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MASTER

THIN-FILM POLYCRYSTALLINE SILICON SOLAR CELLS

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By

Amal K. Ghosh, Tom Feng,
Daniel J. Eustace, and H. Paul Maruska

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Advanced Energy Systems Laboratory

P. O. BOX 45 ■ LINDEN, NEW JERSEY 07036

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PREFACE

This is the third quarterly report of progress on work performed for SERI under subcontract No. XJ-0-9077-1. The period covered is from October 16, 1980 to January 15, 1981.

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OBJECTIVES

The objectives of the project are: 1) to develop cell fabrication procedures to further define the maximum capabilities of the conducting oxide/silicon heterojunction solar cells; 2) to optimize the spray fabrication technique for making reproducible high efficiency cells; 3) to assess the stability and the projected lifetime of the cell structure; 4) to identify through appropriate measurements the effects of grain boundaries and intragrain defects on the electronic transport mechanisms in thin-film polycrystalline silicon; and 5) to determine the feasibility of a large-scale fabrication process.

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1. SUMMARY

1. A model for the stability of the $\text{SnO}_2/\text{n-Si}$ solar cells is presented. This model is capable of explaining most of the observed results and predicts that $\text{SnO}_2/\text{n-Si}$ solar cells operating at temperatures $\leq 100^\circ\text{C}$ can maintain efficiencies $\geq 10\%$ over the expected lifetime of the cells, that is, 20 years.

2. The highest power conversion efficiencies achieved to date for the heterojunction cells are as follows:

Single Crystal Silicon			Wacker Polysilicon		
Type	Area (cm^2)	Eff. (%)	Type	Area (cm^2)	Eff. (%)
$\text{SnO}_2/\text{n-Si}$	4	13.2	$\text{SnO}_2/\text{n-Si}$	4	10.1
$\text{SnO}_2/\text{n-Si}$	20	10.2	$\text{ITO}/\text{n-Si}$	1	11.2
$\text{ITO}/\text{n-Si}$	4	14.1	$\text{ITO}/\text{n-Si}$	4	10.7
$\text{ITO}/\text{n-Si}$	20	10.6	$\text{ITO}/\text{n-Si}$	20	7.6

3. The decrease in the power conversion efficiencies in scaling-up from 4 to 20cm^2 is due to a reduction in short-circuit photocurrent and the fill factor. These losses are related to the sheet resistance of the SnO_2 and ITO films and to the configuration of the grid structure. Our detailed grid optimization study has shown that grid structures can be designed which will significantly reduce these losses.
4. Theoretical analysis of the effects of intergrain barriers on the transport properties of polysilicon indicates that for grain-boundary barrier heights of about 0.1eV or less, a constant recombination velocity can be assumed. However, for larger barriers such an assumption is not valid.

2. A MODEL FOR THE STABILIZATION OF THE PROPERTIES OF $\text{SnO}_2/\text{n-Si}$ SOLAR CELLS

2.1 Introduction

There is general agreement that heterojunction tin oxide-silicon ($\text{SnO}_2/\text{n-Si}$) solar cells offer significant promise for simplifying cell fabrication procedures, while maintaining the high efficiencies of the more conventional diffused p/n structures. This is especially true when the tin oxide is formed by spray hydrolysis, which requires a low temperature ($<400^\circ\text{C}$) and a very short time (<1 minute), and yet which yields cells with efficiencies as high as 13%. However, there is a question about the long term stability of these cells, and in our previous quarterlies¹, as well as in several publications², we have presented the results of some of our stability studies. In these preliminary studies we found that the major instability involved the open circuit voltage. The open circuit voltage for cells under test in sunlight was found to decay in a matter of weeks by about 3 to 5%, but then apparently became constant. On the other hand, the short circuit current was found to be quite stable throughout the tests, and the fill factor only decreased if unprotected electrodes became corroded.

We will now present a more detailed analysis of the stability of $\text{SnO}_2/\text{n-Si}$ cells, and show that changes in photovoltaic parameters can be correlated with redistributions of charges at the interface. Once the interface is stabilized, the properties of the cell become constant. We now have cells under continuous test in sunlight that have maintained invariant open circuit voltages for over a year, even though they showed the usual small decreases during the first few weeks. Furthermore, we will show that there are two mechanisms by which the interface can undergo alterations, one attributable to the light and the other due to heat. In fact, we have found that our cells show no measurable degradations when stored in darkness at room temperature.

2.2 Experimental Results

All of the cells that we will discuss were fabricated by spraying a solution of SnCl_4 onto polished wafers of n-type silicon, used as received from the supplier, which are held on a heated chuck during the deposition.³ For the stability studies, the cells have then been kept for extended periods in various environments, i.e. (a) in air, in total darkness, (b) in flowing nitrogen, in total darkness, (c) in partial vacuum (mechanical pump), in full sunlight, (d) encapsulated in silicone, in full sunlight, (e) in either air, argon, or hydrogen, in an oven. The photovoltaic properties of these cells have been monitored on a regular basis. Illuminated current-voltage measurements (light I-V's) were made using a xenon lamp solar simulator set for AM1 spectrum. At present there are 32 cells in vacuum and 13 cells in encapsulation in sunlight, as well as more than 25 cells in darkness. Other cells have been kept in the oven for heat treatments.

2.2.1 Cells in Darkness

We have kept sprayed $\text{SnO}_2/\text{n-Si}$ cells in darkness for up to almost 3 years now. These cells have been stored in boxes, both in air and in flowing nitrogen, always at room temperature. We have not observed any changes in the properties of these cells under these conditions. It is most significant that the open circuit voltages of all of these cells have remained in the range of 0.61-0.63 V, exactly the same as when they were made. Thus we can expect an indefinite shelf-life for our devices, even without any special storage precautions (other than protecting them from moisture which would corrode the electrodes).

2.2.2 Effects of Extended Illumination

However, when cells are exposed to sunlight for extended periods of time, we find that their open circuit voltages show a small initial decline. At the same time, though, their short circuit currents and fill factors remain constant, so long as the surfaces of the cells are protected from the accumulation of dirt and the corrosive effects of moisture. Thus losses in efficiency are directly attributable to the decreases in open circuit voltage.

For example, the photovoltaic properties of a representative encapsulated cell, which has been exposed to sunlight outdoors for one year, are shown in Figure 1. Although this cell exhibited some initial decrease in current, we have shown conclusively that this loss was due entirely to deterioration of the surface of the encapsulant. The encapsulant was not protected from the environment, and its surface became roughened due to the action of dust particles. More recently, outdoor cells have been kept behind glass shields, and these cells have maintained constant currents. Notice that the open circuit voltages decayed at first, but after about 50 days it became constant.

Overall, we find that individual cells undergo losses in V_{oc} of no more than 5% before stability is achieved. In general, the cells reach equilibrium over a period of one to two months. Thus if a cell is fabricated with an initial efficiency of 12%, it will stabilize in a relatively short time at about 11.5%. In Figure 2 we present data showing the distribution of open circuit voltages of the 32 cells which are kept

FIGURE 1

STABILITY STUDY WITH A SPRAYED SnO_2/Si (SINGLE CRYSTAL) CELL,
ENCAPSULATED AND KEPT OUTDOORS IN SUNLIGHT

Figure 2.

Change in the Open Circuit Voltages
of 32 Sprayed SnO_2 /Silicon Cells
Kept in Sunlight, Protected From Air

in vacuum, first initially and then after 240 days of exposure to sunlight. It is apparent that there exists a range of reduction in the open circuit voltage, from about 10 to 30 mV.

Closer study has shown that the changes in V_{OC} can be directly correlated with changes in the dark current. The dark current-voltage characteristics of our heterojunction $\text{SnO}_2/\text{n-Si}$ cells always exhibit two components. The low voltage portion can be attributed to thermionic emission⁴, while the high voltage portion is governed by the injection/minority carrier diffusion mechanism. The high voltage portion shows a diode quality factor $n=1$, consistent with a diffusion mechanism, while the low voltage portion always has $n > 2.5$. This large n value can be explained by invoking the presence of surface states at the $\text{SiO}_2\text{-Si}$ interface, which have the result that the applied voltage V is divided between the semiconductor depletion region and the SiO_2 interfacial layer. With our good cells, the open circuit voltage corresponds to the $n=1$ portion of the dark I-V curve.

However, after extended exposure to light, the low voltage portion of the dark current has been found to increase in magnitude, as shown in Figure 3. The open circuit voltage thus decreases and is then found to occur in the regime where the dark current has a slope $n > 2.5$, that is, where the thermionic component predominates. Notice that the increase in dark current is the result of an increase in J_0 (dark saturation current) and is not manifested in a change in n . Most important, we find that the open circuit voltage becomes constant (refer to Figure 3).

FIGURE 3.

CHANGES IN THE DARK CURRENT-VOLTAGE
CHARACTERISTIC OF A SPRAYED SnO_2/Si CELL
EXPOSED TO LIGHT FOR SIX MONTHS

These results apply equally well to the cells which were encapsulated with silicone and then exposed to sunlight for extended periods, or those held in partial vacuum in sunlight.

2.2.3 Effects of Heat Treatment

When the sprayed $\text{SnO}_2/\text{n-Si}$ cells are heated to elevated temperatures, there also occur decreases in the open circuit voltage, but the thermal degradation proves to be much more severe than the optical degradation. The rate of degradation depends on the temperature, but we have found that in all cases V_{OC} changes overall from about 0.600 V to less than 0.200V. Subsequent heating, even for months, does not cause further changes. Now in this case the short circuit current also decreases, but by no more than a factor of 5. The degradation is not related to metallization, because cells without grids degrade in the same way when heated. For example, at 350°C it takes about 30 minutes to obtain complete degradation, while at 500°C it takes only 30 sec. According to Reynolds⁵, if the thermal degradation of a cell is due to diffusion or a chemical reaction, then one may express the "time for failure" of the device, t_F , as

$$t_F = t_0 \exp (q E_A/kT) \quad (1)$$

where E_A is the activation energy of the degradation mechanism and t_0 is a constant. Typically, t_F is the time for V_{OC} to decrease by 50%, which we have plotted in Figure 4. The activation energy is 1.5 eV. For comparison, Goodnick et al.⁶ found that for ITO/p-Si cells, the main cause of failure was a loss of fill factor upon heating, and from their t_F vs.

FIGURE 4.
THERMAL DEGRADATION OF
SPRAYED SnO_2/Si SOLAR CELLS.

1/T plot they determined an activation energy of 1.1 eV. Nash & Anderson⁷, in their studies of $\text{SnO}_2/\text{n-Si}$ cells, found that the increase in series resistance at elevated temperatures had an activation energy of 1.3 eV.

From our data, we find that at room temperature it would take roughly 20 million years to lose 50% of the open circuit voltage by the heat degradation process. Even at 100°C , it would take about 500 years to lose just 10% of V_{oc} .

We can learn more about the heat degradation process by once again studying the dark I-V data. Again, the losses in V_{oc} correspond to increases in the dark current. Figure 5 shows the change in dark I-V characteristic for a cell given a short heat treatment at 350°C . Notice that in this case, J_0 remains unchanged, but the slope n starts to decrease. The effect is much more rapid, as noted above, at higher temperatures. Notice in Figure 6 that the dark current increases quite substantially and finally has only a single component with a slope $n=1$. J_0 also finally shows some increase as n approaches unity. Continued heating has negligible further effect. At this point, the dark I-V looks like that of a classic Schottky barrier controlled by thermionic emission currents, without any interfacial layer effects.

The light degradation and the heat degradation are indeed different, as shown in Figure 7. Here a cell was first exposed to sunlight. Notice that after the optical stress, J_0 changed from 10^{-6} A/cm^2 to 10^{-5} A/cm^2 while n remained at 2.8, but after heating at 425°C , n became unity while J_0 remained at 10^{-5} A/cm^2 .

FIGURE 5.

EFFECT OF HEAT TREATMENT AT 350°C
IN AIR ON THE DARK CURRENT-VOLTAGE
CHARACTERISTIC OF SPRAYED SnO_2/Si CELL

FIGURE 6.
CHANGES IN DARK CURRENT-VOLTAGE
CHARACTERISTICS OF SPRAYED SnO_2/Si
AFTER HEATING IN AIR AT 425°C

FIGURE 7.

CHANGES IN THE DARK CURRENT-VOLTAGE
CHARACTERISTIC OF SPRAYED SnO_2/Si (crystal)
CELL AFTER EXTENDED ILLUMINATION

We would like to note that the heat degradation appears not to be influenced by the environment in which the cell is heated. The same degradation in V_{OC} and J_{SC} were found in air, argon, and hydrogen. Figure 8 shows the change in the dark I-V of a cell given a short heat treatment in hydrogen at 380°C, while Figure 9 shows what happens at 425°C in hydrogen. As before, first n decreases, and as it approaches unity, there is some increase in J_0 . It is interesting that heating in hydrogen causes chemical reduction of the SnO_2 , making it more conducting, and thus the degradations seen with heat treatments are not due to resistance losses in the SnO_2 layer.

Finally, we should note that there is an induction period before the thermal degradation sets in. This effect is much more easily noticed at lower temperatures. For example, at 330°C, it takes about 20 minutes before decreases in V_{OC} become apparent, but thereafter the decline is rapid.

2.3 Discussion

First of all, let us note that the silicon wafers are used as-received for our processing, and therefore a thin native silicon oxide layer is present on the surface. This native oxide is generally about 15 Å thick⁸, and it has now been shown conclusively that such films do not have the SiO_2 stoichiometry throughout their thickness, but rather have the form of a suboxide at the interface with the bulk silicon.⁹ This perturbation in the silicon bonding can lead to the formation of surface states at the interface. Thus we are concerned with what amounts to an SOS device

FIGURE 8.

CHANGES IN DARK CURRENT-VOLTAGE
CHARACTERISTICS OF SPRAYED SnO_2/Si
CELL HEATED IN HYDROGEN AT 380°C

FIGURE 9.

EFFECT OF HEATING AN SnO_2/Si
CELL IN HYDROGEN AT 425°C

(SnO₂-SiO₂-Si) which contains interfacial surface charge. The band diagram for our cell configuration is shown in Figure 10. Here Q_{SC} is the semiconductor space charge due to the donors, Q_{SS} is the charge in the surface states, and Q_m is the charge in the SnO₂. Also, ϕ_m is the SnO₂ work function, χ is the Si electron affinity, ϕ_b is the barrier height to electron flow, V_i is the potential drop across the SiO₂ insulator, W is the width of the Si depletion region, V_D is the built in potential, δ is the thickness of the SiO₂ films, and ϕ_0 is the energy (measured from the valence band) below which all surface states would have to be full to achieve a neutral surface.

There are two components to the dark current, one due to electrons emitted over the barrier into the SnO₂ and the other due to hole diffusion in the Si valence band, and they dominate at low and high biases, respectively. The dark I-V characteristics can be represented by the equation

$$J = AT^2 \exp\left(-\frac{\phi_B}{kT}\right) \left[\exp\left(\frac{qV}{n_1 kT}\right) - 1\right] + \frac{q p_n D_p}{L_p} \left[\exp\left(\frac{qV}{n_2 kT}\right) - 1\right]. \quad (2)$$

Here A = Richardson's constant, T = absolute temperature, k = Boltzmann's constant, q = electronic charge, V = applied voltage, n_1, n_2 = diode quality factors for the thermionic and diffusion mechanisms, respectively, D_p = hole diffusion coefficient, L_p = hole diffusion length, and p_n = hole concentration. If there were no insulating film present, both n_1 and n_2

FIGURE 10. ENERGY BAND DIAGRAM OF THE $\text{SnO}_2/\text{n-Si}$ CELL.

would be unity, and the barrier height ϕ_B would simply be the difference between the SnO_2 work function ϕ_m and the Si electron affinity χ (neglecting the image-force lowering of the barrier).

However, the presence of the insulating SiO_2 film causes some interesting changes in the potentials. Let us note, though, that the changes are insignificant unless a considerable density of charged surface states are present. In the absence of surface charge, the voltage across the insulator is given by Gauss' Law:

$$V_i = \delta \frac{\epsilon_s}{\epsilon_i} E_s \quad (3)$$

where ϵ_s , ϵ_i are the dielectric constants of the semiconductor and insulator, respectively, and whose ratio is about 5, and E_s is the electric field just inside the semiconductor, about 10^4 V/cm. Thus for a 15 Å thick insulator, V_i is only a few millivolts. This is also true in the case of a forward bias, which means that in the absence of surface states, essentially all of the applied voltage V serves to decrease V_D .

Consider now the case where surface states are present with a density D_s per cm^2 per eV. We can write two expressions for V_i , one by inspection of Figure 10 and the other by using Gauss' Law (assuming the SnO_2 is as conducting as a metal and will not support a field internally):

$$V_i = - \frac{\delta}{\epsilon_i} Q_m = (\phi_m - \chi) - \phi_B \quad (4)$$

For overall charge neutrality,

$$Q_m + Q_{ss} + Q_{sc} = 0 \quad (5)$$

If we assume that the surface states are only in contact with the semiconductor, i.e., there is no tunnelling from the surface states through the insulator to the SnO_2 , then again from Figure 10

$$Q_{ss} = -qD_s(E_g - \phi_B - \phi_0). \quad (6)$$

That is, the charge is located in the states between ϕ_0 and E_f .

Also

$$Q_{sc} = \frac{2\epsilon_s}{W} V_D \quad (7)$$

from Poisson's Equation in the depletion region. Thus collecting terms,

$$\phi_B = (\phi_m - \chi) + \frac{\delta}{\epsilon_i} [qD_s(E_g - \phi_0 - \phi_B) - \frac{2\epsilon_s}{W} V_D]. \quad (8)$$

Notice that we showed above, Equation (3), that the rightmost term is negligible, and therefore,

$$\phi_B = \frac{1}{n} (\phi_m - \chi) + \left(\frac{n-1}{n}\right) (E_g - \phi_0), \quad (9)$$

where

$$n = 1 + \frac{q\delta}{\epsilon_i} D_s \quad (10)$$

Thus the presence of surface states may increase ϕ_B , the barrier height, and if so, thereby reduce the thermionic dark current, through the effects of n and ϕ_0 in Equation (9).

Again, we can consider the situation under conditions of forward bias. Let us assume the bias V changes the potential of both the depletion region and the insulator, so that

$$\Delta V = (\Delta V_D + \Delta V_i), \quad (11)$$

and the fraction which changes V_D and thus contributes to increasing the dark current is

$$V_D = V_{D0} - \Delta V/n, \quad (12)$$

or

$$\frac{dV_D}{dV} = -\frac{1}{n}. \quad (13)$$

Using Equations (4) and (5),

$$\Delta V_i = \frac{\delta}{\epsilon_i} (\Delta Q_{ss} + \Delta Q_{sc}). \quad (14)$$

Now taking derivatives,

$$\frac{dV_i}{dV} = \frac{\delta}{\epsilon_i} \left(\frac{dQ_{ss}}{dV} + \frac{dQ_{sc}}{dV} \right). \quad (15)$$

Assuming that V_D is a function of Q_{ss} and Q_{sc} as well as V , this can be expressed as

$$\frac{dV_i}{dV} = \frac{\delta}{\epsilon_i} \left(\frac{dQ_{ss}}{dV_D} \frac{dV_D}{dV} + \frac{dQ_{sc}}{dV_D} \frac{dV_D}{dV} \right) \quad (16)$$

For the depletion region,

$$\frac{dQ_{sc}}{dV_D} = \frac{\epsilon_s}{W}, \quad (17)$$

while because the occupancy of the surface states is governed by the position of the Fermi level,

$$\frac{dQ_{ss}}{dV_D} = q D_s. \quad (18)$$

From Equations (11) and (13),

$$\frac{dV_i}{dV} = \frac{1-n}{n} \quad (19)$$

and collecting terms

$$\frac{1-n}{n} = \frac{\delta}{\epsilon_i} \left(-\frac{qD_s}{n} - \frac{\epsilon_s}{W} \frac{1}{n} \right). \quad (20)$$

We showed earlier that the factor $(\delta/\epsilon_i) (\epsilon_s/W)$ is negligible, and thus

$$n = 1 + \frac{\delta}{\epsilon_i} qD_s \quad (21)$$

which is the same as Equation (10) above. Now it is apparent that this n is the diode quality factor n , for the thermionic dark current. It is therefore possible to get an n greater than 1, which means a reduced dark current, if there exists a substantial density of interface states. This is the case treated by Card & Rhoderick for thick oxides.¹⁰

In the case of $\text{SnO}_2/\text{n-Si}$ solar cells it is observed that though the interfacial oxide is thin ($\leq 20 \text{ \AA}$), the fixed surface charge Q_{ss} equilibrates only with Si, which was an assumption in the derivation above. Since n is the ratio of the incremental change in the ratio of applied voltage to diffusion potential, any change in n is reflected in change in the equilibrium of Q_{ss} with the semiconductor. The changes that can affect the equilibrium are the density and distribution of surface state D_s and the oxide thickness δ .

From our experimental results, we may conclude that for the light degradation D_s and δ do not change, because n does not change. However, ϕ_b changes because J_0 changes, according to Equation 2. J_0 changes by about an order of magnitude, and thus, ϕ_b changes from about 0.8 to about 0.74 eV. This indicates that although the density of surface states D_s remains constant, the distribution is not remaining at a constant energy relative to the semiconductor valence band; as a result ϕ_0 changes and thus the band bending in the semiconductor is reduced according to Equation (9). This change in ϕ_0 is attributed to a rearrangement of the bonding in the SiO_x interfacial layer, as a result of light exposure. As ϕ_0 approaches the fermi level, there will occur a neutralization of the surface charge Q_{ss} ,¹¹ and the system as a whole approaches equilibrium. Thus the decreases in V_{oc} due to light are only seen during the equilibration of ϕ_0 .

The situation is different for the heat degradation. Here we can envision two possible explanations for why n tends toward unity. The first is that in some manner the insulator breaks down upon heating, and conducting material comes into direct contact with the silicon, forming a classical

Schottky barrier. This might happen if the SnO_2 were reduced to metallic tin, and the tin penetrated through the SiO_2 . The other possibility, which we consider more likely, is that the excess silicon in the SiO_x portion of the oxide reacts with diffusing oxygen ions, so that the surface state density D_s is decreased.¹² The oxidation process increases δ , but the assumption here is that D_s decreases at a much faster rate than δ increases, and thus from Equation (10), n decreases towards unity.

In addition, we have also noted that for the thermal degradation, the time dependence of the change in n closely follows the time dependence in the change in V_{OC} , with essentially the same induction period, as shown in Figure 11. We wish to use Equation (21) to calculate the time dependence of D_s . First we will assume that there is essentially no change in δ during the induction period in which V_{OC} and n show essentially no changes. Our model is that during this time period, an ionic species, possibly O_2^- , is diffusing across the SiO_2 , under the influence of the field in the insulator. In the example in Figure 11, this induction time is about 16 minutes. Afterwards, we will assume the parabolic growth of the oxide, because the parabolic law has an activation energy of about 1.3 eV, consistent with our results (see Ref. 12, page 29). However, we note from the work of Jorgenson,¹³ that an applied field will essentially double the growth rate, so we will double the constant B in the relationship

$$\delta^2 = Bt \quad (22)$$

where δ is the thickness of the oxide layer and t is the time.

FIGURE 11. THERMAL DEGRADATION OF $\text{SnO}_2/\text{n-Si}$ AT 330°C

The change in δ is shown in Figure 11, where we have also plotted D_S . We note that D_S decreased from 2×10^{13} to 5×10^{12} as the sample degraded. As an added proof, we have recently found that we can affect the rate of change of V_{OC} by applying external biases to cells during the heat stressing. Applying a negative bias to the SnO_2 , which should speed the motion of O_2^- toward the Si interface, reduces the induction period significantly, while applying a positive bias retards the degradation.

There are also some decreases in the short circuit current in heat degraded cells, which may be explained by a photocurrent suppression mechanism such as we observed earlier in the angle of incidence effect.¹⁴ In the present case it could be related to changes in the width δ of the insulating silicon oxide layer.

2.4 Conclusions

There are two degradation mechanisms for $\text{SnO}_2/\text{n-Si}$ solar cells, one due to heat and one due to light. In either case, the degradation reaches a limit after which there are no further changes. The light degradation is evidenced only by a small decrease in V_{OC} (due to an increase in dark current), while heat degradation involves losses in both V_{OC} and J_{SC} . The heat degradation should not be a factor at room temperature and would result in only a 10% loss in performance after 500 years at 100°C . The light degradation causes about a 5% loss in performance, before stability is achieved as the interface approaches equilibrium.

3. Cell Fabrication and Related Studies

The power conversion efficiencies of both $\text{SnO}_2/\text{n-Si}$ and $\text{ITO}/\text{n-Si}$ heterojunction solar cells have been increased. Such improvements were made primarily by reducing the sheet resistance of the SnO_2 and ITO thin films, which resulted in a substantial increase in the fill factor. The highest efficiencies achieved for $\text{SnO}_2/\text{n-Si}$ and $\text{ITO}/\text{n-Si}$ cells using single crystal silicon were 13.2% and 14.2%, respectively. In Figure 12 we have shown the power curves and the photovoltaic parameters of these two cells as measured in a simulated AM1 solar spectrum. In addition, we have also shown the data for a 4-cm^2 $\text{ITO}/\text{n-Si}$ cell using Wacker polycrystalline silicon. It should be noted that although the 10.6% efficiency cell shown in Figure 12 is one of the best 4-cm^2 polysilicon cells we have fabricated, efficiency as high as 11.2% has already been achieved with 1-cm^2 polysilicon cells.

During this quarter, large area 20-cm^2 cells were also fabricated. Power conversion efficiencies of 10.2% and 10.6% were obtained for $\text{SnO}_2/\text{n-Si}$ and $\text{ITO}/\text{n-Si}$ cells, respectively, using single crystal silicon, while for polysilicon the best efficiency was 7.6%. It is evident from a comparison of the data for 20-cm^2 cells presented in Figure 13 and those in Figure 12 for 4-cm^2 that the lower efficiencies of the large area cells are mainly due to lower short-circuit currents and smaller fill factors. Most of the reduction in the short-circuit current observed in the 20-cm^2 cells can be accounted for by

	TYPE	CELL#	AREA(CM ²)	J _{sc} (MA/CM ²)	V _{oc}	FF	EFF. %
SINGLE CRYSTAL	ITO/n-Si	S481D	3.78	29.6	.625	.765	14.1
SINGLE CRYSTAL	SnO ₂ /n-Si	S477D	3.78	30.4	.610	.713	13.2
POLY CRYSTAL	ITO/n-Si	SP51E	3.80	27.6	.551	.694	10.6

FIG. 1. PHOTOVOLTAIC PARAMETERS UNDER AM1 SPECTRUM FOR 4 CM² CELLS

FIG. 2 PHOTOVOLTAIC PARAMETERS UNDER AM1 SPECTRUM FOR 20-cm² CELLS

the larger grid-area coverage, resulting in a reduction in the "active" area. For the 20-cm² cells the grid pattern covers approximately 20% of the total area of the cell, whereas for the 4-cm² cells it covers about 10%. By reducing the sheet resistance of the SnO₂ and ITO films further and by designing an optimum grid pattern we believe the grid-area coverage can be substantially reduced. These approaches are presently being pursued. Finally, regarding the fill factor of the 20-cm² cells, it should be pointed out that the edge or perimeter of the cell must be etched in order to arrive at a high fill factor. This fact is well illustrated in the power curves shown in Figure 14. Before etching, the power curve indicated the presence of a shunting or leakage problem. However, after removing the ITO film from the perimeter of the cell by etching with zinc and HCl, the fill factor increased from 0.57 to 0.71. The slight decrease in the current, after etching, is due to a small reduction in the active area.

The lowest sheet resistance achieved for "undoped" tin oxide film is about 175 ohms. Since the film is about 100 Angstroms, this value of sheet resistance corresponds to a resistivity of 1.75×10^{-3} ohm-cm. To reduce the resistivity further we have been experimenting with fluorine doping. The doping experiment reported in the previous quarter was inconclusive because of the difficulties encountered in using ammonium fluoride. One of the difficulties is the very low solubility of ammonium fluoride in the spray mixture. During this quarter, we have used trifluoroacetic acid

FIG. 3 EFFECT OF EDGE ETCHING ON FILL FACTOR.

($\text{F}_3\text{CCO}_2\text{H}$) to dope the SnO_2 film, thus improving its sheet resistance.

Fluorine doping has resulted in solar cells with slightly larger fill factors.

For example, the $\text{SnO}_2/\text{n-Si}$ cell (S477D) shown in Figure 12 had a 5% by volume concentration of trifluoroacetic acid in the spray mixture. This cell has a fill factor of 0.71. In general, undoped cells have fill factors in the range between 0.65 and 0.70.

The best results that we have obtained for poly- and single-crystal, both for sprayed SnO_2 and ITO as well as for diffused p/n junctions, are compared with theory in Table I.

TABLE 1: Comparison of the best results of sprayed heterojunction and diffused junction cells in both single and polysilicon

POLYSILICON

(Wacker, ~ 1mm grain size)

Solar Cell Parameter	Theory	ITO/n-Si			SnO ₂ /n-Si	Diffused p/n
Area (cm ²)	--	1	4	20	4	4
J _{sc} (mA/cm ²)	30.0	29.8	27.7	23.1	26.6	27.3
V _{oc} (V)	0.540	0.557	0.550	0.510	0.560	0.530
FF	0.780	0.670	0.700	0.646	0.680	0.710
Efficiency (%)	12.6	11.2	10.7	7.6	10.1	10.3

SINGLE-CRYSTAL SILICON

Solar Cell Parameter	Theory	ITO/n-Si		SnO ₂ /n-Si	
Area (cm ²)	--	4	20	4	20
J _{sc} (mA/cm ²)	36	29.6	25.0	30.4	25.0
V _{oc} (V)	0.66	0.625	0.597	0.610	0.600
FF	0.84	0.765	0.710	0.713	0.682
Efficiency	20	14.1	10.6	13.2	10.2

4. Optimization of Grids

The use of metallic grid patterns on the front surface of a solar cell is a well established procedure for reducing the effective sheet resistance of the surface layer. In the case of the heterojunction cells, the grid reduces the path length through which charge carriers must travel laterally in the conducting oxide. Although the grids are very effective in reducing sheet resistance, they can add other resistive components caused by losses in the grid lines themselves, as well as reducing the overall short circuit current by blocking the light where they are applied. By careful design, and using available technology it is possible to optimize the grid design for a variety of conditions to obtain the maximum power output of the cell, consistent with the sheet resistance of the conducting oxide, the resistivity of the grid metal, and the current loss due to shadowing.

We have based our study on a computer optimization plan for the metallization pattern originally developed at Texas Instruments.¹⁵ The following parameters were used for calculating the fractional power loss in $\text{SnO}_2/\text{n-Si}$ solar cells:

1. short circuit current	j	0.03 A/cm^2
2. maximum power voltage	V	0.45 V
3. surface sheet resistance	M	50, 100, 200 ohms/square
4. metal sheet resistance	M*	0.005 ohms/square
5. grid line length	L	2.54 cm (4" cell, 2 busses 2" cell, 1 bus) 3.81 cm (3" cell, 1 bus)
6. grid line width	T	0.001 cm, 0.01 cm, 0.0254 cm, 0.05 cm

Plots consistent with these parameters for a 2" diameter cell are presented in Figure 15. In general, we have arrived at the following conclusions. The narrowest grid line widths will give the smallest fractional power loss, other parameters being equal. For the 4" cell, 2 busses (2" cell, one bus), the loss from grids is about 5.5% for the 0.001 cm wide grid lines. The 0.01 cm wide grids begin to show considerable differences for the different sheet resistivities, and the wider the grids, the greater these differences become. For the 200 ohm/square surface sheet resistivity, the loss rises to 9.5% for a grid line width of 0.01 cm. For the 0.0254 grid line width, the loss rises to 15.8%. Differences between the 3" and the 4" cell are negligible--losses are about 1 to 2% higher for the 3" cell with one bus because of the increased length of grid line.

The overall data are given in tabular form in the accompanying table where the minimum loss values are shown. We are presently preparing new metallization masks in accordance with these results.

FIGURE . FRACTIONAL POWER LOSS VS. GRID REPEAT SPACING
CIRCULAR CELL, TIN OXIDE, 2" DIAM.

Table 1. Minimum Fractional Power Loss for Tin Oxide Cells

entries are fractional
power loss in %

$\frac{M}{L}$ / cm	50 ohms/square				100 ohms/square				200 ohms/square			
	<u>0.001</u>	<u>0.01</u>	<u>0.0254</u>	<u>0.05</u>	<u>0.001</u>	<u>0.01</u>	<u>0.0254</u>	<u>0.05</u>	<u>0.001</u>	<u>0.01</u>	<u>0.0254</u>	<u>0.05</u>
L:												
2.54 cm	5.4	7.1	10.8	15.6	5.4	8.1	13	18.9	5.4	9.6	15.7	22.7
3.81 cm	7.7	8.9	11.9	16.2	7.7	9.7	13.9	19.3	7.7	10.9	16.4	23.1

Bus loss will be an additional approximately 10%.

Total loss for grid plus bus should be below 15%, ideally below 10%.

2.54 cm corresponds to 4" diameter cell, 2 busses, and to 2" diameter cell, 1 bus.

3.81 cm corresponds to 3" diameter cell with one bus.

5. Modelling of Polycrystalline Silicon Solar Cells

The transport properties of polycrystalline silicon have been studied by various researchers using Hall Effect and resistivity measurements. There is a general consensus that grain boundaries play a role in the transport process, but the agreement breaks down when one tries to delineate the exact role of the grain boundary. The doping concentration and the free carrier density do not always coincide. One group believes that grain boundaries can act as a sink for impurity resulting in impurity segregation along the grain boundaries.^{16,17} The other group argues for uniform bulk doping and attributes the difference between doping concentration and free carrier densities to trapping at grain boundaries.¹⁸⁻²¹ Anomalies in Hall mobilities (especially the mobility minimum seen as a function of doping density) have also been attributed to trapping effects at grain boundaries. There appears to be experimental evidence in support of both views.¹⁶⁻²⁴ We believe that in actuality both processes can happen in polycrystalline silicon, and that the dominance of a particular process is dependent on the method of sample preparation and on the doping density. In general, most of the solar cell and transport properties can be explained by assuming bulk doping and subsequent trapping and recombination of carriers at grain boundaries.²⁵⁻²⁷ In modelling transport and photovoltaic properties of polycrystalline silicon solar cells, we have found that most of the device parameters can be calculated to within 10 percent of observed values by treating all grain boundaries to be alike. For AM1 insolation, a single grain boundary recombination velocity of 3.2×10^4 cm/sec has been

estimated. The effective lifetime τ is related to this surface recombination velocity S_0 by the relation

$$\tau_{\text{eff}} = d/6S_0$$

where d is the grain size.

This effective lifetime was utilized for calculating the reverse saturation current due to recombination in the junction space charge region, the diffusion current, the short circuit photocurrent, the open circuit voltage and the fill factor. Excellent agreement was observed between theory and experiment for grain sizes varying over several orders of magnitude.

In deriving equation (23) it was assumed that the polycrystalline silicon, independent of grain size, was 1 ohm-cm material. At such resistivity it was assumed that the doping density was sufficient to preclude the presence of grain boundary barriers, which would prevent electrons and holes from recombining. However, indications are that there continue to exist some grain boundary barriers even for 1 ohm cm material. Our preliminary analysis indicates that equation (23) is still valid for barrier heights of 0.1 eV. For larger barriers the relation may be valid only under some restricted conditions. The surface recombination velocity can no longer be treated as a constant for calculating all device parameters. In addition, grain boundary barriers will increase series resistance

and affect fill factors. The barriers observed in the dark, depending on their magnitude, could be reduced or even eliminated by carrier injection by light and other means.

Based on our detailed study, we conclude the following: (a) at low dopant concentration each grain has a central conducting core surrounded by an insulating space-charge region due to carrier trapping at the boundary; (b) resistivity is mainly dependent on the intergrain boundary barrier, essentially the space-charge region; (c) properties of the intergrain boundary barrier are dependent on doping and on grain size, and the barrier heights and widths can be reduced or removed by impurity doping or by light; (d) carriers recombine efficiently at grain boundaries under flat band conditions; (e) grain boundary passivation studies so far have shown no effect on short circuit photocurrent; (f) the minimum grain size needed for 10% cell is still some where between 200-300 μm .

6. REFERENCES

1. Amal K. Ghosh, Tom Feng, D. J. Eustace, H. Paul Maruska, Quarterly report #1 and #2, SERI Subcontract XJ-0-9077=1, 1980.
2. Charles Fishman, Amal K. Ghosh and Tom Feng, Solar Energy Materials 1, 181 (1979); Charles Fishman, Tom Feng and Amal K. Ghosh, International Electron Devices Meeting, Washington, D. C., December 1978, p. 93.
3. Tom Feng, Amal K. Ghosh, and Charles Fishman, Appl. Phys. Lett. 35, 266 (1979).
4. A. K. Ghosh, C. Fishman, and T. Feng, J. Appl. Phys. 49, 3490 (1978).
5. F. H. Reynolds, Proc. IEEE 62, 212, (1974).
6. S. M. Goodnick, J. F. Wager and C. W. Wilmsen, J. Appl. Phys. 51, 527 (1980).
7. T. R. Nash and Richard L. Anderson, IEEE Trans. Electron Devices ED-24, 468 (1977).
8. S. I. Raider, R. Flitsch and M. J. Palmer, J. Electrochem. Soc. 122, 413 (1975).
9. See, for example, D. E. Aspnes and J. B. Theeten, J. Electrochem. Soc. 127, 1359 (1980).
10. H. C. Card and E. H. Rhoderick, J. Phys. D, 4, 1589 (1971).
11. E. H. Rhoderick, Metal-Semiconductor Contacts, Clarendon Press, Oxford, 1978, page 28.
12. A. S. Grove, Physics and Technology of Semiconductor Devices, John Wiley and Sons, New York, 1967, page 342.
13. Paul J. Jorgensen, J. Chem. Phys. 37, 874 (1962).
14. Tom Feng, Amal K. Ghosh and Charles Fishman, J. Appl. Phys. 50, 8070 (1979).
15. Bernard G. Carbajal, Automated Array Assembly Task, 4th Quarterly Reports, ERDA/JPL Contract NAS-7-100-954405, March 1977.
16. M.E. Cowher and T.O. Sedgwick, J. Electrochem. Soc. 119, 1565 (1972).
17. A.L. Fripp, J. Applied Phys. 46, 1240 (1975).
18. T.I. Kammin, J. Appl. Phys. 42, 4357 (1971).
19. J.Y.W. Seto, J. Appl. Phys. 46, 5247 (1975).

20. G. Baccarani, B. Ricco and G. Spadini, J. Appl. Phys. 49, 5565 (1978).
21. C.H. Seager and T.G. Castner, J. Appl. Phys. 49, 3879 (1978).
22. L.L. Kazmerski, P.J. Ireland, and T.F. Ciszek, Appl. Phys. Lett. 36, 683 (1980).
23. M.H. Mandurak, K. C. Saraswat, and T.I. Kammin, Appl. Phys. Lett. 36, 683 (1980).
24. J.C.M. Hwang, P.S. Ho, J.E. Lewis and D.R. Campbell, J. Appl. Phys. 51, 1576 (1980).
25. A.K. Ghosh, C. Fishman and T. Feng, J. Appl. Phys. 51, 446 (1980).
26. A.K. Ghosh, A. Rose, H.P. Maruska, T. Feng and D. Eustace, Appl. Phys. Lett. 37, 544 (1980).
27. H.P. Maruska, A.K. Ghosh, A. Rose, and T. Feng, Appl. Phys. Lett. 36, 381 (1980).