiO, (n ∼1.65) deposited by thermal evaporation, served as an anti-reflection coating. Figure 4 compares the spectral dependence of reflectivity for bare and SiO (930 Å) coated, Zn$_3$P$_2$ wafers.
MICROELECTRONICS SCHOTTKY BARRIER GRID DEVICE

Fig. 3: Schematic diagram of the Schottky barrier grid device.
Fig. 4: Spectral dependence of reflectivity of bare and SiO coated chemically polished Zn$_3$P$_2$. 
Integration over the AM1 spectrum for wavelengths > 875 nm shows that reflection accounts for 33.4% loss of total photons available. With a 930 Å SiO coverage this loss is reduced to 12.3%.

Figure 5 summarizes the dark and AM1 (ELH -100 mW/cm²) current-voltage behavior obtained for a device with 2.35 μm line width and 12.65 μm line separation (edge to edge) having a net transmission of 80%. The conversion efficiency of this device with A-R coating is 6.08% (total area) and 7.6% corrected for active area. The reverse saturation current of the dark diode was 3.10⁻⁷ A/cm² with a diode factor of 1.9.

Figure 6 plots the spectral dependence of collection efficiency for another device, ZP106W4-C3 n = 4.48% (J_SC = 19.4 mA/cm², V_OC = 0.45V, FF = 0.51) with a 930 Å SiO anti-reflection cover. The collection efficiency of this device, corrected for front surface reflection is presented in Figure 6. Only a slight blue fall-off, indicative of surface recombination is noted. Taking the peak collection efficiency of .65 and the measured J_SC as 19.4 mA/cm² yields a maximum J_SC = 29.8 mA/cm².

D. Conclusions

The results of previous measurements of optical band gap (1.5 eV) and minority carrier diffusion length (≈ 6 μm) have suggested that Zn₃P₂ is an excellent photon absorber - minority carrier generator. The device results reported have been achieved with minimal optimization and in this light the efficiency achieved, 6.08%, is very encouraging. The maximum achievable AM1 current for E_g = 1.5 eV is 30 mA/cm² and hence the efficiency expected for a Zn₃P₂ Schottky barrier device is at most 9.45% (30 mA/cm² x .7 FF x .5V x .9 Transmission). It is stressed that this computation assumes that Schottky
ZP 107-W6
Device D-1
800\% SiO/Mg/Zn$_3$P$_2$
A=2.5 \times 10^{-3} \text{ cm}^2

J_{sc}=19.0 \text{ mA/cm}^2
V_{oc}=50 \text{ V}
FF = 64\%
\eta = 6.08\%

Fig. 5: Light (AM1-ELH-100mW/cm$^2$) and dark I-V of Schottky barrier grid device showing active area efficiency of 7.6\% and total area efficiency of 6.08\%.
Fig. 6: Spectral response corrected for front surface reflection losses (dashed) and uncorrected (solid) for 4.48% SGB device with AM1 $J_{sc} = 19.4 \text{ mA/cm}^2$. 

ZPI06W4 930A SiO/Mg-SBGD

- - - Corrected for %R
Uncorrected
devices will remain pinned at 0.5 V open circuit voltage. Such efficiencies will only be possible with the present device structure if higher current collection efficiencies can be achieved. A theoretical analysis of collection efficiency on device geometry and diffusion length is planned for the next quarter.

III. MINORITY CARRIER DIFFUSION LENGTH

In the previous section experimental results for TMF and stripe geometry magnesium Schottky diodes were presented. Sample to sample variations in the short circuit current resulted in a wide range of device efficiencies. Results on individual wafers however were generally uniform over the surface. Three hypotheses were considered to explain the variation of $J_{sc}$: 1) surface recombination effects 2) variable junction collection efficiency and 3) sample to sample differences in diffusion length. Surface recombination was rejected as a likely explanation for the observed low $J_{sc}$ since spectral response measurements of devices with low $J_{sc}$ exhibited a reduced output over the entire wavelength range rather than a pronounced blue fall off.

The minority carrier diffusion length was measured by a laser beam technique. The 6328 Å He-Ne laser emission was focused to a spot size near the diffraction limit and the current output measured as the spot was scanned towards a collection electrode. Incident power of the laser beam was measured with a calibrated Si cell.

The dependence of current on distance $x$ varied according to relation:

$$ I = I_o \exp(-x/L_n) $$

Where $I_o$ is the maximum collected current. Figure 7 shows a plot of data.
Figure 7: Collected current vs distance for 6328Å laser scan.
taken on a typical magnesium/Zn₃P₂ device. Extrapolation of the current to x=0 and comparison with the known laser incident intensity allowed an absolute measurement of the junction collection efficiency. \( L_n \) was also determined from spectral response measurements on thick samples (quarterly reports 6-7) from the same wafers. Table 1 summarizes measurements on several devices.

### TABLE 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>( L_n, \text{\ um} ) Laser Scan</th>
<th>( L_n, \text{\ um} ) Spectral Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZP118-W4</td>
<td>3.5</td>
<td>1.7</td>
</tr>
<tr>
<td>ZP118-W1</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>ZP37114-W2</td>
<td>8.4</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>7.76</td>
<td></td>
</tr>
</tbody>
</table>

This data indicates that the variability in \( J_{sc} \) is the result of sample to sample variations in \( L_n \). The line space of the grid device must be no more than twice \( L_n \) for optimum current collection and therefore the current output is expected to be controlled by \( L_n \). In the present devices line separation is normally 12 \( \mu \text{m} \) so the 1.7 \( \mu \text{m} \) - 8.8 \( \mu \text{m} \) range of \( L_n \) would certainly account for the observed \( J_{sc} \) variation.

### IV. BARRIER HEIGHT MEASUREMENTS

Since the last reporting of barrier height measurements on Zn₃P₂ (Quarterly Report No. 6), more data has been accumulated for diode contacts of aluminum, magnesium, and beryllium. The variation of observed barrier height with metal species has been fitted to a recently published empirical model more successfully than it can be correlated with metal work function. This empirical model has also been used to predict other candidates
for diode contacts to Zn$_3$P$_2$.

The spectral response system used to take the IPE measurements of barrier height was improved by adding an operational amplifier stage between the sample and the lock-in; this allows a preamplification of the signal by a factor of up to $10^5$ while maintaining zero voltage across the device. The average barrier heights (IPE) from a number of samples with varying surface preparation were as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\phi_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.77 ± 0.09</td>
</tr>
<tr>
<td>Mg</td>
<td>0.81 ± 0.03</td>
</tr>
<tr>
<td>Be</td>
<td>0.73 ± 0.07</td>
</tr>
</tbody>
</table>

The barrier heights from log I-V data reported previously for these metals are in good agreement with the values above. Reexamination of the capacitance data for a large number of magnesium devices revealed little justification for the barrier heights of 1.1 - 1.4 eV as reported previously. The capacitance data for chromium ($\phi_B = 0.4$ eV) and the log I-V data for iron ($\phi_B = 0.5$ eV) appear to be valid, although they are as yet unconfirmed by IPE measurements.

The data for these five metals, plus gold and silver which form ohmic contact to Zn$_3$P$_2$, are plotted versus metal work function$^1$ in Figure 8. The distribution of data points in this plot excludes the conventional linear relation.$^2$ Some recent work on semiconductor interfaces has emphasized the possible chemical nature of the bonding between metals and semiconductors.$^3,4$ Following the empirical correlation suggested by Brillson,$^4$ a plot is made of barrier height versus the heat of reaction per metal atom for the reaction of the metal with the semiconductor to form the appropriate metal phosphide; this is shown in Figure 9. The heats of
Fig. 8: Plot of barrier height of metal/Zn$_3$P$_2$ contacts vs metal/work function.
Fig. 9: Plot of barrier height of metal/Zn$_3$P$_2$ contacts vs $\Delta H_R$. 
reaction are handbook values\(^{(5,6)}\) except for beryllium which was estimated on the basis of its position in the periodic chart, and for chromium, for which a theoretical calculation has been published.\(^{(7)}\) The barrier height shows a step-like change around \(H_R = +1.0\) eV, as do Brillson's data. However for \(\text{Zn}_3\text{P}_2\) which is p-type, the higher barrier heights are associated with the lower values of \(\Delta H_R\). This is just the reverse of the four semiconductors discussed by Brillson which are all n-type.

The empirical correlation shown in Figure 9, allows two tentative predictions to be made. First, it appears that the barrier height attainable with a metal on \(\text{Zn}_3\text{P}_2\) is limited to a maximum of \(\sim 0.8-0.9\) eV. Second, other metals which have \(\Delta H_R > 1.0\) eV/atom are possible candidates for diode formation on \(\text{Zn}_3\text{P}_2\). Three such metals, Ti, Zn, and Ni are indicated in Figure 9, and it is planned to test these in the near future.

V. **THIN Zn\(_3\)P\(_2\) FILMS**

The study of thin \(\text{Zn}_3\text{P}_2\) films prepared by close space transport continued during this quarter with further refinement of growth conditions, characterization of crystallite orientation and measurement of electrical resistivity.

All thin \(\text{Zn}_3\text{P}_2\) films were prepared on \(\sim 13\) μm thick muscovite mica substrates. The rate of growth of films was studied as a function of source temperature over the range 650° C to 725° C, and the substrate temperature was held constant so that \(\Delta T\) (source-substrate) was 107 ± 4°C. The rate of deposition was determined by measuring the resulting average film thickness and using the elapsed growth time. Figure 10 summarizes these data as a plot of log rate (μm/min) vs. \(10^3/T\). The data can be fitted to a straight
Fig. 10: Log rate (μm/min) vs $10^3/T$ for growth of $\text{Zn}_3\text{P}_2$ films.
line as expected for an energy activated process. The expression for the rate dependence (650-725°C) is:

\[ R = 3.63 \times 10^{12} \exp(-2.39/kT) \]  

(1)

where the rate is expressed in \( \mu \text{m/min} \) and the activation energy in electron Volts. For high sticking coefficients (i.e. low substrate temperatures) the rate of growth of the film will be determined by the molecular flux arriving at the substrate. The temperature dependence of the equilibrium pressure should then determine the rate of film growth. For the vaporization of \( \text{Zn}_3\text{P}_2 \):

\[ \text{Zn}_3\text{P}_2 + 3\text{Zn} + 1/2 \text{P}_4 \]  

(2)

\[ K_p = P(\text{Zn})^3 P(\text{P}_4)^{1/2} \]  

(3)

At minimum total pressure (the conditions of the present experiment),

\[ P_{\text{total}} = P(\text{Zn}) + P(\text{P}_4) \text{ and } P(\text{Zn})/P(\text{P}_4) = 6 \]  

(4)

so that

\[ K_p = 729 P(\text{P}_4)^{7/2} \]  

(5)

Since \( K_p \) is determined by the heat of vaporization, \( \Delta H_v \), according to the relation:

\[ \ln K_p = -6.299 \text{ eV/kT} + 77.86 \]  

(6)

It follows from Equations 4 and 5 that the total pressure will have a temperature dependence proportional to \( \exp 2/7(-6.299/kT) \) i.e. \( \exp -1.8 \text{ eV/kT} \). This is within 30% of the activation energy found in the growth experiments, (Eq. 1).

Thin films grown on mica show a strong preferred orientation. Films grown on (HF:HNO₃, 1:3) etched mica exhibit either (220,004) or (303,321,105)
a) thin film (3 um) with strong (303, 321, 105) orientation

b) thin film (3 um) with strong (004, 220) orientation

c) thin film (3 um) prepared on cleaved mica, strong (004, 220) orientation

Figure 11: Scanning electron micrographs of thin $\text{In}_3\text{P}_2$ films on mica
orientations. The latter (Fig. 11a) is accompanied by a flat specular morphology with an apparent grain size in the substrate plane of approximately 6 \( \mu m \) for a 3 \( \mu m \) thick film. The (004,220) orientation is characterized by a non-specular, rough surface (Fig. 11b). Three micron thick films yielded an average grain size of \( \approx 3 \mu m \). The specular (303,321,105) growth was difficult to reproduce and generally occurred at the outer edges of the deposited film, and only with HF etched mica. In contrast, films deposited on freshly cleaved mica yielded only the (220,004) orientation. Figure 11c shows an SEM photograph of a nominally 10 \( \mu m \) thick film with an average grain size of \( \approx 5 \mu m \) (\( T_{source} = 675^\circ C, \Delta T = 107^\circ C \)).

The electrical resistivity of several thin films was measured by a two-probe technique, ignoring contact resistance. The resistance in the plane of the film was measured and an effective dark bulk resistivity calculated from the measured thickness (generally 3-10 \( \mu m \)). The table below summarizes these results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \rho )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPI-19</td>
<td>157 ( \Omega )-cm</td>
<td>2 \times 10^{15}</td>
</tr>
<tr>
<td>EPI-21</td>
<td>210 ( \Omega )-cm</td>
<td>1.5 \times 10^{15}</td>
</tr>
<tr>
<td>EPI-25</td>
<td>397 ( \Omega )-cm</td>
<td>7.8 \times 10^{14}</td>
</tr>
</tbody>
</table>

Since films are grown under conditions of minimum total pressure, \( P(Zn)/P(P_4) = 6 \), the expected resistivity of the single crystal can be calculated from the following relationship using a value of 20 \( \text{cm}^2/\text{V}-\text{sec} \) for carrier mobility\(^{(9)}\)

\[
[h^0] = 2.5 \times 10^{21} \rho(P_4)^{13} \exp(-0.59/kT) \quad (7)
\]

and using the known equilibrium constant for the vaporization of \( \text{Zn}_3\text{P}_2 \).\(^{(9)}\)
A temperature of 573°K is used in this calculation, since it is the lowest temperature at which equilibrium is achieved as the sample is cooled from growth. Making the appropriate substitutions yields an expected carrier concentration of $2.3 \times 10^{15} \text{ cm}^{-3}$ in very good agreement with the measured value for thin films. The lowest resistivity previously obtained for vacuum evaporated thin films was $\sim 10^4 \Omega\text{-cm}$, much higher than expected for the bulk crystal and too large to yield practical photovoltaic devices. The present films, with grain size greater than or equal to the 6-8 μm diffusion length and low, bulk-like resistivity appear well suited for device applications. During the next quarter, effort will be devoted to developing a suitable electrically conducting substrate for prototype devices.
REFERENCES


