UFR 1283 8-2
DOE/ET/20407--T1

EXXON RESEARCH AND ENGINEERING COMPANY

GOVERNMENT RESEARCH LABORATORIES

HETEROSTRUCTURE SINGLE-CRYSTAL SILICON PHOTOVOLTAIC CELL

(Type A, Semiconductor Heterojunction Silicon Devices)

Contract No. E(04-3)-1283

AC03-76ET20407

Annual Report

Period September 28, 1976 - November 30, 1977

Amal K. Ghosh
Tom Feng
Charles Fishman

Exxon Research and Engineering Company

Exxon/GRU.5BEC.77

**government
research**

This work was performed for U.S.
Energy Research and Development
Administration, Division of Solar
Energy, under Contract No. E(04-3)-1283.

P. O. BOX 8 ■ LINDEN, NEW JERSEY 07036

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

	<u>Page</u>
A. OBJECTIVE	1
B. SUMMARY OF IMPORTANT RESULTS	2
C. MAXIMUM THEORETICAL EFFICIENCY	4
D. CELL FABRICATION & RESULTS	5
E. COST ESTIMATES	10
F. RECOMMENDATIONS	11
G. APPENDIX	
Model of SnO ₂ /Si Heterostructure Solar Cell	13

OBJECTIVE

The objective of this contract is to perform an initial fabrication, testing, theoretical, and experimental study, which is necessary to prove and implement the technical and commercial practicability of the described photovoltaic devices in the near future (by 1980).

SUMMARY OF IMPORTANT RESULTS FOR THE
SnO₂/Si HETEROSTRUCTURE SOLAR CELL

I	<u>Efficiency</u>	<u>Exxon</u>	<u>Innotech</u>
	Sprayed	11.04	6.4
	Electron Beam	10.47	9.3
II	Reproducibility	Yes	No
III	Angle of incidence effect with electron beam deposited SnO ₂		
IV	First time theoretical analysis of J _{sc} , V _{oc} and F.F; capability of predicting maximum device efficiency ~ 20%.		
V	Short circuit current losses mainly due to reflection and shadowing. Theoretical fit of experimental action spectra.		
VI	Work function of SnO ₂ determined from photoemission studies. Oxygen adsorption affects work function.		
VII	Dark I-V can be represented by two exponentials related to thermionic and diffusion processes.		
VIII	Barrier height is related to work function differences, insulating oxide thickness and surface density of states.		
IX	Diode constant with the thermionic emission process is related to oxide thickness and surface density of states.		
X	Reverse saturation current for thermionic emissions could remain constant for larger values of diode constant if $\phi_0 \sim 0.3$ eV. ϕ_0 is defined as the energy below which the surface states must be filled for charge neutrality at the semiconductor surface.		

- XI Large diode constants suppress the thermionic emission component of the bucking current and result in larger open circuit photovoltages and fill factors.
- XII The presence of an SiO_x type layer at the SnO_2/Si interface was determined from Auger studies.
- XIII Efficiency is initially reduced by 10% and stabilizes or degradation continues at a reduced rate.
- XIV Diffusion of Al thru SnO_2 into Si could also be a source of degradation.
- XV Initial results indicate that efficiency and other characteristics may be orientation dependent.

MAXIMUM THEORETICAL EFFICIENCY

To compute the maximum efficiency of 21.38%, several assumptions are made. The short circuit current of 38 mA/cm^2 for 100 mW/cm^2 at AM1 is calculated for no reflection or grid coverage losses and a minority carrier diffusion length of 300μ . The series resistance is zero and the cell thickness is 300μ .

The power curve is generated by subtracting the dark current from the short circuit photocurrent. The dark I-V curve has two regions, each having J_0 and diode factor n values. For the theoretical power curve J_{01} is $1 \times 10^{-9} \text{ A/cm}^2$ and J_{02} is 1×10^{-13} . The diode factors for the lower and higher voltage regions are $n=3$ and $n=1$, respectively. The detailed theory is given in the appendix.

This combination of the dark I-V parameters, together with $I_{sc} = 38 \text{ mA}$, results in a cell with $V_{oc} = 0.666 \text{ V}$, fill factor = 0.844 and an efficiency of 21.38%.

PRACTICALLY ACHIEVABLE EFFICIENCY

In a practical cell, there are losses due to reflection, shadowing effects due to grids, series resistance etc. If these losses are taken into account, an efficiency of 15% is still attainable with a SnO_2/Si solar cell.

FABRICATION OF SnO_2/Si
HETEROSTRUCTURE SOLAR CELL

1. Clean wafer.
2. Deposit SnO_2 by electron beam evaporation or spraying.
Thickness: 500 - 700 $\text{\AA}$
3. Heat treatment in air at 300°C for 2-3 hours for electron beam deposited SnO_2 films.
No heat treatment necessary for sprayed films.
4. Evaporate grid electrode Ti - 1000 $\text{\AA}$; Ag - 1 μ .
5. Lap back surface.
6. Evaporate back electrode Ti - 1000 $\text{\AA}$; Ag - 5000 $\text{\AA}$.

Substrate: n type single crystal silicon

1-3 ohm-cm

Cleaning: A-15 min in 9:1 $\text{DIH}_2\text{O}:\text{HF}$
B-SC1 (H_2O_2 , NH_4OH)
C-SC2 (H_2O_2 , HCL)

Source: 99.9% pure SnO_2 powder.

The powder was packed tightly into a 1.5" diameter graphite liner and placed in a multi-hearth electron beam gun.

For the electron beam deposited cell, variations in the deposition rates, heat treatment, thickness, and other processing parameters of SnO_2 affect the properties of the cell and its solar conversion efficiency. However, we have found that highly efficient cells can be made only by depositing the SnO_2 at an angle. The effect of the angle of incidence on the conversion efficiency is shown in Fig. 1. In this plot the angle of incidence of the SnO_2 vapor was measured with respect to the normal of the silicon substrate. It can be seen from Fig. 1 that there is a sharp peak in

the efficiency around 60°. Also shown in Fig. 1 is a plot of the conductivity versus the angle of deposition. From the good match of the two curves, we concluded that one of the factors leading to higher efficiency is the lower resistivity. The sheet resistance of the tin oxide film of these highly efficient cells was on the order of a few thousand Ω /square whereas that of the less efficient ones, that were deposited at the incorrect angles, was on the order of ten thousand Ω /square or higher. For a 500 Å thick tin oxide film, a sheet resistance of a few thousand Ω /square is equivalent to a resistivity on the order of 10^{-2} ohm-cm. We also point out that the transmission spectrum of the SnO_2 is also a function of the angle of deposition; the larger angle depositions gave more transparent films. The smaller angle deposited films gave a deep yellowish color. Transmission for the large angle deposited films was as high as 95% in the visible region of the spectrum.

The SnO_2 in the sprayed cell was deposited onto the silicon through the following chemical reaction:

In order for this reaction to proceed, the SnCl_4 mixture must be sprayed onto a hot surface. This reaction proceeds rapidly at temperatures in the vicinity of 800°C. However, we found that the high temperatures drastically reduce the cell efficiency. We are presently depositing the SnO_2 at 450°C. Antimony was added in the form of SbCl_3 as a dopant to increase the conductivity. We prepared the spray coating material by mixing tin chloride (SnCl_4) into glacial acetic acid and by mixing antimony trichloride (SbCl_3) into methanol. Both mixtures are then mixed together to form the spray coating material. The purpose of the acetic acid and methanol, besides serving as a solvent for SnCl_4 and SbCl_3 , is to modify the rate of reaction; they introduce better reducing conditions for the above reaction to proceed. No subsequent heat treatment is necessary. The spraying was done by a newly

designed programmable system. We believe that the increase in the efficiency, from 1 percent reported earlier, was due to lower temperature, shorter spraying and heating cycle, and a better temperature control. Whether the angle of incidence of the spray mixture has an effect on the efficiency of the cell as in the electron beam deposition is not known at the moment.

For both the sprayed and electron beam deposited cells, the electrodes were deposited by electron beam evaporation in a high vacuum system. Recently we found that Ti/Ag or Ti/Al is a better electrode than the Cr/Al front and Au/Sb back contacts. The Ti/Ag or Ti/Al electrode makes a much better ohmic contact to the silicon than the Au/Sb used by Innotech. Our present electrodes consist of 1000 Å of titanium followed by 2 μ of aluminum as the front contact and 1000 Å of titanium followed by 5000 Å of aluminum for the back electrode.

The efficiency of some cells fabricated by electron beam deposition of SnO₂ and spraying is listed in the Table on page 9. The cells were tested by NASA/Lewis.

FIGURE 1

NASA/LEWIS VALUES

11/3/77

<u>PREPARATION</u>	<u>IDENTIFICATION</u>	<u>AREA (cm²)</u>	<u>J_{sc} (mA/cm²)</u>	<u>V_{oc}</u>	<u>F.F.</u>	<u>EFFICIENCY (%)</u>
Sprayed	S212G	0.99	27.7	0.578	0.666	10.67
Electron Beam	128F	1.01	27.1	0.544	0.705	10.40
Sprayed	S212A	0.91	28.5	0.579	0.658	10.84
Sprayed	S210E	1.0	25.7	0.566	0.672	9.75
Sprayed	S210C	3.95	28.1	0.577	0.681	11.04
Sprayed	S211B	0.91	25.3	0.577	0.703	10.26
Electron Beam	128G	1.0	27.2	0.544	0.695	10.30
Sprayed	32A	0.95	27.4	0.544	0.675	10.06

COST ESTIMATES

The projected cost of single crystal p/n solar cells¹ from ERDA studies are as follows:

1. Photoconductor	\$0.29/Peak watt ²
2. Junction Formation	0.046
3. Metallization	0.101
4. AR Coating	0.033
5. Test & Sort	0.012
6. Inter-connect Encapsulation Packaging	0.114
	<hr/> \$0.596/Peak watt

In SnO_2/Si cells, processes 2 & 4 can be combined and can be done for \$0.02/peak watt resulting in a cell cost of about \$0.537/peak watt. The process is simple and has a better chance of automation.

¹Proc. of ERDA Semi-annual Photovoltaic Program Review Meeting, Si Tech. Programs Branch, San Diego, California, January 18-20, 1977.

²Large Area Czochralski Silicon, ERDA/JPL-954475-76/2 - Texas Instrument Quarterly Report, September 1976 - S.N. Rea and P.S. Gleim.

RECOMMENDATIONS

We have made tremendous progress in the course of our contract study of the SnO_2/Si Heterostructure Solar Cell and would like to continue our work mainly to implement the technical and commercial practicability of the device in the near future.

- (1) In the next phase of the program we would like to scale up the size of the cells from its 1 to 4 cm^2 area to wafers at least 2 inches in diameter.
- (2) One area in which more work is needed to be done is the cell degradation. After an initial drop of about 10 per cent, the degradation is reduced greatly but whether it is completely stopped is not known. The results we have to date are inconclusive. The degradation may be related to the growth of an interfacial oxide or due to diffusion of the metal grid electrode into SnO_2 . Only by properly understanding the degradation mechanism can we prevent it.
- (3) In addition to the above two programs we would like to continue our device modelling studies to be able to improve device efficiency.
- (4) We would like to study the angle of incidence effect in more detail.
- (5) The studies made for single crystals in later stages of the project should be extended to well characterized inexpensive polycrystalline silicon.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

MODEL OF SnO_2/Si HETEROSTRUCTURE SOLAR CELL

This paper presents the model of the cell and will be published
in the Journal of Applied Physics.

SnO_2/Si SOLAR CELLS - HETEROSTRUCTURE OR SCHOTTKY BARRIER
OR MIS TYPE DEVICE*

A. K. Ghosh, C. Fishman and T. Feng
Exxon Research and Engineering Company
P.O. Box 8
Linden, N.J. 07036

The performance of SnO_2/Si solar cells has been measured and analyzed in detail. This has given us an insight into cell characteristics never revealed in the previous studies. Though the device is a junction between two semiconducting materials, SnO_2 and Si, it performs like an MIS device and in the thin oxide limit as a Schottky barrier device.

The dark I-V characteristics are attributed to a combination of thermionic and diffusion processes. The diode constant associated with the former is close to 2 or higher and that associated with the latter is 1. It has been demonstrated that under certain conditions the diode constant can be independent of the reverse saturation current. An MIS type model can explain the spectral response curve, the short circuit photocurrent, the open circuit photovoltage and the light and dark I-V characteristics. A theoretical limit of the efficiency is estimated for the device.

* Part of this paper was originally presented in October, 1977, at the 152nd Fall Meeting of the Electrochemical Society, Inc., in Atlanta, Georgia.

INTRODUCTION

In the last few years, SnO_2/Si and ITO/Si solar cell have been proposed by some¹⁻⁷ as low cost photovoltaic devices. The cost reduction obviously will be in the junction formation step and also in eliminating the antireflection layer. In order that such devices be a viable alternative to p/n junction solar cells, one needs to know more about the capability of the devices. However, no estimates now exist on the maximum efficiency of such cells or what factors limit it.

The system appears to be very appealing. Basically, SnO_2 is deposited onto a single crystal Si substrate by a technique such as electron beam. The processing is a low temperature step and could reduce degradation of carrier life times, a problem observed in some high temperature diffusion processes. The SnO_2 only absorbs in the uv and therefore acts as a window for sunlight. The barrier is located at the interface and should therefore reduce surface recombination and result in larger short circuit photocurrents. Further, at some wavelengths the refractive indices of SnO_2 and Si match so as to make SnO_2 a candidate for an antireflection coating.⁴ It can be expected that a thin layer of SiO_2 will form at the interface during processing and this oxide layer can strongly affect device performance as we shall discuss.

Three parameters are important in analyzing the performance of solar cells: the short circuit photocurrent, the open circuit photovoltage and the fill factor. Each of these parameters is described separately in the present report. The spectral response curves for SnO_2/Si have been theoretically analyzed for the first time to show that holes from the bulk reach the junction by diffusion and that in the junction they are transported by the built-in field of the barrier. It is assumed that for short circuit photocurrent, electrons from SnO_2 tunnel through the SiO_2 layer at the interface between SnO_2 and Si and recombine with the light generated holes. In devices where the SiO_2 layer is too thick and the tunneling transmission coefficient is less than one, the light generated holes recombine with electrons in Si giving rise to photocurrent suppression which is very similar to a series resistance loss.

The open circuit voltage in normal solar cells is dependent on the reverse saturation current, the short circuit photocurrent and the diode constant. The maximum value one can obtain for Schottky barriers is related to the diffusion potential, i.e., the difference in work function between SnO_2 and Si (if surface states do not interfere). However, an interfacial insulating layer can affect the diffusion potential and the magnitude of the open circuit photovoltage and other device parameters. The series resistance of the device can be reduced until the diode constant and the open circuit voltage are the only important parameters that determine the fill factor. The maximum value one could expect from SnO_2/Si solar cells is estimated.

Kajiyama and Furukawa¹ were the first to report about a SnO_2/Si heterostructure solar cell. The cell was only 0.1 percent efficient. The next work of interest is that due to Nishino and Hamakawa², although the efficiency of the device is not known. However, the energy band diagram is very similar to that presently shown in Figure 1.

The best efficiencies reported to date are due to R.L. Anderson,^{3,4} and Grater and others⁵ originally from Innotech. They have reported measured efficiencies close to 10 percent with SnO_2/Si cells. Anderson postulated an energy band scheme similar to that shown in Figure 2 to explain his results. The structure is an MIS type device instead of a normal Schottky barrier type system. According to Anderson the presence of a thin insulating layer in the SnO_2/Si devices can increase V_{oc} by decreasing J_o (the reverse saturation current). Anderson asserts that the dark current is predominantly due to electrons injected over the Si barrier through the oxide. Under illumination, holes are trapped in the potential notch in the valence band, where they recombine either with electrons from the SnO_2 and produce photocurrent, or with electrons from the Si conduction band via interface states and suppress the photocurrent.

Recently, there has been a paper on CVD deposited SnO_2 on a single crystal silicon cell by Kato⁶ et al. However, these cells were not as efficient as Anderson's cells. Another paper of interest has been presented

by DuBow and Burk⁷. Their cell is, however, a heterostructure cell of indium tin oxide and p-silicon.

In analyzing SnO_2/Si cells, the theory of MIS devices is useful. The three most important works are those due to Fonash⁸, Shewchun, Singh and Green⁹ and Card and Yang¹⁰. According to Fonash an interfacial insulating or semi-insulating layer can be used to improve the open circuit voltage and also the light generated carrier response by field shaping. For a given light generated current one would like to obtain the smallest value possible at a given total voltage for the two bucking terms - the thermionic emission and diffusion term. Schewchun et al proposes that the mechanism for current conduction is tunneling through the interfacial insulator. The operation of the cell according to them is based on the concept that they are minority carrier nonequilibrium MIS tunnel diodes. They have presented efficiency as a function of insulator thickness, substrate carrier concentration, surface states and oxide charge. For an insulator thickness of about $10\text{\AA}$ the cell exhibits Schottky diode behavior. According to them a maximum theoretical efficiency of 21% is possible under AM2 illumination for high substrate doping and low interface defect density. According to Card and Yang the increase in open-circuit voltage cannot be explained in terms of an increased n value for the dark current, but derives instead from the effect of the interfacial layer on the tunnel transmission coefficient for the majority carriers. They also predict how the short circuit current and open circuit voltages could be affected by the insulator thickness.

In the course of our presentation it will be shown that some of the important concepts for MIS cells are applicable to SnO_2/Si solar cells. No single mechanism can account for all the results and it is possible there are a number of mechanisms in action, either singly or in concert.

RESULTS AND DISCUSSIONS

The structure of the SnO_2/Si cell is shown in Figure 3. The silicon is an n-type material usually 1-3 $\Omega\text{-cm}$ resistivity and about 10-11 mils thick. After cleaning and etching the polished surface, a layer of SnO_2 is deposited by electron beam evaporation. The layer is about 500-700 $\text{\AA}$ thick. The wafer is then heated in air at 300-350°C for 1-2 hours. The back surface is then lapped and electrodes are put on the front and back, the top electrode being a grid structure as shown in Figure 3(b). For ITO/Si cells⁷ the deposition temperature is between 350-600°C and ITO thickness about 4000 $\text{\AA}$.

The device parameters of some of the cells constructed in the above manner are listed in Table I and II. Table I gives the short circuit photocurrent, the open circuit photovoltage, efficiency and the series resistance of the cells. The incident light was about 100 mW/cm^2 from a solar simulator. The light source is a short arc Xe lamp filtered through a Schott filter. The fill factors measured on the devices when the devices were first fabricated (in 1975) were higher than what we recently measured. The power curve recently measured for one of the devices is shown in Figure 4.

In the cells just described we believe that the SnO_2 is degenerate and behaves essentially as a metallic electrode. There is obviously some difference between the two. For metallic electrodes there is a continuous distribution of energy levels while for SnO_2 there is a band gap so that contact with Si is only through the conduction band. The electron affinity of SnO_2 ¹¹ has been postulated to be around 4.85 ± 0.16 eV by Anderson⁴. The band gap¹¹ of SnO_2 is assumed to be 3.42 eV. The transition at such an energy is attributed to an indirect transition¹². The energy level scheme of SnO_2 and Si are shown in Figure 1 (a) and (b). The Fermi level of n-Si is assumed to be 0.25 eV below the conduction band, which agrees roughly with the assumption that the silicon is 1-3 $\Omega\text{-cm}$ resistivity. We believe the entire depletion region is in silicon as shown in Figure 1 (b). Upon light absorption, holes are transported towards SnO_2 making it positive relative to silicon. Between SnO_2 and Si there is a thin layer of SiO_2 as

shown in Figure 2. Whether the diffusion potential is entirely related to the difference in work functions of SnO_2 and Si or to charged impurity and surface states is not known at present. For the short circuit photocurrent, the photogenerated holes recombine with electrons from SnO_2 which had tunneled through the SiO_2 layer. The recombination occurs through surface recombination states in Si. If the SiO_2 was thick, the tunneling would decrease and the photogenerated holes would be forced to recombine with electrons in Si leading to photocurrent suppression.

The Short Circuit Photocurrent and Related Parameters

Using a Beckman reflectometer, the total reflection from the SnO_2/nSi cell was measured. The wavelength range is from 350 nm to 1000 nm and the reflectance curve is shown in Figure 5. The samples received from Innotech were basically of three distinct colors. They were either a deep blue, a greenish-yellow or a brownish-gold, probably due to varying thicknesses of the SnO_2 . These qualitative differences also appear quantitatively in the reflectance and photoresponse curves. Figure 5 is the reflectance curve for a 4 cm^2 deep blue sample.

The photoresponse curves of the samples were measured over the wavelength range 350nm-150 nm with a tungsten light source and Schoeffel monochromator. A Corning interference filter was inserted at 700 nm to eliminate all second order effects. The light irradiance peak is on the order of $2.5 \times 10^{-3} \text{ W/cm}^2$ and a Keithley electrometer was used to measure the short circuit current. The bandpass for the monochromator is 20nm.

With appropriate analysis it is possible to compute the minority carrier diffusion length in the sample. The long wavelength photoresponse is most sensitive to the diffusion length. To establish a correlation between the short circuit current, I_{sc} , and the diffusion length, a computer modeling of the cell was done.

Beginning with the differential form of the continuity equation, including generation and recombination terms, the current density due to diffusion into and out of a volume can be solved for with appropriate boundary conditions.

The following equations were taken from reference 13 for the computer program. The definition of the terms are the same as in the reference.

$$D_p \frac{d^2 p}{dx^2} - \frac{(P-P_0)}{\tau_p} + \alpha_2 N^1 \exp(-\alpha_2 x) = 0 \quad (1)$$

Boundary conditions

$$P = P_0 \exp(qV/kT) \text{ at } x = \ell_2 \quad (2)$$

where V is the bias voltage across the diode

$$P = P_0 \text{ at } x = d \quad (3)$$

$$J_2 = q \left[\frac{\alpha_2 N^1 \exp(-\alpha_2 \ell_2)}{\alpha_2 + 1/L_n} - \frac{2\alpha_2 N^1 \exp(-\alpha_2 \ell_2) [\exp(-d/L_n) - \exp(-\alpha_2 d)]}{L_n(\alpha_2^2 - 1/L_n^2) [\exp(d/L_n) - \exp(-d/L_n)]} \right] \quad (4)$$

$$J_1 = qN^1 [1 - \exp(-\alpha_2 \ell_2)] \quad (5)$$

J_2 and J_1 are the currents in the bulk and barrier, respectively.

The above equations are very similar to those derived by Gartner¹⁴ for Schottky barrier cells.

Figure 6 shows the different regions of the cell used in our analysis. It is assumed that the quantum efficiency is equal to 1 in silicon. That is, for every photon absorbed, an electron-hole pair is created. Also, anything absorbed in or reaching the junction is collected. Input to the program includes the sample thickness, reflectance vs. wavelength values, incident photon flux vs. wavelength and the absorption constants as a function of wavelength. When the measured photoresponse is entered the program automatically varies the diffusion length until a best-fit is realized. The criterion for the best fit is to minimize the difference between the measured and predicted photoresponse. A fit of such a curve is shown in Figure 7. The generated curve contains 41 points and a plot of the measured and predicted curves is outputted. Next, the program calculates the integrated short circuit current for both the measured and predicted curves. Table III contains the data for 6 of the Innotech cells. The program also

varies the barrier width while varying the diffusion length, but the photo-response was relatively insensitive to the junction width within realistic limits for the junction width. This is understandable, since a 50-150 μ diffusion length and 275 μ cell thickness are large compared with a 0.2 - 2 μ junction width. An increase in junction width would only affect one or two data points in the short wavelength, high extinction coefficient region. The short circuit current values in Table III aren't sunlight values but are the product of the computed or measured quantum efficiencies and the entered photon flux. The deduced diffusion lengths can differ because of varying lifetimes in the bulk Si.

Differences in the predicted and measured integrated short circuit current, in Table III are caused by imprecision in the reflectance data and measurement of the grid coverage. Also, it is implied that the photocurrent collection mechanism in the SnO₂/Si cell is the same as the diffusion model theory. However, the existence of an insulating layer can cause other mechanisms to affect photocurrent collection. For one, the presence of insulating layer can lead to the situation pictured in Figure 2. Tunneling and the trapping of minority carriers at the oxide surface can result in photocurrent collection governed by laws other than straightforward diffusion. Short circuit photocurrents in Table I should not be compared with those in Table III. They were measured under entirely different illuminating spectra.

In the cells (Emdex/Innotech), a major portion of current losses are due to reflection and shadowing effects due to grids. The SnO₂ thin films act as an antireflection coating but is not comparable in performance to those used in commercial p/n junction solar cells. The shape of the spectral response curve was theoretically calculated by taking into account the reflection losses. In most cases it is not necessary to assume an inversion layer at the surface to account for the decrease in spectral response at short wavelengths¹⁵. Furthermore, for these cells we did not observe much photocurrent suppression although this had been suggested in some earlier published work by others.

A graph of J_{sc} vs. light irradiance is shown in Figure 8. The photocurrent is essentially linear with light irradiance. There is a slight deviation at high irradiance. A series resistance or photocurrent suppression could account for this slight deviation. To drive the current through a series resistance the cell must develop a forward bias. This bias increases the current flow in the dark current direction, subtracting from the photocurrent. As the irradiance and photocurrent increase, the bias voltage increases and shunts more photocurrent internally, resulting in a non-linear photocurrent dependence on irradiance.

The Open Circuit Photovoltage

For MIS-Schottky barrier cells¹⁰ in which thermionic emission is the dominant process:

$$J = J_o \exp(-\chi_n^{1/2} \delta) [\exp(qv/nKT) - 1] \quad (6)$$

$$\text{where } J_o = A^* T^2 \exp(-q\phi_b/kT) \quad (7)$$

It can be shown that

$$V_{oc} = \frac{nKT}{q} [\ln J_{sc}/J_o + \chi_n^{1/2} \delta] \quad (8)$$

$$\text{or } V_{oc} = n [\phi_b + \frac{kT}{q} \chi_n^{1/2} \delta + \frac{kT}{q} \ln(J_{sc}/A^*T^2)] \quad (9)$$

If the tunneling transmission coefficient $\exp(-\chi_n^{1/2} \delta) \sim 1$

$$V_{oc} = n[\phi_b + kT/q \ln(J_{sc}/A^*T^2)] \quad (10)$$

There are many papers describing the above equations and discussing means of improving the open circuit voltage. We will only discuss those relevant to our work on SnO_2/Si solar cells. The equations above are capable of explaining only part of our data. According to Cowley and Sze¹⁶ the barrier height (neglecting image force reduction)

$$\phi_b = \gamma (\phi_m - \chi_n) + (1-\gamma) (E_g - \phi_o) \quad (11)$$

and surface state factor

$$\gamma = \frac{\epsilon_1 \epsilon_o}{\epsilon_1 \epsilon_o + q \delta D_s} \quad (12)$$

In the above equations, E_g = bandgap, χ_n = electron affinity, ϕ_m = metal work function, ϕ_o = energy level of surface states measured from valence-band edge and specifies the level below which all surface states are filled for charge neutrality. δ = interfacial oxide thickness ($\text{\AA}$), and D_s = density of surface states $/\text{cm}^2\text{-eV}$, ϵ_i = insulator relative dielectric constant and ϵ_o = free space dielectric constant.

The diode constant n is related to D_s and the interfacial layer thickness δ by the equation¹⁷

$$n = 1 + \frac{\delta}{\epsilon_i \epsilon_o} \left[\frac{\epsilon_s \epsilon_o}{w} + q D_s \right] \quad (13)$$

which holds when surface states equilibrate with the semiconductor and reduces to

$$n = 1 + \frac{q \delta D_s}{\epsilon_i \epsilon_o} = \frac{1}{\gamma} \quad \text{when } w \gg \delta \quad (14)$$

Figure 9 shows the variation of ϕ_b as a function of ϕ_o for different values of n . Equation 14 is plotted in Figure 10. The results indicate that for silicon of barrier height 0.8eV and ϕ_o of 0.3eV, ϕ_b is independent of n . This indicates that the thermionic reverse saturation current I_o is independent of n .

For the different systems just described the reverse saturation current has its origin in the thermionic process. We will show that for SnO_2/Si there are two processes giving rise to the reverse saturation current, one arising from thermionic emission and the other due to diffusion. The diffusion component at small forward bias is usually several orders of magnitude smaller than the thermionic component. These two processes along with the data described in Figures 9 and 10 are important in describing the results. The shape of a typical J-V curve is shown in Figure 11 and the n and J_o values measured for various devices are listed in Table II. The J-V characteristic of SnO_2/Si cells after correcting for series resistance can be represented by the equation

$$J = J_{o1}(\exp qv/n_1 kT - 1) + J_{o2}(\exp qv/n_2 kT - 1) \quad (15)$$

To be able to understand and predict the performance of SnO_2/Si solar cells in addition to J_{sc} one should understand in detail the origin and significance of the different terms in equation (15) eg. J_{o1} , J_{o2} , n_1 , n_2 etc.

In Figure 11 the J-V curves show two slopes. Between 0 to 0.45V the extrapolated $J_o \sim 10^{-6} \text{ Amp/cm}^2$ and n is ≥ 2 . Above 0.45 n is 1 and $J_o \sim 10^{-11} \text{ Amp/cm}^2$. J_o values of the order of $10^{-6} - 10^{-7} \text{ Amp/cm}^2$ can be related to thermionic emission.

$$J_{o1} = A^* T^2 \exp(-q\phi_B/kT) \quad (16)$$

Assuming $A^* = 264 \text{ A/cm}^2/\text{°K}$ and $\phi_B \sim 0.8 \text{ eV}$ it can be shown that $J_{o1} \sim 1.03 \times 10^{-6} \text{ Amp/cm}^2$.

On the other hand J_o values on the order of $10^{-11} - 10^{-12} \text{ Amp/cm}^2$ can be related to diffusion current

$$J_{o2} = \frac{P_n q D_p}{L_p} \sim 1.6 \times 10^{-11} \text{ Amp/cm}^2 \quad (17)$$

If only one of the exponential terms in eq. (15) dominates in the photo-voltaic mode it can be shown

$$V_{oc} = \frac{nkT}{q} \ln(J_{sc}/J_o + 1) \quad (18)$$

As predicted by eq. (18) Figure 12 shows the linear relation between V_{oc} and $\ln J_{sc}$. The slope gives 'n' values which are ~ 1 .

Taking $n=1$ and $J_o \sim 1.6 \times 10^{-11} \text{ Amp/cm}^2$, it can be shown that for $J_{sc} \sim 30 \text{ mA/cm}^2$, $V_{oc} \sim 0.53\text{V}$. Similar values can be obtained if we use larger values of n and its corresponding J_o value.

The results just described are summarized in Figure 13. The dark I-V curves have two components, one originating from the thermionic emission process and the other due to diffusion of holes in silicon. The diode constant due to the thermionic emission is between 1.6 and 2.75 though the reverse saturation current is $\sim 10^{-6} \text{ Amp/cm}^2$. The diode constant of the diffusion component is 1 and the reverse saturation current is $\sim 10^{-11} \text{ Amp/cm}^2$.

Changes in diode constant and barrier height ϕ_B are related to an interfacial layer thickness and surface state density (Fig. 9 and 10). The reverse saturation current due to thermionic emission is dependent on barrier height and can be independent of n if ϕ_0 in equation (11) is about 0.3 eV Fig. 9. For such a condition the diffusion component of the bucking current exceeds the thermionic component at a lower forward bias and shapes the power curve. This results in an increase in photovoltage and fill factor.

Very little information at present is available for the work function and electron affinity of SnO_2 . The only information presently available for a SnO_2 film is from photoemission studies¹⁸ which indicate the electron affinity is about 4.55 ± 0.2 eV and is higher than what has been observed for single crystals. The photoemission studies are done in vacuum. In air the value might well be 4.85 eV. Larger values of work function and electron affinity were observed when O_2 or H_2 was chemiadsorbed on the surface of ZnO . We have done such measurements for SnO_2 and found that the electron affinity with several monolayers of oxygen increases from 4.3 to 4.7 eV. Since these measurements are accurate to 0.2 eV, we believe that the chosen value of 4.85 eV is reasonable.

Fill Factor

The series resistance and dark I-V characteristics determine the fill factors (F.F.) of good SnO_2/Si solar cells. Figure 4 shows the light and dark I-V curves with and without the series resistance. When series resistance is absent, the photocurrent is given by the sum of the currents represented by equations (4) and (5), minus the bucking currents represented by equations (7) and (17), the origins of which, as we already discussed, are thermionic emission and diffusion.

The F.F. by definition is:

$$\text{F.F.} = \frac{J_{mp} V_{mp}}{J_{sc} V_{oc}} \quad (19)$$

where I_{mp} and V_{mp} are the current density and voltage at the maximum power point. This can be obtained by differentiating the equation $P=JV$ and equating it to zero⁽¹⁹⁾. It can be shown for $\frac{dp}{dv} = 0$

$$e^{\alpha V_{oc}} = (\alpha V_{mp} + 1) e^{\alpha V_{mp}}$$

Assuming $V_{mp} \approx V_{oc}$, it can be shown that

$$F.F. = \left(1 - \frac{1}{\alpha V_{oc}}\right) \left(1 - \frac{\ln \alpha V_{oc}}{\alpha V_{oc}}\right)$$

Rothwarf⁽²⁰⁾ has derived a similar equation for the fill factor which differs slightly from the above equation.

For $n = 1$, $V_{oc} = 0.55$ V

$$\alpha V_{oc} = 22.$$

F.F. $\sim$ 0.82

$$\alpha = \frac{q}{nkT}$$

This is the best value of fill factor we could obtain with SnO_2/Si solar cells. But because of series resistance problems, we expect a lower value. The series resistance can occur because of the SnO_2 sheet resistance and metal grid spacing. The series resistance is determined by measuring the dark I-V curves in a straight line region at high forward bias. This value of series resistance can account for the measured lower fill factor than that predicted by the above expressions.

Efficiency

We estimate²¹ the maximum theoretical efficiency of SnO_2/Si solar cells to be close to 20 percent. In calculating the efficiency, the AM1 spectra is assumed to be very similar to the analytical spectra used by De Vos²². To calculate the incident power instead of integrating from 0 to ∞ we have integrated from $0 \rightarrow 1.7 \mu$ to achieve a total incident power density of 101 MW/cm^2 . The curve reported by Moon²³ agrees very well with the proposed analytic spectra. This calculated efficiency assumes no reflection, series resistance, shadowing or other losses. Including realistic values for these losses one can obtain a 15% efficient cell.

Degradation

The SnO_2/Si cells we have studied are not encapsulated. In these unencapsulated cells some degradation is observed with time. Cells which had efficiencies of 9 percent degraded to 7-8 percent in about 2 years. The degradation observed is in the fill factor and to a small extent in the open circuit voltage. Some very small non-linearity is observed in the short

circuit current vs. irradiance curves at high irradiance values. We believe that the degradation may be related to growth of the SiO_2 layer at the interface. Auger depth profiling studies shown in Fig. 16 indicate the presence of Si bonded to oxygen at the interface. More detailed work is necessary to understand degradation and also find whether suitable encapsulation could reduce or eliminate it.

CONCLUSIONS

The performance of the SnO_2/Si solar cell can best be described as that of an MIS device. In the limit when the insulating oxide thickness is such that the tunneling transmission coefficient is one, it behaves like a Schottky barrier. The observed built-in field is all in silicon.

We believe the role of the insulator is such that it reduces the effect of a bucking current due to thermionic emission. Though the theoretical efficiency is higher, we believe a practical cell of 15 percent is achievable. Most of the losses in short circuit photocurrent in present cells are from reflection and shadowing effects. The losses at short wavelengths can be accounted for by reflection.

Diode constants greater than 1 associated with thermionic emission can be attributed to a combination of oxide thickness and surface density of states. It has been shown that larger diode constant values can be achieved without increasing the J_0 value. Thus, larger fill factors and photovoltages can be obtained due to the effects of the oxide layer and surface state density. The fill factors for the devices we have analyzed are lower than the ideal computed values due to the presence of a series resistance.

ACKNOWLEDGMENT

Thanks are due to Irwin Grater and Sy Merrin of Emdex for the early SnO_2/Si devices used in this study and to T. Fischer for the photoemission studies. The authors would also like to thank the Solar Energy Division of the U.S. Energy Research and Development Administration for monitoring and supporting this program under contract No.E(04-3)-1283.

REFERENCES

1. K. Kajiyama & Y. Furukawa, Japan J. Appl. Phys. 6, 905 (1967).
2. T. Nishino & Y. Hamakawa, Japan J. of Appl. Phys., 9, 1085 (1970).
3. R. L. Anderson, Appl. Phys. Letters, 27, 691 (1975).
4. R. L. Anderson, Glass-Si Heterojunction Solar Cells, NSF Grant No. AER74-17631, Final Report, August 31, 1975.
5. I. Grater - Private Communication.
6. H. Kato, A. Yoshida & T. Arizumi, Jap. J. Appl. Phys, 15, 1819 (1976).
7. J. B. DuBow, D. E. Burk, J. R. Sites, Appl. Phys. Letters 29, 494 (1976).
8. S. J. Fonash, J. Appl. Phys 46, 1286 (1975).
9. J. Shewchun, R. Singh and M. A. Green, J. Appl. Phys. 48, 765 (1977).
10. H. C. Card & E. S. Yang, Appl. Phys. Letters 29, 51 (1976).
11. Z. M. Zarzebski & J. P. Marton, J. Electrochem. Sc. 123, 333C (1970).
12. V. K. Miloslavski, Opt. Spectry. 7, -154 (1959).
13. A. G. Milnes & D. L. Feucht - Heterojunctions & Metal Semiconductor Junctions, Academic Press (1972).
14. W. W. Gartner, Phys, Rev. 116, 34 (1959).
15. S. S. Li, F. A. Lindholm and C. T. Wang, J. Appl. Phys. 43, 4123 (1972).
16. A. M. Cowley and S. M. Sze, J. Appl. Phys. 36, 3212 (1965).
17. H. C. Card and E. H. Rhoderick, J. Phys. D: Appl. Phys. 4, 1589 (1971).
18. W. E. Spicer and R. A. Powell, U.S. Army Research Office Contract DAHCO4-74-C-0022, Semi Annual Report, March 31, 1975.
19. J. J. Loferski, IEEE 51, 667 (1963).
20. A. Rothwarf, Technical Report NSF/RANN/AER72-03478 A03/TR75/4 (1975).
21. Amal K. Ghosh, C. Fishman and T. Feng "unpublished".
22. A. De Vos, Energy Conversion 16, 67 (1976).
23. P. Moon, J. Franklin Inst. 20, 583 (1940).

FIGURES

Fig. 1 Energy Level Scheme of SnO_2/Si Solar Cell-Schottky Barrier Mode.

Fig. 2 Energy Level Scheme of SnO_2/Si Solar Cell - MIS mode.

Fig. 3 Structure of SnO_2/Si Solar Cell (a) Side View, (b) Top View.

Fig. 4 Light I-V Curves for SnO_2/Si Solar Cell (2903A).

Fig. 5 Reflection Spectra of Si and SnO_2/Si Solar Cell (2903A).

Fig. 6 The SnO_2/Si Solar Cell Showing the Barrier and the Bulk Region and the Different Terms Used in Theoretically Calculating the Short Circuit Photocurrent.

Fig. 7 The Predicted and Measured Spectral Response Curve.

Fig. 8 Dependence of J_{sc} on Irradiance.

Fig. 9 Barrier Height ϕ_B vs. ϕ_0 for Different Values of n or T

Fig. 10 Diode constant n vs. Oxide Thickness for Different Values of Surface Density of States.

Fig. 11 Forward Bias Characteristic of SnO_2/Si Solar Cell.

Fig. 12 $\ln J_{\text{sc}}$ vs. V_{oc} Plot.

Fig. 13 Ideal Diode Characteristics of SnO_2/Si Solar Cell.

Fig. 14 Dark IV with and without Series Resistance.

Fig. 15 Auger Depth Profile on SnO_2/Si Solar Cell.

TABLE I

Photovoltaic Device Parameters of SnO_2/Si Solar Cells. -
Short Circuit Photocurrent for AM1

Device #	I_{sc} (mA)	V_{oc} (V)	FF	% Efficiency	R_s (Ω)
2903 A (4 cm^2)	125	0.515	0.55	8.8	1.2
2839 A (4 cm^2)	138	0.515	0.40	7.0	1.5
2903 A (1 cm^2)	31.3	0.51	0.48	7.6	2.2
2905 A (1 cm^2)	30	0.505	0.55	8.27	1.97

TABLE II

Reverse Saturation Currents and Diode Constants of SnO_2/Si Cells

Sample #	n	J_o Amp/cm ²
2870 B	1 2.13	1×10^{-11} 7×10^{-7}
2904 A	1.09 2.78	3×10^{-11} 1.4×10^{-6}
2839	0.96 2.25	7.5×10^{-12} 6.5×10^{-7}
2903 A	0.97 2.55	2.5×10^{-11} 1.3×10^{-6}
2871	0.95 2.29	1.5×10^{-11} 1×10^{-6}
2905A	n = 1.25 n = 1.65	8×10^{-8} 1.1×10^{-6}

TABLE III*

Experimental and Theoretical Short Circuit Currents and
Diffusion Lengths of Holes Determined for SnO_2/Si Cell.
The Short Circuit Photocurrent is for an Arbitrary Irradiance.

Sample	Measured Short Circuit Current (per cm^2)	Predicted Short Circuit Current (per cm^2)	Predicted Dif- fusion Length
2839A ₂ (4 cm^2)	36mA	43mA	50 μ
2904A ₂ (1 cm^2)	38mA	39mA	110 μ
2904B ₂ (1 cm^2)	33mA	35mA	100 μ
2903A ₂ (1 cm^2)	42mA	39mA	130 μ
2905A ₂ (1 cm^2)	34mA	37mA	50 μ
2903A ₂ (4 cm^2)	39mA	43mA	70 μ

*Normally a larger short circuit current is obtained for a larger diffusion length, unlike the table indicates. The cell color, and hence the reflection, varied from sample to sample. The reflection was included to predict the short circuit current and could therefore lower the predicted value of the cells with high diffusion lengths.