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THEORETICAL MODELS OF EFFICIENCY FOR POLYCRYSTALLINE THIN FILM SOLAR CELLS

DE-AC-1-79ET 23107

Quarterly Progress Report No. 3

August 1 - October 30, 1980

December, 1980

INSTITUTE OF ENERGY CONVERSION
University of Delaware
Newark, Delaware 19711

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By
Ines Pereyra
and
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THEORETICAL MODELS OF EFFICIENCY FOR POLYCRYSTALLINE THIN FILM SOLAR CELLS

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1. SUMMARY

The calculation of the short circuit current and the open circuit voltage for a shallow p-n homojunction of Zn_3P_2 was completed.

The contributions of the three regions of the cell (n-layer, space charge region and p-layer) were considered.

The parameters varied were the thickness of the n-layer, the diffusion length, the surface recombination velocities and the carrier concentration.

The model assumes a shallow, abrupt p-n homojunction. Reflection losses are not taken into account.

The spectral response, the short circuit current and the open circuit voltage are predicted as functions of the material parameters for AM1.5 illumination.

A paper was prepared and was presented in the meeting of the A.V.S. held at Detroit on October 14-17.

2. SPECTRAL RESPONSE

The spectral response was calculated as a function of x (width of the n -layer), N_A and N_D (impurity concentrations) and diffusion length.

The equation for the contributions of the three layers are:⁽¹⁾

$$\eta_n = \alpha(\lambda)L_p / ((\alpha(\lambda)L_p)^2 - 1) ((K_p L_p + \alpha(\lambda)L_p) / (K_p L_p \sinh(X/L_p) + \cosh(X/L_p)))$$

$$- (\exp(-\alpha(\lambda)X) (K_p L_p + \tanh(X/L_p))) / (K_p L_p \tanh(X/L_p) + 1)$$

$$- \alpha(\lambda)L_p \exp(-\alpha(\lambda)X)$$

$$\eta_W = \exp(-\alpha(\lambda)X) [1 - \exp(-\alpha(\lambda)W)]$$

$$\eta_p = \alpha(\lambda)L_n / ((\alpha(\lambda)L_n)^2 - 1) (\exp(-\alpha(\lambda)(X+W))) ((\alpha(\lambda)L_n) - \tanh(Y/L_n))$$

$$- (\alpha(\lambda)L_n \exp(-\alpha(\lambda)Y)) ((\cosh(Y/L_n))^{-1}))$$

Where:

α = absorption coefficient

W = width of the space charge region

λ = wave length

Y = width of the p -layer

L = diffusion length

K = surface recombination velocity

X = width of the n -layer

In Figures 1, 2 and 3 the dependence of the overall collection efficiency on N_A , N_D , L_n , L_p and X can be observed.

For a given value of W (given by N_A and N_D), the collection efficiency diminishes uniformly with the width of the n-layer for short wavelengths. For long wavelengths that is not the case, and due to the intensity of the incoming flux at any wavelength, this can cause an optimum width for the total current.

The collection efficiency does not appear very sensitive to the values of N_A and N_D , although there is a slight shift for medium wavelengths.

3. SHORT CIRCUIT CURRENT

J_{sc} was computed by integration of the collection efficiency weighted by the incident flux at AM1.5.*

An optimum width for the n-layer was found (see Figures 4 and 7). The maximum value of the current is not very dependent on the diffusion length, but the position of the maximum is very sensitive on the value of the diffusion length. The optimum width ranges from 0.8μ to 0.4μ when the diffusion length changes from 5μ to 2μ .

* Terrestrial Photovoltaic Measurement Procedures, (June 1977), NASA T. M. # 73702.

4. OPEN CIRCUIT VOLTAGE

V_{oc} is estimated from the dark diode current and the short circuit current. The dark diode current is calculated as the superposition of the space charge recombination and minority carriers diffusion. Solving from these, one gets:

$$V_{oc} = \frac{2kT}{q} \ln \left[\left[\left(\frac{J_{orec}}{2J_{od}} \right)^2 + \frac{J_{sc}^{1/2}}{J_{od}} \right] - \frac{J_{orec}}{J_{od}} \right]$$

Where:

J_{orec} = dark saturation current due to recombination in the space charge region

J_{od} = dark saturation current due to minority carriers diffusion

$$J_{orec} = q \frac{n_i D}{L^2} W$$

$$J_{od} = q \frac{D}{L} n_i^2 \left[\frac{1}{N_A} + \frac{1}{N_D} \coth \left(\frac{X}{L} \right) \right]$$

D is the minority carrier diffusion coefficient
 n_i is intrinsic carrier concentration

In Figure 5 we can see that V_{oc} decreases uniformly as function of the n-layer width. Also for a given value of N_D the higher the value of N_A , the higher V_{oc} .

But what one looks for is the optimum value of the power ($J_{sc} \times V_{oc}$). In Figure 6 one can observe that this optimum depends on W (N_A , N_D) and on the diffusion length.

5. CONCLUSIONS

An optimum width was found for the n-layer, together with upper limits for the short circuit current and open circuit voltage. These and the theoretical curves for the spectral response V_{oc} vs X and J_{sc} vs X will be compared with experimental results for Mg diffused Zn_3P_2 devices.

It might be that some refinement should be done with respect to the abrupt junction approximation. Also considerations on fill factor will be made, to complete estimates on limits of efficiency.

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FIGURE 1

SPECTRAL RESPONSE Vs WAVELENGTH

FIGURE 2

SPECTRAL RESPONSE Vs WAVELENGTH

FIGURE 3

SPECTRAL RESPONSE Vs WAVELENGTH

FIGURE 4

J_{sc} Vs WIDTH OF n LAYER

FIGURE 7

Width of n Layer (μm)
 J_{sc} Vs WIDTH OF n LAYER

A PINHOLE MODEL FOR METAL-INSULATOR-
SEMICONDUCTOR SOLAR CELLS*

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1. INTRODUCTION

An important class of solar cells under active study¹ for potential low-cost terrestrial use, is the metal-insulator-semiconductor structure (MIS). The feature that makes these devices more attractive than the simple metal semiconductor Schottky diode is the observed⁽¹⁻⁵⁾ and predicted⁽⁶⁻¹²⁾ increase in open circuit voltage that is a consequence of the presence of the insulating layer. The insulating layer causes a reduction in the dark saturation current as compared to a Schottky device prepared with the same metal and semiconductor, and if no reduction in short circuit current and fill factor results, produces an increase in open circuit voltage and cell efficiency. There is a rather narrow range in insulator thickness δ ($10 \text{ \AA} < \delta < 20 \text{ \AA}$) in which higher efficiency can be obtained.⁽⁹⁻¹²⁾

The key issue involved in understanding the behavior of MIS devices and hence in designing higher efficiency MIS solar cells is what mechanisms produce the lower saturation current. A number of models have been proposed⁽⁶⁻⁸⁾ with varying degrees of success.⁽⁹⁻¹²⁾ Basic to all the models is the question

of how minority and majority carriers pass through the insulating layer. The mechanism usually assumed is tunneling,^(7,8,13) although trap assisted minority current flow has been suggested as a feature which would be beneficial.⁽⁹⁾ Aside from this common feature of tunneling, the various models place different emphasis upon a number of features of the junction region. These include the density and nature of interface states at the semiconductor insulator interface, the distribution of voltage between interface states and the depletion region of the semiconductor, the storage of charge in the insulating layer and the sign of such charge, the carrier transfer rates between interface states and the metal and between the interface states and the majority carrier band, and the effects of light on the interface state occupation. While all of these factors may be relevant in some of the devices studied, here we shall address only the question of how the carriers traverse the insulating layer.

In the experimental MIS structures it has been found that the peak in open circuit voltage and efficiency occurs when the insulating layer is less than $20 \text{ \AA}$ thick.^(8,9) In most of the devices fabricated the insulating layer is a native oxide of the semiconductor (SiO_x on Si, and mixtures of GaAsO_4 , As_2O_3 and Ga_2O_3 on GaAs), formed by heating, deposition, or chemical processes. The metal layer is then deposited upon the insulating layer. It is well known^(14,15) that it is quite difficult to obtain uniform thickness in layers so thin, and that small regions (pinholes) completely free of the insulator occur. Indeed, it has recently been recognized that such pinholes must occur^(14,15) and some of the negative effects they might produce have been explored. In contrast to the approach that pinholes are an inherent

negative factor in MIS solar cells, we find that they can be the means by which the minority and majority carriers pass through the insulating layer. They are thus the controlling elements that determine the open circuit voltage and efficiency that can be achieved; and to understand both the present devices and produce better ones we have studied the limitations produced by the size and distribution of the pinholes.

2. CURRENT FLOW IN SCHOTTKY AND MIS DIODES

Figure 1 shows the band picture for a p-type MIS solar cell. The expression for the diode current based on a simple tunneling picture is: ^(8,10)

$$j = A^* T^2 \exp(-\phi_{BP}/kT) \exp(-\chi_V^{\frac{1}{2}} \delta) [\exp(qV_S/kT) - 1] \quad (1)$$

where A^* is the Richardson constant for holes ($A^* = 120(m_h^*/m_o) \text{ amp/cm}^2 \text{ } ^\circ\text{K}^2$) and V_S the voltage drop across the semiconductor, with V the voltage across the cell, given by $V = V_S + V_i$, where V_i is the voltage drop across the insulator. In the limit that $\delta \rightarrow 0$ eq. (1) is the expression for an ideal Schottky diode. We note that the tunneling factor $\exp[-\chi_V^{\frac{1}{2}} \delta]$, with χ in eV and δ in $\text{\AA}$, simply reduces the current by a numerical factor from the Schottky value. While Eq. (1) is a plausible model for current transport across the insulator the experimental results indicate a current inconsistent with the bulk values of χ_V and χ_C expected for the insulators used (χ_V and χ_C are the interfacial barrier heights below the valence band and above the conduction band respectively). Card and Rhoderick ⁽⁸⁾ in considering SiO_2 on Si find that although $\chi = 3.15$ eV for bulk SiO_2 , to fit the data to the model χ must be assumed to vary with δ , the thickness of the oxide. The variation of χ with δ is such that in the range of δ over which the short circuit is observed not

to decrease significantly (up to $\sim 20 \text{ \AA}$), χ remains below 0.25 eV. Card and Rhoderick offer two explanations for this discrepancy. First they argue that for a layer which is on the order of 10 atomic layers or less one should not expect to define a band structure in a conventional sense. Second they argue that if a potential barrier can be defined it will not be constant over the entire contact area.

Studies of superlattices⁽¹⁶⁾ suggest that nearly bulk band structure is attained within a few atomic layers. Hence the argument that failure to reach bulk properties accounts for the low $\chi_v^{\frac{1}{2}}$ δ values has no strong theoretical or experimental basis. If this were so it would also mean that theoretical expressions were of little use unless $\chi_v^{\frac{1}{2}}$ vs δ could be determined by some means other than fitting the current-voltage curves.

There is, however, increasing evidence that thermally grown oxide layers on Si are non-stoichiometric^(14,17,18) with a composition SiO_x ($1 < x < 2$) within a region of $20 \text{ \AA}$ from the Si interface. One would thus expect that χ_v might indeed vary with thickness for layers prepared in this way but values as low as 0.25 eV are still not anticipated.

The second argument that the barrier height is not uniform is reasonable, in that layers less than $100 \text{ \AA}$ thick generally have "pinholes" or discontinuities^(19,20) which in the case of the usual fabrication of MIS devices would be filled with metal, as the metal is deposited on the insulating layer. The metal semiconductor contacts at such regions would be true Schottky diodes. If we assume that the χ_v and χ_c values are near their bulk values for the insulator, then all the diode-current would be carried by flow through the

"pinhole" Schottky regions until the pinhole density fell to nearly zero.

Based upon such a picture one recovers Eq. (1) but with the factor $\exp$

$-\chi_v^{\frac{1}{2}} \delta$ replaced by (A_p/A) , where A_p is the area of pinholes and A the total

area of the junction. The empirical variation of $\chi_v^{\frac{1}{2}} \delta$ with δ is then a

manifestation of the decreasing density of pinholes with insulator thick-

ness. The insulator simply reduces the contact area through which current

can flow.

3. QUALITATIVE FEATURES OF THE PINHOLE MODEL OF MIS DIODES

Based upon the arguments outlined in Section 2 the most likely current mechanism for flow through the interface appears to be Schottky contacts at pinholes in the insulating layer. The consequences of this picture can be given qualitatively:

1) Since the area of Schottky contact is reduced the total current through a given area for a given voltage is reduced.

2) For a solar cell if the short circuit current were undiminished from the Schottky value (see below) then the lower diode current cited in (1) would yield a higher open circuit voltage by $\Delta V_{oc} = \frac{kT}{q} \ln A/A_p$.

3) The short circuit current should not be reduced even when the diode current is substantially reduced due to a fundamental asymmetry between majority and minority current flow. (See Appendix) This asymmetry can be seen easily in Figure 1. Majority carriers (holes) which reach the barrier in a region other than a pinhole will be reflected back from the insulator into the bulk semiconductor and this retreat is aided by the direction of the electric field i.e. the majority carriers are moving up hill and when they are reflected by the insulator barrier they go back down the hill. The minority carriers (electrons) on the other hand, after being reflected by the insulator are maintained by the field near the barrier until they diffuse to a pinhole and reach the metal i.e. the minority carriers are moving down hill and after reflection from the insulator cannot make it up the hill again and accumulate at the bottom eventually finding their way to a pinhole. If the density of pinholes becomes too low the current will no longer be

capable of being carried without the density of minority carriers reaching such high values that they begin to diffuse back into the bulk semiconductor where they recombine. An estimate of the ratio (A_p/A) at which j_{sc} should begin to diminish is obtained by noting that the minority current crossing the metal semiconductor contact is $j_{minority} \approx q \frac{v_{th}}{4} n_j$ where v_{th} is thermal velocity and n_j the density of minority carriers at the pinhole. For undiminished short circuit current flow over the whole device area the condition is:

$$j_{sc} = q \frac{v_{th}}{4} n_j \frac{A_p}{A}$$

The short circuit current is due to diffusion from the bulk and is given by:

$$j_{sc} \approx q \frac{L}{\tau} n_{bulk}$$

Hence

$$n_j = \frac{4}{v_{th}} \frac{L}{\tau} n_{bulk} \frac{A}{A_p}$$

Since n_j is supplied by diffusion from regions around the pinhole and these in turn by diffusion from the bulk (aided by the space charge field) at some point minority carriers from the region around pinhole will begin to diffuse back to the bulk rather than to the pinhole or the space charge will become so large as to repel additional carriers. A rough estimate of when this should occur is $n_j = n_{bulk}$ or

$$\frac{A_p}{A} = \frac{4}{v_{th}} \frac{L}{\tau} = \frac{4}{v_{th}} \left(\frac{kT}{q} \frac{\mu}{\tau} \right)^{\frac{1}{2}}$$

For p-Si with $L_n \approx 2 \times 10^{-2}$ cm $\tau_n = 2 \times 10^{-5}$ sec and $v_{th} = 10^7$ cm/sec,

$A_p/A \approx 4 \times 10^{-4}$, $\Delta V_{oc} = 0.20$ V; while for n-Si with $L_p = 2 \times 10^{-4}$, $\tau_p = 10^{-8}$ sec,

$v_{th} \approx 10^7$ cm/sec, $A_p/A \approx 8 \times 10^{-3}$, $\Delta V_{oc} = 0.125$ V. These increases are in the range observed in MIS solar cells at the value of δ at which j_{sc} begins to decrease,⁽³⁾ and indeed higher V_{oc} is reported on p-type material than on n-type.⁽⁹⁾

4) Since the variation in pinhole area with the thickness of the insulator will depend on how the insulator is formed, the sensitivity of V_{oc} to oxide formation technique in MIS structures is readily explained.

4. ESTIMATES OF LIMITS OF EFFICIENCY

As in ordinary p-n junction solar cells we can write the efficiency of the pinhole MIS as

$$\eta = \frac{V_{oc} j_{sc} FF}{P_{in}}$$

where V_{oc} is the open circuit voltage, j_{sc} the short circuit current, FF the fill factor of the current voltage curve and P_{in} the power contained in the incident light (usually AM1 or its equivalent). Our picture of the operation of the device yields

$$V_{oc_{max}} = V_{oc \text{ Schottky}} + \frac{kT}{q} \ln(A/A_{p_{min}}) = V_{oc}^0 + (\Delta V_{oc})_{max}$$

where $A_{p_{min}}$ is the minimum area of the pinholes consistent with undiminished short circuit current. Hence for j_{sc} we have

$$j_{sc} = j_{sc}^0$$

We also expect that for $A_{p_{min}}$ the fill factor will not be seriously affected due to the series resistance associated with the spreading resistance.⁽¹⁵⁾ We can even anticipate a slight increase in FF associated with the higher V_{oc} . Assuming that j_{sc} doesn't have a strong voltage dependence produced by the change in junction field and space charge width, the maximum efficiency expected can be written as

$$\eta_{max} \approx \left(\frac{V_{oc} j_{sc} FF}{P_{in}} \right) \approx \eta_0 \left(1 + \frac{(\Delta V_{oc})_{max}}{V_{oc}^0} \right)$$

where η_0 is the value expected for a Schottky solar cell composed of the same metal and semiconductor as the pinhole MIS. Since $V_{oc}^0 \leq 0.5 \text{ V}$ for most

Schottky solar cells and $\Delta V_{oc} \leq 0.2$ V, increases in efficiency of up to 40% can be achieved. The resulting efficiencies will be roughly of the same magnitude as predicted for p-n junctions of the semiconductor based⁽¹⁰⁾ upon minority carrier diffusion controlling V_{oc} .

5. DISCUSSION

While the model proposed here for MIS solar cells, depends upon naturally occurring pinholes in the thin oxides to form the Schottky diode contacts that carry both the dark and light generated currents, more reliable and higher efficiency cells should be readily obtained by growing thicker oxides, or depositing insulating layers, and artificially producing "pinholes" of the appropriate density and size. The estimates of higher V_{oc} and the area of pinholes needed to carry undiminished short circuit current must be refined by detailed calculations. In the Appendix we have outlined the equations that must be solved to determine the minority and majority carrier densities and from these, the current densities and necessary pinhole areas will be obtained. These calculations are needed to determine the limits of efficiency more precisely and to guide the design of efficient solar cells based upon this model.

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Equilibrium electron band diagram for p-MIS cell.

Figure 1

APPENDIX

3.1 Equations Controlling the Minority and Majority Carriers Concentrations in the Depletion Region for an n-type MIS Device.

In the depleted region ($0 \leq Z \leq W$) the continuity equation and Poisson's equation lead, under the assumption that $N_D \gg p$, to:

$$\frac{\partial^2 p}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial p}{\partial \rho} - x \frac{\partial p}{\partial x} + \frac{\partial^2 p}{\partial x^2} - p = 0 \quad A.1.1$$

Where

$$\rho = \frac{r}{\left(\frac{kT}{q^2 N_D} \epsilon \epsilon_0 \right)^{\frac{1}{2}}}$$

and

$$x = \frac{(z-w)}{\left(\frac{kT}{q^2 N_D} \epsilon \epsilon_0 \right)^{\frac{1}{2}}}$$

This equation controls the spatial variation of the density of minority carriers ($p(\rho, x)$).

For majority carriers continuity and Poisson's equations give:

$$\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial n}{\partial \rho} + x \frac{\partial n}{\partial x} + n = 0 \quad A.1.2$$

The usual technique of separation of variables leads to the following one dimensional equations:

For holes (minority carriers) where $p(\rho, x) = h_p(\rho) g_p(x)$

$$\frac{d^2 h_p}{d(K_p^{\frac{1}{2}} \rho)} + \frac{1}{K_p^{\frac{1}{2}} \rho} \frac{dh_p}{d(K_p^{\frac{1}{2}} \rho)} - h_p = 0 \quad A.1.3$$

$$\frac{d^2 g_p}{dx^2} - x \frac{dg_p}{dx} + (K_p - 1) g_p = 0 \quad A.1.4$$

Where K_p is the separation constant to be determined by the boundary conditions.

For electrons (majority carriers), $n(\rho, x) = h_n(\rho) g_n(x)$

$$\frac{d^2 h_n}{d(K_n^{\frac{1}{2}} \rho)} + \frac{1}{K_n^{\frac{1}{2}} \rho} \frac{dh_n}{d(K_n^{\frac{1}{2}} \rho)} - h_n = 0 \quad A.1.5$$

$$\frac{d^2 g_n}{dx^2} + x \frac{dg_n}{dx} + (K_n + 1) g_n = 0 \quad A.1.6$$

So the radial equation is the same for majority and minority carriers. This equation will give the allowed values of the separation constant (K_p, K_n) through the boundary conditions.

3.2 Boundary Conditions: The conditions are that the total hole current, and the total electron current through the external wall of the cell ($r=r$; $\rho=\rho_c$) should be zero.

$$\left. \frac{\partial p(x, \rho)}{\partial \rho} \right|_{\rho=\rho_c} = 0; \quad \left. \frac{\partial n(x, \rho)}{\partial \rho} \right|_{\rho=\rho_c} = 0 \quad A.2.1$$

While at the semiconductor - oxide interface

$$(Z = 0; X = - \frac{W}{(\frac{kT\epsilon\epsilon_0}{p^2 N_D})^{\frac{1}{2}}} = x_0)$$

The condition is:

$$J_p \Big|_{x=x_0} = q S (p-p_e) \quad \text{A.2.2}$$

Where S is the surface recombination velocity. S will assume different values depending on whether there is oxide present at the interface or not for $r < r_p$ there is no oxide, so

$$S = \frac{v_{th}}{4}$$

for $r > r_p$ there is oxide and

$$S = 0$$

The solution of these equations with the boundary conditions indicated is quite complex and is not completed at this time. One result which falls out easily is that due to difference in signs for minority and majority carriers in Eqs. A1.4 and A1.6 the density of minority carriers increases as one goes into the space charge region while for majority carriers the density decreases. This is simply the mathematical representation of the fundamental asymmetry discussed in Section 3

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