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DEPOSITION, FABRICATION AND ANALYSIS OF POLYCRYSTALLINE
SILICON MIS SOLAR CELLS

Final Report, January 1—December 31, 1979

By
Wayne A. Anderson

March 1980

Work Performed Under Contract No. AC03-79ET23044

The State University of New York at Buffalo
Electrical Engineering Department
Amherst, New York

MASTER

U.S. Department of Energy

Solar Energy

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OBJECTIVES

Several objectives have been set for this research project. Fabrication studies are planned on single crystal and polycrystalline silicon slices (250 μm thick) to achieve efficiency values of 14% and 12%, respectively, for MIS device having areas $> 2 \text{ cm}^2$. Further analysis of these devices will include conduction mechanisms and modelling, surface state analysis, and environmental testing.

Thin silicon films (20-30 μm) will be deposited on heated metal substrates using electron beam and induction heating techniques. These films will be evaluated using SEM, X-Ray, TEM, Auger, and SIMS studies. MIS devices will be used to evaluate conduction mechanisms and grain boundary effects.

ANY OPINIONS, FINDINGS, CONCLUSIONS, OR RECOMMENDATIONS IN THIS PUBLICATION ARE THOSE OF THE AUTHOR AND DO NOT NECESSARILY REFLECT THE VIEW OF THE DEPARTMENT OF ENERGY.

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1. SUMMARY

Cr-MIS solar cells are fabricated using the structure $730 \text{ \AA} \text{ SiO}_2 \text{ AR coating} / 1 \text{ \mu m Al grid} / 50 \text{ \AA} \text{ Cu} / 30 \text{ \AA} \text{ Cr} / 20 \text{ \AA} \text{ SiO}_2 / \text{silicon}$. Recent studies show the importance of surface preparation and interfacial oxide thickness. Distilled and deionized water is important in the final rinsing procedure. An interfacial oxide thickness of $15\text{-}20 \text{ \AA}$ is optimum and may be achieved by ramping to $550\text{-}600^\circ \text{ C}$ in air. Photovoltaic response of 0.56 V , 34 mA/cm^2 , and a fill factor of 0.75 have been attained. Peak efficiency values for 2 cm^2 cells (active area with 10% grid shading) are 13.2% for polished single crystal (xtal), 11.5% for chemically polished (only) single crystal, and 9.0% for Wacker polycrystalline silicon (poly.-Si) substrates. A consistent fabrication technique has been established using a 1 pump-down process for depositing all top layers. A planar etch has been shown to work well in surface preparation of poly.-Si. Laser-scan studies reveal current loss at grain boundaries of poly.-Si but a generally uniform generation in the MIS solar cell.

Conduction mechanism studies have been made using I-V-T measurements from 77° K - 400° K . These studies indicate the Cr-MIS cell to be a majority carrier device dominated by majority carrier tunneling via interface states at room temperature with majority carrier tunneling through the oxide + space charge region occurring at lower temperatures. These mechanisms are present in Cr-MIS cells on both single crystal and polished poly.-Si substrates. Cells on non-polished poly.-Si exhibit trap limited conduction which is certainly an undesirable process.

Data from the conduction mechanism studies were used as the basis for a computer model in MIS solar cell design. This model also included

interface state effects, the effects of thin metal films, recombination, grain boundaries, doping level, series resistance, etc. This model showed that the optimum Cr-MIS cell should be designed using $0.5 \Omega \cdot \text{cm}$ p-type $\langle 100 \rangle$ Si, $N_{\text{SS}} < 5 \times 10^{11}/\text{cm}^2\text{-eV}$, $15\text{-}20 \text{ \AA}$ interfacial oxide, $25\text{-}30 \text{ \AA}$ Cr, $50 \text{ \AA}$ Cu, $1\text{-}2 \mu\text{m}$ Al grid, and $730 \text{ \AA}$ SiO A/R coating. Poly.-Si should have grains $> 50 \mu\text{m}$ and $G_{\text{SS}} < 10^{12}/\text{cm}^2\text{-eV}$. Efficiency values of up to 16% on single-crystal Si and 13% on poly.-Si should be possible to achieve. Each design variable has a certain sensitivity in its influence on V_{oc} , J_{sc} , FF, and efficiency. These are discussed herein. Electronic measurements and a second computer model show N_{SS} to be significantly influenced by choice of silicon substrate and that $N_{\text{SS}} > 1 \times 10^{12}/\text{cm}^2\text{-eV}$ will significantly reduce V_{oc} . It is also shown that $t_{\text{ox}} > 20 \text{ \AA}$ can seriously reduce FF.

Thin ($20\text{-}30 \mu\text{m}$) silicon films have been deposited on low cost (stainless steel or Ti) substrates for use as an economical semiconductor in terrestrial solar cell fabrication. The substrates are heated to $400\text{-}500^\circ \text{C}$ prior to a $1 \mu\text{m}$ Al deposition and then a $20\text{-}30 \mu\text{m}$ silicon deposition (at a rate of $1.5 \mu\text{m}/\text{min.}$) using e-beam heating. An ohmic contact has been formed meaning that the top layers can be immediately deposited to quickly form a MIS solar cell. Material studies indicate $5 \mu\text{m}$ dia. columnar structure containing $500\text{-}5000 \text{ \AA}$ $\langle 110 \rangle$ crystallites. Impurity content is in the ppm range. SEM, Auger, SIMS, X-ray, TEM and microprobe analyses were used in these studies. Electrical studies show carrier trapping to limit photovoltaic performance. MIS cells on these films exhibit $J_{\text{sc}} = 1.5 \text{ mA}/\text{cm}^2$ and $V_{\text{oc}} = 100 \text{ mV}$. Clearly, larger grain size is required to improve on these results.

Reliability studies have included Auger analysis radiation tolerance and shelf life degradation effects. Auger profiles indicate that 150°C heat treatment will not change the Cu-Cr-oxide-silicon profile. Proton

irradiation (1 MeV) $> 1 \times 10^{11}/\text{cm}^2$ begins to reduce V_{oc} and J_{sc} . Similar effects were seen for electron and neutron irradiation. Trapping and surface state losses have been clearly revealed. Recently fabricated cells using a revised procedure indicate little shelf life degradation over a period of several months for a properly fabricated MIS cell.

2. INTRODUCTION

Cr-MIS solar cells are being studied as possible low-cost candidates for terrestrial solar cells. The MIS process utilizes thin metal layers and low-temperature techniques. Diffusion and photolithography are not required in the process. All materials are readily available for large-scale applications. In the existing process, all top layers may be deposited in a matter of minutes utilizing a one-pump-down fabrication sequence. The process is readily applied to any kind of semiconductor as is evidenced in our laboratory using single crystal silicon, poly.-Si, amorphous silicon, and polymers.

This report includes a discussion of MIS cell fabrication techniques, photovoltaic response data, I-V-T analysis to reveal conduction mechanisms, a detailed computer model, optimum MIS solar cell design, surface state effects, Auger studies, reliability studies and e-beam deposition of thin silicon films. The most important features of our work during 1979 include the one pump-down fabrication process, establishing a consistent fabrication sequence, achieving 13% efficiency on 2 cm² area, an evaluation of conduction mechanisms, establishing a detailed computer model and setting up an improved e-beam system to deposit thin silicon films.

Several studies remain to be completed to fully evaluate the potential of the Cr-MIS cell. A better grid design is required to boost total area efficiency to > 13%. Passivation of grain boundaries is necessary to increase efficiency in poly.-Si. Different Schottky metals and interfacial oxides must be studied to evaluate the ultimate potential of MIS cells. Further reliability studies are needed to fully evaluate MIS solar cell stability. E-beam deposited Si films must be studied for depositions on 550-600° C substrates at $< 1 \times 10^{-6}$ Torr to improve grain size and achieve higher efficiency.

3. MIS SOLAR CELL FABRICATION AND PHOTOVOLTAIC RESPONSE

3.1 Photovoltaic Data on MIS Cells

MIS solar cells have been fabricated having the structure SiO (A/R coating) / Al grid / 50 Å Cu / 30 Å Cr / 22 Å SiO₂ / silicon substrate / Al ohmic contact. Details of fabrication have been previously reported⁽¹⁾ and are pictorially shown in Figure 1. The 5 Å Cr layer is no longer used since the Cr-Cu-Al grid - SiO layers are deposited in one pump down of the vacuum system. This new deposition system utilizes 6 substrate holders, 6 masks, and 6 evaporation sources, all of which may rotate with respect to each other. Total fabrication time is now reduced to about 3 hours with further reductions possible in the future.

In recent studies the effects of D.I. H₂O quality, ohmic contact formation, and metal deposition conditions have been examined and optimized. More recently, the interfacial oxide formation was studied by removing the oxide grown during ohmic contact formation (600° C in air) and growing a new oxide at temperatures < 600° C. A photoresist step was used to protect the back Al ohmic contact. A tabulation of these results is given in Table 1 showing the effects of heat treatment and substrate on device performance. During this study the Cr deposition rate, vacuum, and AR design were not optimum which accounts for an efficiency < 10%. The increase in and then levelling off of V_{oc} , J_{sc} , FF, and efficiency with oxide thickness (temperature) agrees quite well with our computer predicted curves shown in Section 5 herein. These trends in experimental data are shown in Figure 2. These trends show a range of heat treatment temperatures of 550° C - 600° C where solar cell performance is optimum. This corresponds to a 2 Å - 5 Å difference in oxide thickness centered about an average value of 20 Å as indicated by ellipsometry measurements.

Figure 1 Diagram of a Cr-MIS Solar Cell

TABLE 1
Effect of Interface Oxide Thickness on Photovoltaic
Performance of MIS Solar Cells

Cell	Heat Treat	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	P_o mW/cm ²
101, <100>1	None	0.04	15.4	0.28	0.17
102, <100>5	400° C	0.20	19.7	0.52	2.04
103, <100>5	500	0.40	26.1	0.65	6.8
104, <100>5	550	0.50	27.8	0.68	9.4
106, <100>5	580	0.53	28.7	0.63	9.6
107, <100>5	600	0.52	27.8	0.65	9.4
108, <100>1	580	0.53	28.0	0.66	9.8
105, Poly	580	0.485	20.0	0.67	6.5
109, Poly	580	0.50	21.5	0.67	7.2
110, Poly	580	0.49	23.6	0.64	7.4
133, Hamco <100>	580	0.56	28.0	0.73	11.5

Typical illuminated I-V curves for two of these cells is shown in Figure 3. It is encouraging that a similar quality is seen in both cases where one cell is on a single crystal Si substrate and one is on a polycrystalline Si substrate. The lower J_{sc} in poly-Si is attributed to grain boundary effects. These data are meant to show consistency in the process and do not represent our optimum results. It is also encouraging that these recent cells apparently do not degrade with time although more time is needed for a full evaluation.

The last entry in Table 1 is for a MIS cell on <100> p-Si from a 5" diameter as-sawn wafer from Hamco Corp. in Rochester, N.Y. This silicon was polished in our laboratory using a plamar etch (as reported later in

FIGURE 3. Illuminated I-V Curves for
Cr-MIS Solar Cells on Xtal and poly.-Si.

this section). Deionized (18 m Ω), distilled water was used in final cleaning rather than the deionized, lab grade water normally used. This cell exhibited a higher fill factor and V_{oc} than previous cells, even though the silicon was not mechanically polished. A higher V_{oc} is attributed to reduced surface state density from using a better water rinsing procedure. A higher fill factor is attributed to the use of an Ag layer over the Al grid to lower device resistance. This result is significant in that it shows the MIS process to be applicable to potentially lower cost silicon.

Finally, Figure 4 shows the illuminated I-V curve for a 13.2% efficient MIS cell on single crystal silicon. This is one of the highest efficiency values reported for a true MIS cell and was designed based on the computer program discussed in Section 5.

3.2 Surface Preparation of MIS Solar Cells on Polycrystalline Silicon

Studies are continuing to extend the MIS process on single crystal Si substrates to poly.-Si. Past performance has shown cells on poly-Si to be lower in efficiency due to lower V_{oc} (0.52 V rather than 0.60 V) and lower J_{sc} (22 mA/cm² rather than 26 mA/cm²) to give a peak efficiency of about 9% rather than 13%. These differences may be attributed to grain boundary effects, lower diffusion length in the silicon, or interface state effects due to the condition of the silicon surface. A study of etching effects on the silicon surface for Wacker poly-Si slices is given below.

An optical microscope study was made of polished Wacker poly-Si and of finished MIS solar cells on this material. Figure 5 shows numerous twin boundaries within a single grain and then one twin boundary within a grain on a finished MIS cell. These twin boundaries can easily be a source of current loss in a finished solar cell. Another study (Figure 6) shows

13.2% Efficient Solar Cell

$$V_{oc} = 0.57 \text{ V}$$

$$J_{sc} = 34 \text{ mA/cm}^2$$

$$\text{Fill Factor} = 0.68$$

$$\text{Area} = 2 \text{ cm}^2$$

FIGURE 4. AM1 illuminated I-V curve for a 13.2% efficient MIS cell

FIGURE 5. Twin Boundaries on Wacker
Poly.-Si.

Twin boundaries within a grain. These boundaries
are separated by 5-10 μm . (200X)

Grain boundaries within a diode. (200X)

FIGURE 6. Surface Conditions on Polished
poly.-Si Compared to Xtal-Si.

Parallel grains. Brighter area is metal covered.
Surface roughness $\approx 30 \mu\text{m}$. Notice a twin boundary
running along one grain boundary. Also notice the
difference in texture outside the grain boundaries.
(200X)

Comparative surface of a <100> Si polished with
CP4. Etch pits $\approx 5\text{-}10 \mu\text{m}$. Surface is very smooth,
suggesting that the grains in poly-Si are of different
orientations to cause surface roughness in those
samples. (200X)

that adjacent grains may have a different crystallographic orientation as evidenced by a different texture after etching with CP4A. A similar etching process was applied to a single crystal $\langle 100 \rangle$ Si wafer resulting in a very smooth surface having a few smaller etch pits. Finally, Figure 7 shows how the surface condition is duplicated on the surface of a 1000 Å metal grid line. Grain boundaries and surface roughness are reproduced in the metal even though the metal is opaque. CP4A has been observed to increase the severity of grain boundaries which probably reduces J_{sc} in poly-Si cells.

One solution to this problem is to use a planar etch which has an equal etch rate in all crystallographic directions.⁽²⁾ A possible planar etch solution consists of 8% HF, 75% HNO₃, and 17% CH₃OOH. This etchant was observed to give a much smoother silicon surface and reduce the severity of preferential etching at grain boundaries.

MIS solar cells on this planar etched Wacker poly.-Si have given efficiency values ranging from 6% to 9% for a 2 cm² area. J_{sc} varies from 19 to 24 mA/cm² depending on metal thickness and A/R coating while V_{oc} varies from 0.49 - 0.55 V. Past data have shown a fill factor variation from 0.30 - 0.64 with an average of 0.52 for a total of 12 cells. Obviously, there was a problem with the fill factor in past cells which has since been resolved by our new oxide growth process as outlined in Section 3.1. This new process has produced solar cells having fill factors consistently in the 0.63 - 0.73 range and efficiency values consistently higher as well.

3.3 Laser Scan Studies

Most analysis work has involved MIS devices on the Wacker poly.- substrate. Small diodes on grain boundaries exhibit higher n-values and lower barrier height (ϕ_B) when compared to similar devices on single

FIGURE 7. Duplication of Si. Surface in
Metal of a Finished Solar Cell.

Grain boundary crossing the grid line. Dark areas are covered with A/R coating. Surface roughness $\approx 30 \mu$ caused by preferential etching of CP4 and is reproduced in metal layer which is $\approx 1000 \text{ \AA}$ thick. Notice different texture in two grain surface, indicating different orientation. (200X)

Twin boundaries within the diode area. Bright region is the diode area, while the dark region is bare silicon. Boundary separation $\approx 5 \mu$. (200X)

crystal substrates (refer to simplified equation 1)

$$J \approx A^* T^2 \exp\left(-\frac{\phi_B}{kT}\right) \left| \exp\left(\frac{qV}{nkT}\right) - 1 \right| \quad (1)$$

This effect may be caused by an increased interface state density or recombination centers associated with grain boundaries. This type of interface state influence was shown in past work.⁽³⁾

A laser scan study of poly.-Si was conducted to evaluate the photocurrent loss at grain boundaries for these MIS devices. A single line scan in Figure 8 illustrates the lower current generated in poly.-Si compared to the single crystal variety. A 3 mW, 6328 Å, 0.003 inch diameter beam was used in this analysis. The key observations include overall reduced current in the poly-Si substrate and further reduced response at grain boundaries (which would be more pronounced if a smaller spot size were used). A more thorough study was conducted at the National Bureau of Standards (by Dr. D. E. Sawyer) which revealed more vivid details of grain boundary effects (see Figure 9). The intensity modulated scan shows grain boundaries as dark regions on the photograph. An amplitude modulated scan shows grain boundaries and grid lines as minima in the contour plots. It is estimated that on the average, grain boundaries cause a loss of current within $\pm 40 \mu\text{m}$ or one diffusion length of the grain boundary center. Some grain boundaries exhibit much more current loss than others as is evident on the photograph.

FIGURE 8. 6328 Å Laser Line Scan of MIS Solar Cells

FIGURE 9. 6328 Å Laser Area Scan of MIS Solar Cells
using Polycrystalline Silicon

6328 Å laser scan
of polycrystalline
Si revealing grain
boundary recombination
(with 70 mA current
bias).

6328 Å laser scan
of polycrystalline
Si indicating a
general uniformity
of generation.

4. I-V-T ANALYSIS OF MIS SOLAR CELLS

4.1 Analysis of MIS Cells on Single Crystal Silicon

A detailed analysis of conduction mechanisms has been made for MIS cells on crystalline silicon.⁽⁴⁾ This analysis is essential to an understanding of device operation and results in J-V equations for use in computer aided designs. In the present experiments, the dark J-V characteristics of the cells (Figures 10 & 11) were digitally recorded at different temperatures, T. Using the (J, V, T) matrix, $\log \left(\frac{J}{T^2} \right)$ was plotted against $(1/kT)$ at each bias (Figures 12 & 13) and $\log J$ was plotted against V at each temperature. The slope of the plot of Figures 12 and 13 gave the activation energy at each bias point and from the mid-bias extrapolation of the latter plot (which gives J_0), the function $(kT) \ln \left(\frac{A^* T^2}{J_0} \right)$ was plotted against the temperature. The mid-bias extrapolation eliminated the effects of shunt resistance and space charge recombination on J_0 . The behaviour of these plots characteristically reveals the conduction mechanisms.

Activation energy as a function of applied bias is plotted in Figure 14 for temperatures above 250° K. This energy is calculated using the relation $\epsilon_{ac} = - \partial[\ln(J/T^2)] / \partial(1/kT)$. At a moderate forward bias, the activation energy can be represented by $\epsilon_{ac} = (\phi_B - qV)/n$, with $\phi_B = 0.815$ eV and $n = 1.19$ in this case. This leads to $J \sim T^2 \exp\left(-\frac{\phi_B}{nkT}\right) \left[\exp\frac{qV}{nkT} - 1\right]$. The value of ϕ_B is also confirmed from the high frequency (1 MHz) C-V measurements. It also corresponds to the value of $kT \ln \left(\frac{A^* T^2}{J_0} \right)$ in the higher temperature region of Figure 15. At a small forward bias, the activation energy appears to become bias independent and saturates at about 0.5 eV. It should be remembered that at small forward bias, generation-recombination in the depletion region and the shunt currents become important in silicon.

FIGURE 11. Reverse Log I-V (T) for a MIS cell
on xtal Si

FIGURE 12. $(I/T^2) - (1/kT)$ as a function of positive bias voltage

FIGURE 13. $(I/T^2) - (1/kT)$ as a function of negative bias voltage

Activation Energy
(eV)

Temperature > 250°K

FIGURE 14. Activation energy as a function of bias

Applied Bias (V)

$$kT \ln \left(\frac{A^* T^2}{J_0} \right) \text{ (eV)}$$

FIGURE 15. $kT \ln (A^* T^2 / J_0)$ vs temperature for a MIS cell on crystalline Si

devices. However, a generation-recombination term will give $\epsilon_{ac} = (\phi_B - qV)/n$ with $n \approx 2$. Such a mechanism seems to dominate only in a very limited region. A shunt resistance, on the other hand, would behave like $R_{sh} = R_{sh}(0) \exp[\frac{\epsilon_{ac}(R_{sh})}{kT}]$, with a bias independent activation energy. The shunted current component will therefore, show an activation energy $\epsilon_{ac}(R_{sh})$ which is bias independent. In the reported cell, this energy is about 0.5 eV. This is further confirmed by the activation energy plot for a reverse bias. The difference of 0.1 eV between the plateau values of the activation energy in small forward bias and reverse bias, is believed to be the back contact barrier height. The back contact was aluminum, alloyed at 600° C with p-Si. Evidently, this contact is not perfectly ohmic, but a barrier height of 0.1 eV does not affect the performance by a large amount. Also in Figure 14, we see a tail in the high bias region. This is mainly because of series resistance. Due to the series resistance, the activation energy is obtained using $(\phi_B - qV + IR_s)/n$, where R_s is the series resistance and I is the current. Some high field tunneling effects could also modify this region of the activation energy plot.

The above results at $T > 250^\circ \text{ K}$ are not surprising for a MIS solar cell. However, at this point of analysis it is not clear whether the device is surface state controlled or tunnel controlled at higher temperature, because both mechanisms predict majority current, $J \sim T^2 \exp(-\frac{\phi_B}{kT}) [\exp(\frac{qV}{nkT}) - 1]$. Minority carriers can also control the device characteristics.⁽⁵⁾ In a recent publication⁽⁶⁾ it has been demonstrated that Al-SiO_x-(p-Si) solar cells are minority carrier devices. However, for minority carriers, $J \sim T^3 \exp(-\frac{E_g}{kT}) [\exp(\frac{qV}{nkT}) - 1]$ and therefore, the activation energy should be equal to the silicon band gap, E_g . Our experiments on Cr-MIS solar cells have never given an activation energy

equal to E_g . Even the plot of short circuit current vs open circuit voltage gave activation energy similar to ϕ_B , instead of E_g . It is then apparent that these devices are not minority carrier controlled. This difference in the mode of operation is further discussed in the following paragraphs. The exact current conduction mechanism is distinguished by plotting $kT \ln \left(\frac{A^* T^2}{J_0} \right)$ vs T , as shown in Figure 15, and discussed below.

At temperatures below 250° K, the observed $J - V$ characteristics differ significantly from the expected behaviour. As can be seen from Figure 15, the function $kT \ln \left(\frac{A^* T^2}{J_0} \right)$ decreases with temperature and eventually extrapolates to a zero value at 0° K. This is in sharp contrast to the relatively constant values at higher temperatures. As shown below, this corresponds to a different conduction mechanism.

Normally it is assumed that the majority carriers tunnel through the interfacial oxide barriers to the semiconductor band edge at the insulator-semiconductor surface. The tunneling through the space charge region is neglected.⁽⁷⁾ However, some majority carriers can tunnel through both the oxide barriers and the space charge region. For these carriers, the barrier width is the sum of the oxide layer thickness and the depletion layer width. The overall shape of the barrier will depend on the band bending in the oxide interface and the space charge region, with the metal fermi level and the semiconductor band edge in the quasi-neutral region being the tunnel levels. We have made calculations for this type of tunneling, assuming a parabolic band bending in the space charge region and a rectangular insulator barrier. The details of these calculations will be presented elsewhere. The resultant expression for

the current density in a p-type semiconductor is

$$J_1 = A^* T^2 \left(1 + \frac{kT}{E_{00}}\right)^{-1} p_i^{(1)} \cdot \frac{N_A}{N_V} \left[\exp \frac{qV}{nkT} - 1\right]. \quad (2)$$

Here $E_{00} = \frac{\hbar q}{2\pi} \sqrt{\frac{N_A}{\epsilon_s m^*}}$ and $p_i^{(1)} = \exp\left(-\frac{2\sqrt{2m^*}}{\hbar} \sqrt{\chi + \phi_B - V - \phi_d} \delta_{ox}\right)$,

ϕ_d being the doping potential. Other notations are as usually defined.

For low to medium biases, the total current is given by

$$J = J_1 + J_2 + J_3 + J_4$$

where $J_2 = A^* T^2 p_i^{(2)} \exp\left(-\frac{\phi_B}{kT}\right) \left[\exp \frac{qV}{nkT} - 1\right]$ (3)

$$J_3 = A^* T^2 f(N_{ss}) \exp\left(-\frac{\phi_B}{kT}\right) \left[\exp \frac{qV}{nkT} - 1\right]$$

$$J_4 = q n_{min} (L_{min}/\tau_{min}) \left[\exp \frac{qV}{nkT} - 1\right]$$

In the above expressions, $p_i^{(2)} = \exp\left(-\frac{2\sqrt{2m^*}}{\hbar} \chi^{\frac{1}{2}} \delta_{ox}\right)$, J_2 is the current due to the majority carriers tunneling over the oxide barrier to the semiconductor band edge.⁽⁷⁾ J_3 is the current due the majority carriers tunneling via interface states. $f(N_{ss})$ is a function of surface state density and their capture cross-section. For uniformly distributed surface states, $f(N_{ss}) = \sqrt{6\pi} N_{ss} \sigma_{ss} \Delta E_{ss}$, where N_{ss} is the number of surface states/area per eV, σ_{ss} is their capture cross-section and ΔE_{ss} is the energy spread of these states. J_4 is the minority carrier current, with n_{min} being the minority carrier density and L_{min} and τ_{min} being the diffusion length and lifetime for these minority carriers.

For mechanism 1 (J_1), the function $kT \ln \left(\frac{A^* T^2}{J_0}\right)$ reduces to zero at 0° K and increases almostly linearly with temperature. For mechanisms 2 and 3 (J_2 and J_3), this function again increases linearly with temperature, but the intercept at 0° K is ϕ_B . For mechanism 4 (J_4), the inter-

cept at 0° K will be E_g . Therefore, from Figure 15, it is evident that below 250° K , mechanism 1 is dominant. Our calculations show that mechanism 2 could be dominant over mechanism 1 only for low doping and higher temperatures. Also, at higher temperatures, mechanism 3 could be dominant over mechanism 2, depending on the surface state density, capture cross-section and oxide interface thickness. Therefore, in many devices the validity of mechanism 2 could be limited to a small region of temperature and bias. Indeed, the calculations for our devices indicate that mechanism 3 dominates over mechanism 2. It can also be shown that minority carriers will govern the device characteristics for $0.4 \Omega\text{-cm}$ p-Si cells if the surface state density is below $10^{11} \text{ cm}^{-2}\text{eV}^{-1}$. For $10 \Omega\text{-cm}$ p-Si, this limit on surface state density is around $10^{13} \text{ cm}^{-2}\text{eV}^{-1}$. In practice, it is possible to get surface state densities of 5×10^{12} – $10^{13} \text{ cm}^{-2}\text{eV}^{-1}$. For this reason, these devices made on $0.4 \Omega\text{-cm}$ p-Si, are mostly majority carrier controlled, while those reported in reference 4 (made on $10 \Omega\text{-cm}$ Si) are minority carrier controlled. It is interesting to note that by proper selection of doping density, efficient solar cells can be fabricated for both majority and minority carrier controlled cases. In Figure 15, we have plotted the theoretical curve for $kT \ln\left(\frac{A^* T^2}{J_0}\right)$ with $J_0 = J_{01} + J_{02} + J_{03} + J_{04}$. Since experimental J_0 was obtained by mid-bias extrapolation of the $\log J$ vs V plot, which eliminated the shunt resistance and space charge recombination effects on the measurement of J_0 , these two effects were not included in theoretical calculations. In these calculations, the semiconductor doping was assumed to be $N_A = 5 \times 10^{16} \text{ cm}^{-3}$ and ϕ_B is 0.82 eV , as obtained from C-V measurements. Other values are $x = 3.65 \text{ eV}$, $m^* = 0.55 m_0$, $A^* = 32 \text{ A/cm}^2\text{-}^\circ\text{K}^2$, $\epsilon_s = 11.8 \epsilon_0$, $\delta_{ox} = 15 \text{ \AA}$, $f(N_{ss}) = 1$. As can be noted, the theoretical function corresponds well to the experimental data. Calculations show

that while mechanism 1 is responsible for the I-V characteristics below 250° K, mechanism 3 is dominant at higher temperature for this particular set of parameters.

4.2 An Analysis of MIS Solar Cells on Polycrystalline Silicon

The previous section gave information concerning the analysis of MIS solar cells on single crystal silicon using results of low temperature I-V tests. Majority carrier tunneling via interface states was shown to be a dominant dark current mechanism at room temperature with majority carrier tunneling through the oxide + space charge region occurring for lower temperatures. A similar study was performed for MIS cells on poly.-Si as outlined below.

Data for a MIS solar cell on unpolished Wacker poly.-Si are shown in Figures 16 and 17. These data are indicative of a device whose current flow is controlled by a Gaussian trap distribution. The I-V characteristic is given by⁽⁸⁾

$$I \propto V^B \quad (4)$$

which is typical of space charge limited conduction. If the trapping states are filled, the value of B should be 2.0 and the I-V data would follow the Mott-Gurney relationship. The plot in Figure 17 indicates that the traps are filled at high temperature ($B = 2$) and at lower temperatures the fraction of unfilled traps is given by

$$\frac{N_T}{N_0} = \exp\left(-\frac{E}{kT_c}\right) \quad (5)$$

where E is energy above the conduction band and $T_c = (B-1) T$ is the characteristic temperature associated with the traps. This is not a desirable conduction process in that the traps act as recombination

FIGURE 17. B in $I \propto V^B$ vs Temperature for
a Cr-MIS Cell on Unpolished poly.-Si.

centers for the photo-generated carriers and also will clamp the Fermi level to the trap level thus reducing V_{oc} . Polishing of the silicon is necessary to remove this effect and provide for a logarithmic I-V relationship to produce a higher efficiency solar cell.

A similar analysis was performed on MIS cells made from polished Wacker poly.-Si as shown in Figures 18 - 21. Log I-V data with temperature as a parameter are shown in Figure 18 and are similar to data for a MIS cell on single crystal silicon. Convergence at high bias and low bias is caused by series and shunt resistance, respectively. The activation energy plot of Figure 20 is derived from Figure 19 and also shows behavior similar to that for a cell on single crystal silicon. A plot of $kT \cdot \ln\left(\frac{A \cdot T^2}{J_0}\right)$ vs temperature (Figure 21) then reveals that at low temperature the current flow is governed by tunneling via oxide interface and space charge regions whereas at higher temperatures, tunneling via interface states is the dominating factor. This behavior is similar to that of a cell on single crystal silicon indicating a promising future for solar cells on polycrystalline silicon in meeting the D.O.E. efficiency goals.

FIGURE 21. $kT \ln (A^* T^2 / J_0)$ vs Temperature
for Cr-MIS Cell on Polished poly.-Si.

Polished Wacker Poly. #22

5. A COMPUTER MODEL FOR MIS SOLAR CELL DESIGN

A computer model was developed to optimize the design of MIS solar cells on crystalline silicon. This model accounts for all known design variables and uses information concerning properties of the various materials as part of the solar cell construction. Knowledge of the conduction mechanisms including surface states, tunneling, diffusion length and recombination is also included. This knowledge was gained from I-V-T measurements on our Cr-MIS solar cells as previously reported herein in Chapter 4. Some of the key equations used in this analysis are contained in the following paragraph.

Several current equations are required to completely describe MIS solar cell behavior. Minority carriers in the bulk are given by

$$J_S^e(\lambda) = f J_L(\lambda) - \frac{qD_n}{L_n} n_{po} \tanh\left(\frac{H-W}{L_n}\right) \left[\exp\left(\frac{V_a}{n}\right) - 1 \right] \quad (6)$$

$$\text{where } V_a = \frac{qV + IR_s + qV_{ox}}{kT} \cdot f = \frac{A_s}{A_T} T$$

The minority carrier tunnel current is given by

$$J_T^e = A_e^* T^2 p_{ie}(t_{ox}) \exp\left[-\frac{E_{gs} - \phi_{bp}}{kT}\right] \cdot \left[\exp\left(\frac{V_{ox}}{V_T}\right) - 1 \right] \quad (7)$$

whereas the majority carrier tunnel current may be expressed as

$$J_T^h = A_h^* T^2 p_{1h}(t_{ox}) \exp\left(-\frac{\phi_{bp}}{kT}\right) \left[\exp\left(\frac{V_a}{n}\right) - 1 \right] \quad (8)$$

Surface state current is then a function of surface state density (N_{ss}) and capture cross-section (σ_{ss}) as given by

$$J_T^S = J_{03} (N_{ss}, \sigma_{ss}) \left[\phi_{bp} - V_a \right] \left[\frac{\exp\left(\frac{V_a}{n}\right) - 1}{1 + \frac{J_{03} \tau}{q N_{ss}} \exp\left(\frac{\phi_d}{n k T}\right)} \right] \quad (9)$$

Finally, recombination current may be expressed as

$$J_r = \frac{\pi q n_i w}{2 \tau_n} \frac{kT}{(\phi_{bp} - \phi_d)} \exp\left(\frac{\Delta E_{gs}}{2kT}\right) \left[\exp\left(\frac{V_a}{2kT}\right) - 1 \right] \quad (10)$$

The effect of interface states between Cr and the semiconductor is given by⁽⁹⁾

$$\phi_{bp} = \gamma (X_e + E_{gs} - \phi_m') + (1 - \gamma) \phi_0 \quad (11)$$

$$\text{where } \frac{1}{\gamma} = 1 + \frac{q N_{ss} t_{ox}}{\epsilon_i}$$

$$\phi_m' = \phi_m - \frac{Q_{fix} t_{ox}}{\epsilon_i}$$

$$Q_{fix} = 5 \times 10^{11} / \text{cm}^2 \text{ positive fixed charge in oxide}$$

$$\sigma_{ss} = \text{capture cross-section for surface states}$$

$$= 10^{-16} \text{ cm}^2$$

Lifetime effects must include grain boundary contributions in poly.-Si.

These effects are governed by the following equations:

$$\tau_n = \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} \right)^{-1} \text{ in bulk} \quad (12)$$

due to shallow traps, deep traps, radiative recomb.

$$\tau_{ng} = \frac{L_g}{v_{th} G_{ss} \sigma_{ss} (E_{fn} - E_{fp})} \exp\left(-\frac{V_D}{V_T}\right) \text{ due to grain boundary} \quad (13)$$

where G_{ss} = density of states at grain boundary

= 10^{11} , 10^{12} , 10^{13} for low, mid, large angle

L_g = length of square grain

Mobility reduction due to grain boundaries is given by

$$\mu_{ng} = \frac{L_g}{\sqrt{6\pi}} \frac{v_{th}}{V_T} \exp\left(-\frac{V_D}{V_T}\right) \quad (14)$$

Finally, the sheet resistance of thin metal films may be calculated using

$$R_s = \frac{4}{3} \frac{\rho_b/d}{\frac{d}{\Lambda} \ln\left(\frac{d}{\Lambda}\right)} \quad (15)$$

where ρ_b = bulk resistivity

d = metal thickness

$\Lambda = 450 \text{ \AA}$ for Cu and Cr

The computer design shows⁽¹⁰⁾ an optimum Cr-MIS cell to use $10^{17}/\text{cc}$ B-doped p- <100> Si. The interface state density (N_{ss}) should be $< 5 \times 10^{11}/\text{cm}^2\text{-eV}$. A 15-20 $\text{\AA}$ silicon oxide is to be grown on top of the Si. Depositions of 25-30 $\text{\AA}$ Cr (having $\phi_m \approx 4.2 \text{ eV}$), 50 $\text{\AA}$ Cu, 1-2 μm Al grid, and 730 $\text{\AA}$ SiO A/R coating will then complete the solar cell. A grid line spacing of 0.25 cm should be adequate to give a good fill factor. An SiO A/R coating is not the best but does represent a coating which is easily and cheaply deposited. This solar cell should give $J_{sc} = 27 \text{ mA/cm}^2$, $V_{oc} = 0.64 \text{ V}$ and $FF = 0.80$ to produce an efficiency of about 14% on single crystal silicon. Similar depositions on high quality poly.-Si should give an efficiency of about 12% if $G_{ss} < 10^{12}/\text{cm}^2\text{-eV}$ and grain size $> 50 \mu\text{m}$.

Variations in design parameters can significantly influence solar cell performance. The Cu thickness is a significant factor in A/R coating

design whereas the Cr thickness is less important. The A/R coating thickness should increase by 12 Å per 1 Å decrease in Cu thickness. This sensitivity is to be expected since the A/R coating is adjacent to the Cu. Likewise, the optimum grid finger spacing depends heavily on Cu thickness but not on Cr thickness. This spacing would decrease by 60 μm per 1 Å decrease in Cu thickness. The Cu film accounts for most of the high conductance necessary for a good fill factor. J_{SC} decreases by 0.2 mA/cm² for each 1 Å increase in Cr thickness since Cr has poor optical transmittance compared to the Cu. V_{OC} does not appear to be a strong function of the thickness of either the Cu or Cr film. Fill factor (FF) decreases from a 0.82 to 0.74 as the Cu thickness decreases from 50 to 20 Å. The optimum AM1 efficiency in Figure 22 is then seen to be a strong function of Cr thickness due to the effect of J_{SC} .

Metal work function has a strong influence on V_{OC} as would be expected and as shown in Figure 23. This also indicates the importance of the doping density of Si in that an optimum exists at about $1 \times 10^{17}/\text{cm}^3$. J_{SC} and fill factor decrease for doping $> 1 \times 10^{16}/\text{cm}^3$ as would be expected from the doping dependence of minority carrier mobility. A combination of these effects predicts an absolute maximum efficiency of about 16% for $\phi_m = 4.2$ eV and $N_A = 1 \times 10^{17}/\text{cm}^3$ ($\rho = 0.5 \Omega - \text{cm}$).

The most critical factor for crystalline silicon appears to be the combination of interfacial oxide thickness (t_{ox}) and interface state density (N_{ss}). J_{SC} will drop for $t_{ox} > 20$ Å, especially for $N_{ss} > 1 \times 10^{12}/\text{cm}^2\text{-eV}$. The ideality factor (n) may be estimated by the simplified expression.⁽⁹⁾

$$n = 1 + \frac{qt_{ox} N_{ss}}{\epsilon_i \epsilon_0} \quad (16)$$

and increases significantly for $t_{ox} > 12$ Å while $N_{ss} > 1 \times 10^{12}/\text{cm}^2\text{-eV}$. The most unpredictable result is found in the dependence of FF, V_{OC} , and

FIGURE 22. Air Mass One Efficiency vs
Cr Thickness for a Cr-MIS Cell.

FIGURE 23. V_{oc} vs ϕ_m for a Cr-MIS Cell.

efficiency on t_{ox} and N_{ss} as shown in Figures 24 - 26. For $\delta > 12 \text{ \AA}$ and $N_{ss} > 1 \times 10^{12}/\text{cm}^2\text{-eV}$ there is an unexpected dip in FF and V_{oc} , which thus decreases efficiency. It is also possible to find a peak in V_{oc} for $1 \times 10^{11}/\text{cm}^2\text{-eV} < N_{ss} < 1 \times 10^{12}/\text{cm}^2\text{-eV}$ but for $N_{ss} > 1 \times 10^{12}/\text{cm}^2\text{-eV}$ a strong and undesirable variation with t_{ox} is seen. These results predict an optimum MIS cell performance when $N_{ss} < 1 \times 10^{12}/\text{cm}^2\text{-eV}$ and $12 \text{ \AA} < t_{ox} < 18 \text{ \AA}$. Note that t_{ox} on the diagrams is the effective electronic thickness which is less than the actual oxide thickness.

A similar analysis was made for poly.-Si with grain size (L_g) and grain boundary interface density (G_{ss}) as parameters. Theoretical data from this study are given in Figures 27-31 and compared with theoretical data from Exxon⁽¹¹⁾ and our experimental data on Wacker poly.-Si. The Exxon curve is calculated for $G_{ss} = 1.6 \times 10^{13}/\text{cm}^2\text{-eV}$. These figures show the potential for $J_{sc} = 25 \text{ mA/cm}^2$, $V_{oc} = 0.60 \text{ V}$, $FF = 0.75$, to give an efficiency of 11.25% when $L_g = 50 \text{ }\mu\text{m}$ and $G_{ss} < 5 \times 10^{12}/\text{cm}^2\text{-eV}$. The Exxon curves give somewhat lowered values since they used $G_{ss} = 1.6 \times 10^{13}/\text{cm}^2\text{-eV}$. The experimental data point for the MIS cell on Wacker poly.-Si falls well within the range of theoretical predicted values. Figure 31 is significant in that it shows the importance of the combination of doping density (N_A) and G_{ss} in predicting optimum efficiency. It is essential for $G_{ss} < 10^{12}/\text{cm}^2\text{-eV}$ to achieve an efficiency $> 10\%$ unless N_A is quite restricted. This suggests the importance of grain boundary passivation in achieving the D.O.E. efficiency goal using poly.-Si.

Finally, a summary of these findings is contained in the loss mechanism chart of Figure 32. The top four losses (72%) are intrinsic to the use of silicon. Reflection, grid shadow, resistance, doping, and band-gap effects account for a 24% loss which would be about the same in p-n junction cells.

FIGURE 27. J_{sc} vs Grain Diameter
(Computer Data)

FIGURE 28. V_{oc} vs Grain Diameter
(Computer Data)

FIGURE 29. Fill Factor vs Grain Diameter

(Computer Data)

FIGURE 30. Efficiency vs Grain Diameter

(Computer Data)

FIGURE 31. Efficiency vs Doping

Density (Computer Data)

FIGURE 32. Loss Mechanism Chart for MIS

Solar Cells

Transmission, interface, and surface state losses account for 35% and are basic to the MIS design. These give a combined loss of 87% to predict an efficiency of roughly 13%. Further losses in poly.-Si due to grain boundary effects predicts an efficiency of roughly 10%. Improved grid design, A/R coating, and transmission loss can increase efficiency values to a maximum limit of 16% on single crystal silicon and 13% on poly.-Si.

6. INTERFACE STATE ANALYSIS FOR Cr-MIS DIODES

Several previous publications^(1,3) outline our work involving interface state magnitude and distribution in the energy gap for Cr-MIS solar cells. Small area diodes were tested using a lock-in-amplifier system to determine device capacitance and conductance as a function of bias and frequency. These data were then analyzed by computer to obtain interface state data as shown in Figure 33. These data are for devices having a structure shown in Figure 1 with the exception of a 40-60 Å interfacial oxide rather than 25 Å and a much smaller area. The dependence of substrate choice on interface state density is apparent. These results are important as evidenced by the equation⁽¹²⁾,

$$V_{oc} = 0.65 - 1.05 \times 10^{-15} \delta \cdot D_s \quad (17)$$

where δ = oxide thickness in Å and D_s = interface state density in states/cm²-eV. This trend of decreased V_{oc} with increased D_s has also been experimentally verified by fabrication of devices on various silicon substrates.

A computer solution of the steady state diffusion equation was designed which accounted for interface oxide thickness, interface state distribution, Schottky metal selection, tunneling probability, and various time constants. This program was established to produce an illuminated I-V curve as pictured in Figure 34 with interface state distribution (shown in Figure 33) for various substrates as a parameter. The dependence of V_{oc} on D_s is clearly seen and parallels the experimental data. A similar curve in Figure 35 uses interfacial oxide thickness as a parameter and indicates a decreased fill factor for $\delta > 15$ Å (effective oxide thickness as seen by an electron) as has been experimentally verified. These results clearly show the importance of surface preparation and oxide thickness in MIS solar cell performance.

FIGURE 33. Interface State Density Distributions on Cr-MIS Solar Cells

IV CURVE OF MIS SOLAR CELL

FIGURE 34. Computer Model of an Illuminated
I-V Curve for a Cr-MIS Solar Cell on
Various Silicon Substrates

IV CURVE OF MIS SOLAR CELL

FIGURE 35. Computer Model of an Illuminated I-V Curve for a Cr-MIS Solar Cell Having Various Oxide Thickness

7. AUGER STUDIES ON SILICON MIS SOLAR CELLS

Auger electron spectroscopy and ion sputtering techniques were used to investigate the free surface composition of polycrystalline silicon and MOS (metal oxide semiconductor) solar cells fabricated on polycrystalline silicon. A thin silicon oxide layer was observed on the free silicon surface. Carbon and oxygen were found chemisorbed to the surface for a surface layer of 10 to 20 Å. It is generally believed that the native oxide layer on free Si surface is about 20 Å. We found that this surface oxide layer was not really silicon oxide but a mixture of silicon oxide and oxygen atoms chemisorbed to the Si surface. For the MOS silicon solar cell, chromium atoms were found in the silicon dioxide layer. Chromium and oxygen atoms diffused into the silicon surface for a layer of ~ 35 Å. Chromium and oxygen both diffused throughout the copper layer and copper diffused through the chromium layer to the Cr-SiO₂ interface.

The experiments were conducted in an ultra-high vacuum (UHV) system equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and ion sputtering gun. A schematic diagram of the UHV system is shown in Figure 36. Samples were mounted in the main chamber and then the system was pumped to 10^{-10} Torr. Surface compositions of both free polycrystalline silicon and MOS solar cell surfaces were studied by AES with a CMA (cylindrical mirror analyzer). Ion-sputtering AES profiles were taken to study the composition of metal layers and silicon-diode and silicon layers. Complete Auger profiles were taken at metal-metal, metal-oxide and oxide-semiconductor interfaces to carefully examine the interdiffusion of the layers.

An Auger profile was taken of a polycrystalline silicon virgin surface.⁽¹⁰⁾ This surface is contaminated by carbon and oxygen. No energy shift of the

FIGURE 36. Schematic Diagram of the UHV Auger System.

high energy Si-Auger peaks were observed. We also did not observe an energy shift of the low energy Si peak. The low energy peak was weak because the surface is covered by carbon and oxygen and the low energy Auger peak has a very shallow ($< 10 \text{ \AA}$) electron escape depth. A very weak shift Si low energy peak was observed when the low energy part of the profile was amplified. This indicated that only a very small portion of the Si atoms were oxidized to SiO_2 at the surface. The oxygen peak was greatly reduced after a few seconds of ion sputtering. This confirmed that the oxygen atoms on the silicon surface were mostly due to chemisorption.

The surface composition was studied for a Cr-Cu-Cr MOS polycrystalline solar cell. The chromium surface had a very large amount of oxygen and it was found that oxygen existed throughout the two chromium layers in the solar cell. The oxygen atoms were introduced into the chromium layers on purpose during the device fabrication to reduce the work function of chromium and thus to increase the open-circuit voltage of the cell. AES profiles were taken at various positions during the ion sputtering of the solar cell. Positions at which these profiles were taken are indicated in Figure 37 from a to f corresponding to these positions. Figure 37 is the ion-sputtering AES profile showing the composition of the cell from the chromium surface to the polycrystalline silicon. It is clear that oxygen and chromium existed through the whole cell and diffused into the silicon for a thickness of 35 to 40 $\text{\AA}$. Large amounts of oxygen were detected in both chromium layers. This could reduce the work function of chromium but would probably increase the series resistance of the Cr layer to $3 \text{ K}\Omega/[\text{cm}]$. The increase of resistivity of chromium by this oxygen must have been modified by the copper atoms diffused into the chromium layers as shown in Figure 37. The diffusion of copper atoms into the chromium layer

FIGURE 37. AES Profile by Sputter

the Cr-Cu-Cr-Oxide-Si Cell

Peak - Peak Auger Signal

may slightly increase the resistivity of the chromium, but decrease the overall sheet resistance to $20 \Omega/\square$. In general, the boundary between the copper and chromium layers was difficult to define because of the interdiffusion of copper and chromium into each other. The SiO_2 layer between the chromium and silicon layers is very difficult to define. The oxygen signal at this region seemed to associate with the chromium signal rather than with the silicon signal. Careful study indicated that the silicon Auger signal was mostly contributed from elemental silicon rather than from SiO_2 .

Stability of MIS solar cells at elevated temperatures has been a controversial item for some time. This question was previously considered^(13,14) and has again been recently studied as well. An Auger profile was taken of a Cr-Cu-Cr MOS device (from the same run as that of Figure 37) after heating at 150°C for 4-1/2 hours. This profile is shown in Figure 38 and indicates no additional interdiffusion of metals. A similar study after 600°C heat treatment shows a complete change in the profiles as shown in Figure 39. This effect is of course to be expected. Our electronic test data suggest that these MIS cells will not catastrophically degrade for $T < 250^\circ \text{C}$.

FIGURE 38. Auger Profile After Heating

a Cr-Cu-Cr-Si Diode to 150° C.

FIGURE 39. Auger Profile After Heating a
Cr-Cu-Cr-Si Diode to 600° C.

8. THIN POLYCRYSTALLINE SILICON FILMS BY E-BEAM DEPOSITION

8.1 Deposition of Polycrystalline Silicon

Polycrystalline silicon films are formed by e-beam deposition of silicon from a water cooled copper crucible.^(1,15) A diffusion pumped Denton vacuum system having a DEG-801 electron gun was used in the first phase of this study. Figure 40 shows a diagram of the experimental configuration inside of the bell jar. Stainless steel or Ti substrates are polished using 0.02 μm alumina, rinsed in water, and ultrasonically degreased in detergent. The cleaning procedure is completed by rinsing in warm D.I. water, immersion in propanol, and drying in a N_2 stream. Four substrates may be used simultaneously in each deposition.

The evaporation procedure consisted of the following steps: pump to 5×10^{-7} Torr, heat substrate to 320°C , heat e-gun filament, activate Ti getter pump, preheat Si charge with e-gun, evaporate Al with e-gun, deposit Si @ 1.5 $\mu\text{m}/\text{min.}$, and discontinue deposition after 12-15 minutes. A detailed study of heat exchanges during deposition was made⁽¹⁶⁾ to predict the final substrate temperature during deposition and compare theoretical with experimental data. It was particularly important to determine the proximity to the Al-Si eutectic (577°C). Boron concentration in the deposited film was controlled by using a pre-doped source.

8.2 Structure and Composition of E-Beam Deposited Si Films

A systematic investigation was undertaken to evaluate the Si films with respect to crystallinity, growth processes, impurity level, and crystal orientation.^(17,18) The scanning electron microscope (SEM) was a useful tool in studying gross structure, topography, and growth processes.

A. electron gun
(schematic)	J. substrates
B. trajectory of beam	K. heater front plate
C. silicon charge	L. heater assembly
D. water-cooled Cu
crucible	M. spring-loaded
substrate clamp
E. cooled collar	N. tungsten heater
F. crucible cap	O. steel collar
G. Al source	P. glass bell jar
H. shutter	Q. crystal monitor
I. shield	R. port to diffusion
pump and trap

FIGURE 40. Diagram of Electron Beam Deposition System

Figure 41 shows the as-deposited edge of an e-beam evaporated Si film clearly showing columnar growth. A study of the fractured edge of such a film (Figure 42) indicates that the film bulk is free of large voids. Columnar growth was observed for substrate temperatures ranging from 250° C to 510° C. Melt formation and a change of film morphology occurred for $T > 510^{\circ} \text{C}$. The existence of columns in the bulk was confirmed by performing the deposition on a Si substrate and then fracturing through the deposition. A Sirtl etch revealed the existence of columns at the fractured edge. The column widths were constant for films of thickness $> 5 \mu\text{m}$. Some films were annealed for 1 hour at 450° C but did not exhibit significant grain growth.

SEM micrographs were used to reveal the existence of Si growth centers on the Al surface during early stages of growth. Figure 43 shows the fairly uniform formation of Si growth centers on the Al surface. The X-ray Line scan of Figure 44 clearly identifies each growth center to be Si. It appears that the existence of a growth center at a particular point reduces the probability of another center appearing in the neighborhood of that point. Al has been clearly detected between growth centers. The growth centers appear to be caused by the precipitation of Si crystallites at the Al-Si interface when the Al film becomes saturated with Si. This predicts a decrease in surface density of growth centers with decreased deposition rate and thus an increased column diameter. It has also been revealed that the surface density of growth centers conforms to the density of columns in the final film.

FIGURE 41. As-Deposited Edge Showing Columnar Growth of an e-beam Deposited Si Film

FIGURE 42. Fractured Edge of an e-Beam Deposited Si Film

FIGURE 43. SEM Micrograph Showing Si Growth Centers

FIGURE 44. X-Ray Line Scan Identifying Si Growth Centers

Secondary Ion Mass Spectrometry (SIMS) was used for thin-film depth profiling and microanalysis.⁽¹⁵⁾ These studies were conducted at the Johns Hopkins Applied Physics Laboratory. Samples for this analysis were prepared with the configuration 16.0 μm Si / 2.1 μm Al / Ti substrate. Si deposition was performed at 7×10^{-6} Torr, 450-473° C, and at 0.93 $\mu\text{m}/\text{min}$. The Si source had a resistivity of 0.006 $\Omega\text{-cm}$ (2×10^{19} B atoms / cm^3). A defocused ion beam was used during SIMS analysis to insure uniform depth removal.

The boron concentration was found to be $1 \times 10^{18}/\text{cm}^3$ using a previous calibration based on Si wafers having a known resistivity. This compares to a boron concentration of $2 \times 10^{19}/\text{cm}^3$ in the source silicon used during e-beam deposition. The elements O and C are thought to be residual gas related. Other impurities may be attributed to the glass bell-jar, the system, the crucible, the substrate, or personnel (such as Na). A revised system design should reduce many of the impurity levels. For example, Ti of the order of 7×10^{13} atoms/ cm^3 has been reported⁽¹⁹⁾ to reduce the efficiency of n^+p solar cells from 10.5% to 6.1%. Our level of $\text{Ti} > 1 \times 10^{16}/\text{cm}^3$ could be a serious problem in achieving a reasonable minority carrier diffusion length. It may be necessary to explore a new substrate material if this is the present source of Ti in the silicon.

X-ray diffraction studies were conducted with the express purpose of resolving the question of crystallinity of these thin Si films. Visual inspection of the films was not conclusive. The spectral response of solar cells made from these films gave a long wavelength cutoff of 0.8 μm indicative of a large bandgap (amorphous Si) or very poor diffusion length. A low doping efficiency ($\rho \geq 1000 \Omega\text{-cm}$ for 1×10^{18}

B atoms/cm³) could also be indicative of an amorphous material. A Philips-Norelco diffractometer with 1.790 Å Co K_α radiation was used in x-ray studies. The x-ray lines indicate the existence of several Si peaks corresponding to a crystalline structure. One sample was studied repeatedly after removing successive layers of silicon by grinding. Results of this study indicate the film bulk to be crystalline since the peak heights remained at the same order of magnitude. (Peak heights would have increased if crystallinity existed only at the Al-Si interface).

Questions concerning grain size and preferred orientation were answered by careful analysis of the X-ray data. A summary of these data is given in Table 2. Sample NS36 was deposited at room temperatures directly onto the Ti substrate and appears to be amorphous. Broad diffraction peaks have been observed by others^(20,21) on amorphous silicon which is indeed the case here. Samples deposited with a high background pressure ($> 1 \times 10^{-5}$ Torr) also exhibited broad peaks indicating little or no crystallinity. Samples deposited with good vacuum, Al-coated substrates, and when using a Ti sublimation pump did exhibit definite crystallinity with crystallite diameters of about 500 Å. It is essential that oxygen be removed from the vacuum system to permit formation of larger crystallite size.⁽²²⁾ These data also indicate the development of a $\langle 110 \rangle$ preferred orientation with increasing film thickness. This is illustrated by an increased magnitude of the (220) / (111) intensity ratio. It was also observed that the (111) peak width varied inversely with the initial Si deposition rate measured 2 minutes after initiating the deposition. It is possible that a low initial deposition rate permits oxidation of the Al layer in regions of high surface density to produce a high density of small (111) crystallites. A high initial deposition rate prevents oxidation from taking place and permits the formation of

Table 2

X-RAY DIFFRACTION DATA

X-Ray Diffraction Data for Polycrystalline Silicon Films

Sample	t(μm)	r_i	P_i	r_i/P_i	peak heights			$\Delta (2\theta)$			$\frac{I_{220}}{I_{111}}$
					(111)	(220)	(311)	(111)	(220)	(311)	
NS29 ^{**}	14.0	104	2.6	40.0	127	104	83	0.2	0.3	0.35	1.23
NS32	19.0	240	14	17.1	55	125	63	0.4	0.35	0.45	1.99
NS36 ⁺⁺	6.0	--	--	--	2	0	0	5.0	--	--	--
NS49	16.0	80	7.4	10.8	43	83	30	0.7	0.4	0.5	1.10
NS50	4.0	88	18	4.9	28	23	--	0.8	0.6	--	0.62
NS60	21.0	176	9	19.6	61	140	74	0.3	0.3	0.3	2.30
NS61 [*]	20.0	96	6.8	14.1	24	45	19	0.8	0.3	0.5	0.70
NS62	19.8	112	7.2	15.6	47	145	40	0.6	0.35	0.5	1.80
NS63 [*]	8.0	168	17	9.9	23	28	36	0.5	0.4	0.35	0.97
NS64	8.5	208	20	10.4	50	69	28	0.4	0.35	0.5	1.21
NS66	17.5	400	18	22.2	60	140	73	0.25	0.3	0.4	2.80
NS67 ^{**}	23.5	264	2.8	94.3	12	90	50	0.2	0.25	0.4	9.40
NS68 ^{**}	14.4	112	5	22.4	38	53	40	0.25	0.3	0.4	1.67
NS69 ^{**}	1.3	--	--	--	50	8	--	0.2	0.3	--	0.24

t: silicon thickness (μm) r_i : initial deposition rate ($\text{\AA}/\text{sec}$) P_i : initial pressure ($\times 10^{-6}$ Torr) $\Delta (2\theta)$: line broadening

* Si on Ti (no Al underlayer)

** Ti getter pump used

+ deposited at room temperature

NS69 annealed in vacuo (90 mins at 420°C)

larger seed crystals. It appears that the effects of initial Al-Si interactions are propagated upwards during deposition to influence the entire Si film.

Transmission electron microscopy (TEM) studies were conducted to learn more concerning the crystalline nature of these thin silicon films. A beam voltage of 200 kV corresponds to a relativistic electron wavelength of $0.0251 \text{ \AA}$ and Bragg angles of about 0.5° . Unsupported silicon flakes were obtained from samples NS65 by bending the Ti after Si deposition. This film had been previously deposited on a 500° C Ti substrate at 7×10^{-6} torr (without an Al overlay). The Si flakes were picked up on a SiO coated Cu microscopy grid. The spotted ring pattern of Figure 45 clearly identifies the polycrystalline nature of the film. Application of the Bragg condition for small angles identified interplanar spacings of 3.12, 1.91, 1.64, and $1.35 \text{ \AA}$. These values identify the 111, 220, 311, and 400 interplanar spacings of Si. The dark field electron micrograph of Figure 46 reveals diffracting crystals of the order of $500 \text{ \AA}$. Similar studies of Si films deposited on an Al-coated Ti substrate have revealed $0.5 \text{ }\mu\text{m}$ crystallites.

A summary of the materials aspects of e-beam Si deposition studies is in order at this point. SEM micrographs have revealed the columnar nature of growth with $5 \text{ }\mu\text{m}$ diameter columns for 20-30 μm thick films. An x-ray line scan revealed the Si growth centers in an Al underlayer. SIMS analysis was used to obtain boron doping concentration and to reveal impurities in the ppm range. X-ray diffraction studies revealed the crystalline nature of these films with a $\langle 110 \rangle$ preferred orientation. TEM studies gave further evidence of crystallinity and revealed $500 \text{ \AA} - 5000 \text{ \AA}$ crystallites depending on deposition conditions.

FIGURE 45 TEM Diffraction Pattern for e-Beam Deposited Si

FIGURE 46. TEM Dark-Field Micrograph @ 50,000 X

8.3 Electrical Properties of E-Beam Deposited Silicon Films

Small grain poly-Si. may be considered to have an energy band structure similar to that of crystalline silicon.⁽²³⁾ But, the defective crystal structure gives a high concentration of states in the energy gap with a donor state located at 0.25 eV and an acceptor state at 0.48 eV above the valence band edge.⁽²⁴⁾ These states cause ion doped poly-Si to be p-type, and act as recombination centers to reduce carrier lifetime by three orders of magnitude compared to crystalline silicon.

Film resistivity has been determined as a function of doping. A 20 μm Si film must have $\rho < 400 \Omega\text{-cm}$ to give a voltage drop $< 0.01 \text{ V}$ when $J = 25 \text{ mA/cm}^2$. A lower resistivity is required for optimum V_{oc} . Room-temperature measurements of surface resistivity for e-beam deposited thin film silicon films were made by the spreading resistance technique.⁽²⁵⁾ The spreading resistance (R_s) is given by

$$R_s = \frac{V}{I} = \frac{\rho}{4r_0} \quad (18)$$

where r_0 = radius of the flat circular contact and ρ is semiconductor resistivity. Here, r_0 is experimentally determined using a semiconductor of known resistivity. Figure 47 shows room temperature resistivity (corrected for finite film thickness⁽²⁶⁾) for several thin film depositions made with and without the use of a Ti pump. Boron concentration was based on a SIMS calibration and knowledge of boron content in the Si source. Experimental data points qualitatively agree with the theoretical curve of Seto.⁽²⁷⁾ A carrier trapping model was assumed with a grain size of $270 \text{ \AA}$ and a surface state density of $3.3 \times 10^{12} \text{ cm}^{-2}$ located 0.37 eV above E_v . This model predicts a rapid change in resistivity

with boron concentration given by

$$N \approx Q_t/L \quad (19)$$

where N = boron concentration (cm^{-3}), Q_t = grain boundary trap density (cm^{-2}) and L = crystallite diameter (cm). If $LN < Q_t$, the crystallites are completely depleted of free carriers which gives a high resistivity. In Figure 47, samples NS68 and NS29 show resistivity values below the curve. These samples were deposited while using a Ti getter pump which has been shown to give increased crystallite diameter ($500 \text{ \AA}$ compared to $200 \text{ \AA}$ without the pump). These two samples seem to be described by $LN > Q_t$ indicative of a lowered grain boundary trap density ($5 \times 10^{11} \text{ cm}^{-2}$ rather than $1 \times 10^{13} \text{ cm}^{-2}$) which could be related to a low-angle grain boundary rather than a high-angle grain boundary.

Temperature variation of conductivity was studied after depositing 0.0044 cm^2 gold electrodes on the top surface of the film to form an ohmic contact. Conductivity measurements were conducted in a temperature range of -145°C to $+15^\circ \text{C}$. Results of some of these measurements are shown in Figure 48. The thermionic-emission current density for a voltage V_g across a grain boundary is given by⁽²⁷⁾

$$J = \frac{1}{4} \bar{p} \bar{v} q \exp(-q\phi_B/kT) [\exp(qV_g/kT) - 1] \quad (20)$$

where $\bar{p}$ = avg. hole conc.

$$\bar{v} = \sqrt{8kT/\pi m^*}$$

ϕ_B = grain boundary potential barrier

We may assume an applied voltage (V_A) to be distributed over many grain boundaries such that at each grain boundary $V_a \ll \frac{kT}{q}$. Then, using $J = \sigma V_a$,

$$\sigma = Lq^2 \bar{p} (2\pi m^* kT)^{-1/2} \exp(-q\phi_B/kT) \quad (21)$$

FIGURE 47. Resistivity vs doping for e-beam poly-Si

where L = grain size

This becomes $\sigma \propto \exp[-(E_F - E_V)/kT]$ for $LN_A < Q_t$ (22)

or $\sigma \propto T^{-1/2} \exp[-q\phi_B/kT]$ for $LN_A > Q_t$ (23)

where Q_t = grain boundary trap density

A plot of $\log \sigma$ vs $\frac{1}{kT}$ produces a line of slope $E_F - E_V$ if $LN < Q_t$ and $q\phi_B$ if $LN > Q_t$. Thus, by examining Figure 48, we see that $E_F - E_V \approx 0.38$ eV for sample NS34 and $q\phi_B \approx 0.091$ eV for samples NS68. The former is limited by available carrier density while the latter by grain boundary potential barrier, ϕ_B . Again, the benefit of a Ti sublimation pump is clearly seen.

Cr-MIS diodes and solar cells were fabricated in the usual manner⁽¹²⁾ except that the ohmic contact was formed during Si deposition. Dark I-V characteristics were measured for a diode formed on a 750 Å crystal-lite film. By subtracting the bulk resistance contribution we may derive the log J-V plot of Figure 49 which gives $\phi_B = 0.52$ eV and $n = 2.6$. The high n-value may be due to a thick oxide in the MIS structure or recombination in the depletion region. A plot of $\frac{1}{C^2}$ vs V , shown in Figure 50 gives $\phi_B = 0.47$ eV, in good agreement with the result from I-V data.

MIS photovoltaic cells were fabricated on the 20-30 μm poly-Si films using the standard procedure. An example of a typical fabrication sequence is given in Table 2. Dark and light I-V data for device No. NS34A is shown in Figure 51. Digital multimeter readings gave $V_{oc} = 85$ mV and $J_{sc} = 1.01$ mA/cm². J_{sc} did show a linear increase with increased lamp intensity.

20 - 30 μm E-BEAM DEPOSITED SILICON

FIGURE 48. $\sigma - 10^3/T$ for e-beam poly-Si

20 - 30 μm E-BEAM DEPOSITED SILICON

FIGURE 49. Log J-V plot for a MIS cell on e-beam poly-Si

20 - 30 μm E-BEAM DEPOSITED SILICON

FIGURE 50. $1/C^2 - V$ plot for a MIS cell on e-beam poly-Si

TABLE 3

Processing Sequence for Thin-Film Silicon MIS Photovoltaic Cell # NS34A

Film or Processing Step	Material	Vacuum deposition or other processing parameters					Cr/Cu/Cr Sheet Resistivity
		Evaporation	Pressure x 10 ⁻⁶ Torr	Temperature (° C)	Time (Sec)	Thickness (μm or Å)	
Substrate	Ti	1)mechanical polish, 2)rinse, 3)clean ultrasonically in detergent, 4)rinse, 5)propanol dip, 6)blow dry in N ₂ .					
Underlayer	Al	e-beam	9.0	343	60	2.0 μm	--
Semiconductor	Si*	e-beam**	7.4	485	750	11.0 μm	--
Si Surface Treatment/Oxide Growth		1)mechanical polish, 2)anneal (1 hour at 540° C), 3)HF etch, 4)thermal oxide (5 mins. at 560° C); cool					
Masking		Mask for deposition (5 x 7 0.00519 cm ² array)					
Schottky Metal	Cr	thermal	30	RT	93	39.8 Å	23.8 kΩ/[]
Conductive Layer	Cu	thermal	12	RT	15	68.2 Å	29.3 Ω/[]
Oxidation Barrier	Cr	thermal	--	RT	8	9.3 Å	35.2 Ω/[]
Masking		Remask					
Contact (.0013 cm ²)	Al	thermal	18	RT	64	1.4 μm	--

* Si source contains 2×10^{19} boron atoms/ cm^3

** defocused beam

$I = 0$

0.001 mA/div.

$V = 0$

0.02 V/Division

FIGURE 51. Dark and Light I-V Data for Device #NS34A Having a Solar Area of 0.004 cm^2 . AM1 illumination.

A summary of data obtained for various MIS cells on poly-Si thin films is shown in Table 4. A few significant features should be discussed at this point. Cells NS29 and NS30 gave good diode characteristics but no photovoltaic response due to the lack of a thermal oxide between Cr and Si. Cells NS32A-C show the importance of a 600° C oxide on photovoltaic response. This effect is attributed to a reduction in surface dangling bonds through chemical combination. Cell NS34C is inferior to cells NS34A & B due to greater stress in the Si caused by a stainless steel rather than Ti substrate. Data in this table show the importance of the Ti substrate, 600 Å oxide, defocused e-beam (samples NS66 and 68), and the use of a Ti getter pump during Si deposition.

Spectral response data were taken to gain information regarding minority carrier diffusion length. MIS diodes on the thin poly-Si films were tested in this study. A Spex model 1670 monochromator (courtesy of Dr. H. Card of Columbia University) was used to obtain the curve shown in Figure 52. An integration of the test data

$$J_{SC} = q \int_{0.4 \mu m}^{0.8 \mu m} n(\lambda) \text{ Q.E. } (\lambda) d\lambda = 1.18 \text{ mA/cm}^2 \quad (24)$$

was compared to the experimental AM1 value of $J_{SC} = 1.01 \text{ mA/cm}^2$ and found to agree within experimental expectations. Two absolute measurements were made using glass absorption filters at 0.40 μm and 0.52 μm . The beam power was measured using a MIS cell previously calibrated at NASA-Lewis Research Center. A fair agreement is seen between these two sets of data. In general, a low infrared response is observed which is easily attributed to a low minority carrier diffusion length caused by the small crystallite size.

TABLE 4

20 - 30 μm E-BEAM DEPOSITED SILICON

Device Parameters, Including Deposition Conditions, Surface Treatment, and Photovoltaic Response

Sample	Substrate	Beam Power (kW)	Final Rate/ Vacuum ($\text{\AA}/\text{Sec}/\mu\text{ Torr}$)	Surface Treatment				Total Cr Thickness ($\text{\AA}$)	Photovoltaic Response	
				Mech. Polish	Anneal	HF	Thermal Oxide		J_{sc2} (mA/cm^2)	V_{oc} (mV)
NS29	s-s	1.50	77					570	0	0
NS30	s-s	1.44	--					66	0	0
NS32A	s-s	1.73	57			X	550	75	0.27	16.5
B	s-s	1.73	57				R.T.	54	7×10^{-6}	1.2
C	s-s	1.73	57			X	600	56	0.80	46.4
NS34A	Ti	1.53*	22	X	X	X	560	49	1.01	85.0
B	Ti	1.53*	22		X	X	580	46	1.27	94.0
C	s-s	1.53*	22	X		X	580	46	0.58	38.0
NS37	Ti	1.37	19		X	X	600	50	0.39	9.7
NS38	Ti	1.56	4.0				550	50	0.01	5.0
NS41	Ti	1.41	16			X	580	53	0	0
NS48A	Ti	0.77	2.4		X	X	580	--	0	0
B	Ti	0.77	2.4			X	580	--	~ 0	0.29
NS49A	Ti	1.15	23			X	560	52	0.4	65.0
B	Ti	1.15	23		X	X	560	52	0.4	54.0
NS66A	Ti	1.60*	13			X	120	60	0	0
B	Ti	1.60*	13			X	580	60	1.27	90.5
NS68	Ti	1.70*	19			X	580	58	1.53	90.0

*denotes defocused e-beam

FIGURE 52. Spectral response curve for a
MIS cell on e-beam poly-Si

8.4 Phase II - A New E-Beam Deposition System

The previous two sections have presented work on phase I of the effort to obtain 20-30 μm thick, polycrystalline silicon films on a low-cost metal substrate. An ohmic contact is formed during deposition so that only the top layers need be deposited to complete fabrication of the solar cell. Both structural and electronic properties have been reported on the phase I work and indicate the need to increase substrate temperatures, increase chamber vacuum, and reduce impurity content to improve on film quality. Solar cells were fabricated on these initial films to produce $V_{\text{oc}} \sim 100 \text{ mV}$ and $J_{\text{sc}} = 1.5 \text{ mA/cm}^2$, without an A/R coating.

Phase II is now underway in that a new e-beam system is operational using a stainless steel vacuum chamber. The chamber is now pumped by a liquid nitrogen baffled, 9" oil diffusion pump. This is now being modified by the addition of a titanium getter pump and an ion pump to reduce contamination and improve on the present 5×10^{-6} Torr vacuum capability. A very stable substrate heater is now operational which can handle four - 1" square substrates and achieve a temperature of 500-600° C. The Airco-Temesca electron gun is very stable and capable of continuous operation for long periods of time. An automatic rod feed permits the continuous deposition of many series of films if desired.

A summary of some of the initial runs made in this system is given in Table 5. A very good film adhesion was seen in all cases, unlike in the previous work. The vacuum was not as good as desired but did remain quite stable during deposition. An Al layer over the stainless steel was necessary to produce a columnar structure. Non-coated stainless steel resulted in a very polished but amorphous film.

TABLE 5

E-Beam Deposited Thin-Film Silicon Data

Film ID	Substrate	Vacuum (Torr)	Substrate Temp. (° C)	Aluminum (Yes or No)	Voltage (kV)	Emission Current (mA)	Time (min)	Thickness (μ m)	Observations
9-7SS/A179	Stainless Steel	2×10^{-5}	60	Yes	5	400	10	≈ 20	Good Adhesion Columnar
9-20SS/A179	Stainless Steel	5×10^{-6}	445	Yes	5.5	400	12.5	≈ 15	Good Adhesion Columnar
9-21SS/A179	Stainless Steel	1.2×10^{-5}	445	Yes	5.5	400	11	≈ 4	Good Adhesion Columnar
9-27SS/A179	Stainless Steel	3.8×10^{-5}	475°	Yes	5.5	450	10.5	≈ 8	Good Adhesion Columnar
9-28SS/A179	Stainless Steel	1.8×10^{-5}	470°	Yes	5.5	450	10	-	Good Adhesion Columnar Dither Control Used
10-2SS/79	Stainless Steel	1.8×10^{-5}	445°	No	5.5	400	6.5	-	Amorphous Film

Samples 9-20, 9-21 and 9-27 have been examined by a scanning electron microscope (SEM). Sample 9-20 is the best film when it comes to uniformity and close packing of the columns. Film 9-21 is 1/4 the thickness of 9-20 and was deposited at 1/4 the rate. There are more large columns at the slow rate but the columns are not tightly packed. A few very large (40 μm) Si clumps were observed on film 9-20. These clumps may be due to abnormal growth or splattering of Si from the melt. An electron microprobe surface scan revealed only silicon and no impurities for the films reported herein. More detailed Auger and ion probe studies are now being conducted.

Once the proper deposition conditions have been achieved (vacuum, rate, substrate temperature) we will begin electronic studies of the films. The immediate work will involve film depositions and material evaluation to obtain crystalline films having a structure suitable for solar cell fabrication.

9. RELIABILITY STUDIES ON MIS SOLAR CELLS

Very few studies have been made (in general) to evaluate the overall stability of MIS solar cells. One prior publication⁽¹³⁾ outlines environmental effects seen for the Cr-MIS solar cell. Another important area of study deals with the ability of MIS solar cells to withstand various forms of nuclear radiation. This information can be important when cells are exposed to radiation from the Van Allen Belt (Solar Satellite Power System), solar flares, or nuclear detonations.

9.1 Radiation Effects on MIS Solar Cells [This work was not funded by D.O.E.]

Proton damage was explored using a Van de Graaff generator as a proton source. The proton is a particularly destructive particle due to its positive charge and heavy mass. Electrostatic beam scanning was utilized in distributing the defocused beam over the active area of the solar cell. Figure 53 shows AMI illuminated I-V curves with proton fluence as a parameter (using 1.0 MeV protons). The V_{oc} and J_{sc} values were influenced by proton fluence (ϕ) as described by the equations

$$V_{oc} = 0.53 - 0.067 \log\left(1 + \frac{\phi}{2.96 \times 10^{11}}\right) \quad (25)$$

and

$$J_{sc} = 24.0 - 9.2 \log\left(1 + \frac{\phi}{2.96 \times 10^{11}}\right) \quad (26)$$

Spectral response was also determined as a function of proton fluence as described in Figure 54. The decrease in infrared response may be attributed to decreased diffusion length caused by extensive bulk damage and described by the equation

$$\frac{1}{L_n^2} = \frac{1}{L_{no}^2} + 1.69 \times 10^{-2} \phi \quad (27)$$

where L_n = diffusion length in μm and L_{no} = initial diffusion length in μm . A more complete summary of changes in solar cell parameters due to proton irradiation is given in Table 6.

FIGURE 53. Illuminated I-V Curves with Proton Fluence as a Parameter

FIGURE 54. Spectral Response as a Function of Proton Fluence

Table 6

MIS Solar Cell Device Data as a Function of Proton Fluence

SAMPLE	Proton Energy (MeV)	Dosage (p/cm ²)	V _{oc} (volts)	J _{sc} (mA/cm ²)	Effi- ciency %	ϕ_b (volts)	n	L _n (microns)	Peak Response Wavelength (microns)
410	1.0	0	0.52	29.8	11.56	0.802	3.50	82.5	0.80
		1.17×10^{12}	0.465	15.3	3.66	0.864	2.14	5.0	0.60
		7.28×10^{12}	0.418	9.9	1.93	-	-	2.5	0.52
		1.27×10^{13}	0.412	9.9	1.90	0.862	2.16	2.0	0.52
424	1.6	0	0.53	24.0	9.70	0.890	2.60		
		2.6×10^{12}	0.49	15.1	4.60	0.880	-		
		5.5×10^{12}	0.47	12.6	3.60	0.880	2.3		
		1.5×10^{13}	0.43	11.3	2.80	0.887	2.2		
		3.3×10^{13}	0.39	5.6	1.10	0.880	2.2		

Electron irradiations were performed at Bell Telephone Laboratories, Murray Hill, New Jersey, using a Van de Graaf machine. Dark and illuminated I-V curves for dosages of 0 and $1.1 \times 10^{16} \text{ e}^-/\text{cm}^2$ using 1 MeV electrons showed a reduced efficiency at these radiation levels. The dark I-V data indicate an increased n-value and reduced ϕ_B after e^- irradiation. The reduced spectral response is similar to that seen during proton irradiation.

Bulk damage effects for e^- radiation is noted at higher fluences than for p^+ irradiation. The critical fluence for $1.3 \Omega \text{ cm}$ n/p silicon solar cells was found to be $2 \times 10^{15} \text{ e}^-/\text{cm}^2$.⁽²⁸⁾ Data on MIS cells are quite similar to this reported level. Bulk damage is evidenced by a reduced diffusion length and peak spectral response. Bulk damage effects for e^- are less than those for p^+ since the e^- are lighter and pass entirely through the wafer thus retaining some of the incident energy.

Surface state measurements on MIS diodes as a function of substrate choice and type of Schottky metal were previously reported.^(29,30) A similar approach has been used in testing MIS diodes prior to and after proton and electron irradiations. Figure 55 shows surface state density variation in the gap before and after an irradiation of $1 \times 10^{13} \text{ p}^+/\text{cm}^2$ using 1.0 MeV protons. The increase in interface state density with irradiation is to be expected. It is observed that the increase in N_{ss} occurs at a radiation level of the same order of magnitude as the N_{ss} level itself which is to be expected. A similar effect occurs for 1 MeV electrons at a fluence of $1 \times 10^{16} \text{ e}^-/\text{cm}^2$. The increase in N_{ss} may be linked to the observed decrease in V_{oc} for a MIS solar cell as has previously been

FIGURE 55. Surface State Variation for
Cr-MIS Cell Due to 1.0 MeV Proton
Irradiation

shown⁽¹²⁾ by the equation

$$V_{oc} = 0.65 - 2.1 \times 10^{-14} N_{ss} \quad (28)$$

which predicts a decrease in V_{oc} to 0.44 V for $N_{ss} = 1 \times 10^{13}/\text{cm}^2$ -eV.

The effects of alpha particles on solar I-V performance were also observed. A relatively low dosage of $1.7 \times 10^{12} \alpha/\text{cm}^2$ caused a significant decrease in efficiency from 10.3% to 6.3% due mainly to a decreased J_{sc} . This has been attributed to a significant decrease in diffusion length from 60 to 22 μm . Results from a similar study using 14 MeV neutrons indicates a significant decrease in efficiency at a fluence of $8.2 \times 10^{12} \text{ n}/\text{cm}^2$. This decreased efficiency is shown to be related to both a decreased V_{oc} and J_{sc} caused by interface state and diffusion length degradation. A dosage of $10^{15} \text{ photons}/\text{cm}^2$ using Co^{60} gamma rays gave a slightly decreased efficiency due to a reduction in J_{sc} . This was linked to a decreased spectral response. The damaging effects of a γ - ray are due to the creation of secondary electrons and pair production and parallel that of electron damage. γ - rays were also observed to deepen the color of the antireflection coating. This effect is known as "color centers" and is believed to be due to the excitation of orbital electrons to the conduction band.

In summary, these studies indicate the radiation sensitivity of Ce-MIS cells to be comparable to that of p-n junction cells.

9.2 Environmental Stability of Cr-MIS Solar Cells

We have previously reported^(13,14) that properly encapsulated Cr-MIS cells do not significantly degrade with normal terrestrial environmental exposure. We have also shown that improperly fabricated (dirty surfaces, poor film quality) or poorly encapsulated MIS cells will degrade as might

be expected. A study has recently begun to more carefully evaluate the stability of Cr-MIS solar cells. Some preliminary data were shown in Table 7. These cells exhibit fairly consistent photovoltaic characteristics over several months of testing. These data represent shelf life degradation studies. Future tests will evaluate exposure to illumination, evaluated temperature, and humidity.

TABLE 7
Some Preliminary Recent Reliability Data for
Cr-MIS Solar Cells

<u>Cell</u>	<u>Date</u>	<u>V_{OC} (V)</u>	<u>J_{SC}[*] (mA/cm²)</u>	<u>FF</u>	<u>Efficiency (%)</u>
A-XTAL	8/22/79	0.53	28.5	0.71	10.7
	9/21/79	0.525	26.0	0.69	9.4
	10/ 8/79	0.522	28.0	0.67	9.8
	11/26/79	0.54	26.0	0.72	10.0
	12/18/79	0.53	28.0	0.65	9.6
B-XTAL	9/21/79	0.51	24.0	0.72	8.8
	10/ 8/79	0.505	26.0	0.69	9.0
	11/26/79	0.52	25.0	0.72	9.4
	12/18/79	0.51	26.0	0.70	9.2
C-POLY	9/21/79	0.51	22.0	0.61	6.8
	10/ 8/79	0.50	23.5	0.61	7.2
	11/26/79	0.53	23.0	0.62	7.6
	12/18/79	0.51	24.0	0.61	7.5

* Simulated AM1 illumination using an ELII lamp.

10. CONCLUSIONS AND RECOMMENDATIONS

The following major conclusions can be drawn from the work reported herein.

1. An efficiency in excess of 13% for xtal-Si and in excess of 10% for poly.-Si is achievable using the Cr-MIS design for large area solar cells.
2. Conduction mechanism studies indicate majority carrier tunneling via interface states to dominate at room temperature.
3. The optimum Cr-MIS cell is designed using 0.5 Ω -cm p-Si having a <100> orientation, $N_{ss} < 5 \times 10^{11}/\text{cm}^2$ -eV, $G_{ss} < 10^{12}/\text{cm}^2$ -eV (for poly.-Si), and grain diameter $> 50 \mu\text{m}$. A 15 - 20 Å interfacial oxide, 25 - 30 Å Cr, 50 Å Cu, 1 - 2 μm Al grid, and 730 Å SiO₂ A/R coating complete the design using $< 10\%$ grid shading.
4. E-beam deposited thin Si films must be formed using substrate temperatures in excess of 500° C, a vacuum $< 10^{-6}$ Torr, and a rate $> 1 \mu\text{m}/\text{min}$. to achieve grain diameter $> 10 \mu\text{m}$.
5. Auger profile studies indicate the Cu-Cr-SiO₂ profiles to be unchanged when heated to $< 150^\circ \text{C}$.
6. Nuclear radiation studies show the Cr-MIS solar cell to be comparable to p-n junctions in response to several forms of irradiation (p^+ , e^- , n, γ , α).

The following recommendations are made for future research emphasis.

1. Grid and A/R modifications are necessary to consistently achieve $> 10\%$ efficiency on poly.-Si.
2. Grain boundary interface state density and capture cross-section must be characterized to evaluate grain boundary effects on solar cells in general.
3. The Cr-MIS process must be carefully applied to ribbon silicon, web silicon, silicon on ceramic, various types of poly.-Si, and e-beam deposited silicon.

4. Different types of low work function metals should be evaluated for use with p-type silicon.
5. E-beam deposited silicon studies should continue using higher substrate temperature and better vacuum to improve on crystallite size.
6. Reliability studies must be carefully conducted to evaluate the long-term stability of MIS solar cells.

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