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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE THIN FILM
SILICON SOLAR CELLS

Final Report, June 30, 1979—June 29, 1980

By
B. L. Sopori

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Motorola, Inc.
Phoenix, Arizona

U.S. Department of Energy

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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE
THIN FILM SILICON SOLAR CELLS

FINAL REPORT

FOR THE PERIOD

30 JUNE 1979 - 29 JUNE 1980

PRINCIPAL INVESTIGATOR: B.L. SOPORI

NOVEMBER 1980

MOTOROLA, INC.
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PREPARED FOR THE

UNITED STATES
DEPARTMENT OF ENERGY
DIVISION OF SOLAR TECHNOLOGY
AND
SOLAR ENERGY RESEARCH INSTITUTE
UNDER DOE SUBCONTRACT NO. AC-01-79ET-23104

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1.0 OBJECTIVES

The objectives of this program were:

1. To develop appropriate measurement techniques to facilitate a quantitative study of the electrical activity of structural defects and at a grain boundary (G.B.) in terms of generation-recombination, barrier height, and G.B. conductivity.
2. To characterize G.B.s in terms of physical properties such as angle of misfit and local stress, and to correlate them with the electrical activity.
3. To determine the influence of solar cell processing on the electrical behaviour of structural defects and G.B.s.
4. To evaluate polycrystalline solar cell performance based on the above study, and to compare it with the experimentally measured performance.

Work done during this contract period initially emphasized development of measurement and sample preparation techniques, so that meaningful measurements could be performed on substrates and devices. Measurement techniques developed for device/substrate analysis are,

- (i) The surface photovoltage technique for measurement of minority carrier diffusion length, cell characterization, and process control.
- (ii) The current phase-shift technique for measurement of minority carrier lifetime.
- (iii) Automatic spectral response measurement.
- (iv) Two wavelength laser scanning.
- (v) Voltage pick-off probing for grain boundary characterization.

In applying these techniques (supplemented by more conventional measurements such as I-V characterization) it was realized, early on, that surface preparation was extremely important. Consequently, a technique for polishing polycrystalline silicon was developed which has the following attributes:

- (i) surface is free from polishing damage
- (ii) maximum grain-to-grain-to-grain height variation, $\delta_{\max} < 0.05 \mu\text{m}$.
- (iii) No "grooving" at the G.B.s takes place.

This polishing technique uses a novel procedure, based on surface photovoltage, to monitor surface damage. This polishing technique enables us to measure optical parameters of ribbon such as specular reflection coefficients, band edge absorption coefficient, and effects of oxygen incorporation in polycrystalline silicon.

These measurements showed: (a) reflection coefficient of RTR ribbon is the same as that of single crystal Si (b) absorption in RTR ribbons at wavelengths

close to the band edge is higher than that of single crystal Si. This could be explained on the basis of residual stress in RTR ribbon. (c) Microscopic stresses, particularly near G.B.s, were observed by IR birefringence. (d) High concentrations of oxygen ($\sim 10^{19} \text{ cm}^{-3}$) could be incorporated into ribbons. (e) Oxygen precipitation was observed at G.B.s in RTR ribbon. (f) The pressure of oxygen resulted in highly resistive G.B.s. Even though it may be regarded as a G.B. passivation technique, a high oxygen concentration was found to yield high stacking fault densities and very large stresses at G.B.s.

Considerable effort was directed towards analyzing structural defects in both RTR ribbons and Wacker Silso wafers. Major emphasis was on utilizing chemical etching and IR microscopy for defect delineation so that defects over large areas could be conveniently determined. This analysis was believed to be a prerequisite for determining influences of various defects and G.B.s on photovoltaic behaviour.

Two approaches were used to determine influences of defects/G.B.s on photovoltaic mechanisms: (i) Large area cells (typically 1 cm x 2 cm) were analysed for local variations in minority carrier diffusion length and photoresponse. The cells were then defect etched to correlate these parameters with substrate structure. Although this procedure yielded much information regarding local photo-current losses at twins and G.B.s we found that quantitative analysis (of the influences of defects/G.B.s) could not be done easily with large area cells. (ii) To overcome this difficulty we developed a simple four-step process for fabricating high quality small diodes on p-type silicon substrates.

Arrays of small area diodes (50 mil diameter), fabricated on polished RTR ribbons and Wacker Silco wafers, were analysed to determine dependences of type and density of defects/G.B.s. on solar cell parameters. From the resultant

data it appears possible to predict cell parameters if the substrate defect structure is known. Conversely, it appears feasible to determine upper limits on the densities of defects to permit the fabrication of high efficiency cells.

In order to determine the effects of G.B. misfit angle on photovoltaic parameters, it was necessary to develop a simple (optical) technique for determination of crystal orientation. This technique is very well suited for the determination of grain orientations in polycrystalline silicon even when grain sizes are small ($\sim 50 \mu\text{m}$). Furthermore, twins can be easily identified by this technique. Grain orientations measured by this technique agree very well with x-ray Laue results. Investigation of influences of G.B. misfit are now the subject of a continuing study.

We have also investigated various electronic and physical mechanisms associated with defects/G.B.s that contribute to photovoltaic losses. Initial results show that defects/G.B.s contribute to increases in dark current with a major contribution of recombination in the space charge region. Tunnelling currents have also been observed.

Currently there is considerable interest in polycrystalline silicon substrates because of their potential for low-cost solar cells. Although fairly good efficiency solar cells can be fabricated on polycrystalline silicon substrates with present technology, the optical and electronic processes taking place in this material are not well understood. In particular, the presence of defects/grain boundaries (G.B.s) profoundly affects the electrical properties of these materials as compared to equivalently doped monocrystalline silicon. The presence of defects/G.B.s in a solar cell results in photovoltaic losses. An understanding of these loss mechanisms which influence the attainable efficiencies of solar cells, is important in order to improve substrate quality as well as to determine the most appropriate processing steps for cell fabrication. Appropriate measurement techniques are necessary to evaluate the cell degradation mechanisms associated with each type of defect and G.B.

This report describes the work we have carried out towards achieving the objectives of the program. The report is divided into sections, each of which describes various sub-task investigations.

4.0 MEASUREMENT TECHNIQUES

We have continued development of several non-destructive optical techniques useful for the characterization of substrates and devices, and for solar cell process control. Parameters measured by these techniques include minority carrier diffusion length (lifetime), junction depth, inhomogeneities (both lateral and in-depth), process induced parametric effects and spectral response. These measurement techniques are currently used on routine basis (although still within a laboratory). A major emphasis has been placed on utilizing these techniques for measurements within small areas of cells and substrates, as well as on small area devices.*

4.1 SURFACE PHOTOVOLTAGE (SPV) FOR MEASUREMENT OF DIFFUSION LENGTH (L)

This technique can be used on bare substrates, partially processed solar cells, or completed solar cells. The method consists of determining the spectral dependence of the photo-signal generated due to the presence of a depletion type region at the surface of unprocessed substrates, or at the p-n junction of processed cells ($0.8 \mu\text{m} \leq \lambda \leq 1.0 \mu\text{m}$).** It can be shown that in order to maintain a constant photo-signal, the intensity I_λ of the incident light (of wavelength λ) is given by

$$I_\lambda (1-R) = \text{constant} (\alpha^{-1} + L) \quad (1)$$

where R and α are reflection and absorption coefficients respectively. I_λ is measured in photons/sec. Hence a plot of $I_\lambda (1-R)$ vs α^{-1} is a straight line whose intercept on the α^{-1} -axis gives the diffusion length L .

*It is shown later in this report that small area devices offer distinct advantages in determining the effects of G.B.s and structural defects.

** Measurements on solar cells can be done using open circuit voltage or short circuit current as photo signals. The techniques are referred to as open circuit photovoltage (OCPV) or short circuit photocurrent (SCPC) respectively.

The conventional procedure for this measurement is well described in the literature (1,2). A schematic program of the set-up is shown in Figure 1a. The incident (filtered) light is chopped and split into two beams -- a sample beam and a reference beam. The reference beam is focussed onto a photo-detector which is calibrated to measure light intensity incident at the sample. The photo-signal from the sample is measured using a lock-in amplifier. Measurements on unprocessed wafers are carried out using a capacitive coupling scheme as shown in Figure 1b. A typical $I_{\lambda} (1-R)$ vs α^{-1} plot is shown in Figure 2.

It has been shown that the conventional SPV technique can be used for high resolution ($\sim 10L$) measurements by focussing the optical beam (diameter = d). This, however, necessitates some correction being made (depending on D/L) to determine the diffusion length (2). With high resolution, this technique is well suited for diffusion length mapping in polycrystalline ribbons provided that the uniformity of the material extends to regions larger than the beam size.

4.1.1 APPLICATIONS

The SPV/OCPV technique has many applications for material/cell characterization and process control.

4.1.1.1 EVALUATION OF SUBSTRATE QUALITY

The presence of impurities and defects are known to strongly influence the minority carrier diffusion length, L . Hence the SPV technique can be used to monitor substrate quality via measurement of L . For example, Figure 3 shows a typical dependence of L on dislocation density (in RTR ribbons). Substrate quality can also be determined in terms of lateral variations in L values. Figures 4 and 5 show typical variations in diffusion length in Cz silicon wafers. Figure 6 shows L variations in polycrystalline RTR ribbon.

FIGURE 1a: SCHEMATIC DIAGRAM OF THE SPV TECHNIQUE

FIGURE 1b: SKETCH OF THE SAMPLE HOLDER

FIGURE 2: $I_{\lambda}(1-R)$ VS. α^{-1} PLOT FOR A HOMOGENEOUS SILICON WAFER

FIGURE 3: DIFFUSION LENGTH -- DISLOCATION DENSITY CORRELATIONS

FIGURE 4: VARIATION OF DIFFUSION LENGTH IN SILICON WAFERS (Cz) WITH AND WITHOUT DISLOCATIONS.

FIGURE 5: VARIATION OF DIFFUSION LENGTH (MEASURED BY SPV) IN A Cz GROWN Si WAFER WITH SWIRL DEFECTS.

FIGURE 6: SKETCH OF AN RTR RIBBON SHOWING L-VALUES (IN μm) IN VARIOUS REGIONS. DOTS REPRESENT MEASUREMENT USING A SMALL OPTICAL BEAM: AND THE DASHED CIRCLE REPRESENTS THE REGION OF MEASUREMENT BY A LARGE BEAM.

4.1.1.2 PROCESS CONTROL

This technique is well-suited for monitoring the effects of various solar cell processing steps because L can be measured before and after each step. It is well established that processes like diffusion, ion-implantation, thermal annealing, etc. can influence L either through impurity incorporation/gettering or defect incorporation/annihilation. Table 1 shows results of each measurement on a set of 3 wafers which went through some solar cell processing steps. Each wafer was split in two and the two sets of half-wafers were sent through different sequences of cell processing.

4.1.1.3 CELL CHARACTERIZATION

All solar cell characteristics (I_{SC} , V_{OC} , FF) can be directly related to L . Measurement of L in a solar cell can be used to predict cell performance; it can also be used as a diagnostic process if the cell performance departs from that expected from its L value. Our measurements of silicon solar cells have shown that if the cell is uniform, there is a good agreement between calculated and measured dependences of I_{SC} on L ; Figure 7 shows such a correlation. A major source of disagreement, $I_{SC}(\text{measured}) < I_{SC}(\text{theoretical})$, was found to be due to cell non-uniformities.

4.1.1.4 CELL NON-UNIFORMITIES

The OCPV/SCPV technique can be used to determine both lateral as well as in-depth inhomogeneities in solar cells. In-depth inhomogeneities in the base region (e.g. sometimes a layer of high recombination is introduced near the junction as a result of diffusion or ion-implantation annealing) are manifested as curvature in the $I(I-R)$ vs α^{-1} plots as seen in Figure 8 (also discussed in

THREE Cz SILICON WAFERS

$\rho = 1 \Omega\text{-cm.}$

TABLE 1
INFLUENCE OF VARIOUS PROCESSING STEPS ON DIFFUSION LENGTH

FIGURE 7: DEPENDENCE OF SHORT CIRCUIT CURRENT DENSITY FOR TEXTURED SILICON SOLAR CELLS ON CARRIER DIFFUSION LENGTH (AM1 ILLUMINATION).

FIGURE 8
OCPV CURVES OF TWO CELLS
WITH IN-DEPTH
NON-UNIFORMITY

reference 3). This technique can also be extended to measure the junction depth in a cell.

4.2 THE CURRENT PHASE SHIFT (CPS) TECHNIQUE

This method is based on the fact that when a modulated light source illuminates a semiconductor, the carriers generated exhibit a phase-shift with respect to the incident light. The phase-shift is a function of τ (in addition to other parameters like surface recombination velocity, modulation frequency, absorption coefficient) and can be measured as a phase difference between the incident light and the short circuit current. A simple experimental setup used for this measurement is shown schematically in Figure 9. A long wavelength LED (GaAs or GaInAs) is modulated and the light focussed on the sample. For unprocessed substrates a Schottky (Hg) contact is made on the back side. The short circuit photocurrent is fed to a lock-in amplifier to display the phase. The reference signal to the lock-in can be either a current driven signal to the LED or from a separate high speed photo-detector which receives part of the light. It has been shown that in this arrangement (and with certain other easily satisfied requirements) the phase-shift ϕ is given by

$$\tan \phi = \omega\tau/2 \quad (2)$$

where ω is the angular frequency of modulation.

This technique has the advantage that the absorption coefficient need not be known. However, to make high resolution measurements, certain corrections must be made (depending on the contact size and the surface recombination velocity) to determine the true lifetime. These corrections are discussed in (4) for the arrangement shown in Figure 9. We have observed that results of the CPS technique agree well with the SPV measured value of L (using appropriate values of D in the relation $L = \sqrt{D\tau}$).

FIGURE 9: SCHEMATIC OF THE CURRENT PHASE-SHIFT METHOD FOR LIFETIME/DIFFUSION LENGTH MEASUREMENT.

Measurements on solar cells can be made by illuminating the p-n junction side directly (which also improves the S/N ratio). This also offers the added advantage of being able to use different wavelengths of illumination to generate the carriers up to different distances away from the junction and, hence, probing in-depth inhomogeneities.

4.3 SOLAR CELL SPECTRAL RESPONSE

The spectral response of a solar cell may be taken under D.C. or A.C. conditions. Under D.C. conditions the light from a solar simulator may be filtered by discrete narrow band optical filters before illuminating the cell. The short circuit current, under each (narrow band) wavelength region is then measured. Under A.C. conditions, weak chopped light is used (often from a monochromator) accompanied by a synchronous detection system. A.C. response can be measured under light bias to establish actual cell operation conditions (e.g. by AM1 illumination). Figure 10 shows a schematic of the automatic measurement set-up in the Motorola Solar Energy R&D Optics Laboratory. The light source is a double-beam spectrometer (Cary 17). Signals (from the cell and the reference light detector) are multiplexed, digitized, and sent to the computer. A reference run is made with a flat (pyroelectric) detector in the sample compartment; this measures the spectral distribution of light intensity as a ratio A_1 given by

$$A_1 = \frac{\text{Flat detector}}{\text{Reference signal}}$$

Next, the flat detector is replaced by a solar cell and ratio A_2 is determined:

$$A_2 = \frac{\text{Cell output}}{\text{Reference signal}}$$

FIGURE 10: SCHEMATIC OF AN AUTOMATIC SPECTRAL RESPONSE MEASUREMENT SYSTEM.

The spectral response is then given by

$$S. R. = \frac{A_2}{A_1}$$

Sensitivities obtained in the A.C. response are very high; consequently small device measurement can be done very effectively. Figure 11 shows responses of two diodes: Figure 11a is for a 50 mil diode (D_1) fabricated on a single crystalline Cz wafer; Figure 11b is for a 50 mil diode (D_2) fabricated on a Wacker Silso poly silicon wafer. The diffusion length in D_1 was measured to be $\sim 70 \mu\text{m}$. Measurement made on a single (large) grain in the Wacker Silso poly substrate gave a diffusion length value of $65 \mu\text{m}$. However, a comparison of the spectral responses of D_1 and D_2 clearly indicates a lower effective diffusion length for D_2 .

4.4 TWO WAVELENGTH LASER SCANNER

The laser scanner used for imaging cell/substrate photoresponse is shown schematically in figure 12. Light from either of the two HeNe lasers, one operating at $1.15 \mu\text{m}$ and the other at $0.6328 \mu\text{m}$, can be selected by mirror M_1 . The selected beam is focussed on the sample, which is located on a computer-controlled X-Y translation stage. This arrangement allows distortion-free imaging of the beam, which is in contrast to distorted imaging normally occurring in the mirror deflection type of scanners. The signal from the sample, either voltage or current, is processed to give a display in one of the following modes: (a) line scan (b) Z-modulation raster imaging or (c) isometric display.

Figure 13 shows line scans taken across a polycrystalline cell at two different wavelengths. The structure of the electrode, and the scan direction, are also shown. Short wavelength response reflects p-n junction properties,

FIGURE 11a: SPECTRAL RESPONSE OF A SMALL AREA SINGLE CRYSTAL CELL (D₁)

FIGURE 11b: SPECTRAL RESPONSE OF A SMALL AREA POLYCRYSTALLINE CELL (D₂)

FIGURE 12: SCHEMATIC OF THE FOCUSED LASER SCANNER (FLS)

FIGURE 13: LINE-SCAN OF A SOLAR CELL AT TWO DIFFERENT WAVELENGTHS (CELL #956S-2)

whereas long wavelength response is proportional to the local value of minority carrier diffusion length (3). Figures 14a and 14b show Z-modulation photoresponse images of cells fabricated on two types of substrates, Wacker Silso poly and Motorola RTR ribbons respectively. Figure 14a shows that the response of each grain is uniform; however, there are significant variations in the responses from different grains. Figure 14b (a high contrast photograph) shows the loss in photoresponse in the regions of structural defects.

Figure 15 shows an isometric display of the photoresponse of a 50 mil (diameter) diode fabricated on a polycrystalline substrate. The effects of G.B.s in lowering the response can be quantitatively measured.

We are also extending laser scanning to unprocessed wafers. In this case the laser beam is chopped and the a.c. (surface photovoltage) signal is capacitively coupled. This process is somewhat similar to SPV measurement; it can be done only on polished samples. Moreover, it is necessary that the spacing between sample surface and electrode be uniform in the region of scan. An electrode configuration developed for this purpose is shown in Figure 16. Major parts of the assembly are marked. A line scan of the photoresponse of an unprocessed ribbon (taken at $\lambda = 1.15 \mu\text{m}$) is shown in Figure 17. The amplitude variation is proportional to the diffusion length variation in the ribbon.

(a)
CAST POLY CELL

(b)
RTR RIBBON CELL

FIGURE 14: Z-MODULATION PHOTORESPONSE IMAGES OF CELLS
FABRICATED ON (a) WACKER SILSO POLY (b) MOTOROLA
RTR RIBBON. (b) IS A HIGH CONTRAST PICTURE TAKEN
TO BRING OUT SMALL CHANGES IN INTENSITY - AMPLITUDE
DIFFERENCE IN PHOTO-SIGNAL BETWEEN BRIGHT AND DARK
REGIONS IS ONLY ABOUT 20%.

FIGURE 15: ISOMETRIC DISPLAY OF PHOTORESPONSE
FROM A 50 MIL DIAMETER DIODE.

FIGURE 16: VACUUM CHUCK AND ELECTRODE ASSEMBLY FOR PHOTO-RESPONSE IMAGING OF UNPROCESSED WAFERS.

FIGURE 17 LINE-SCAN OF SPV RESPONSE DUE TO FOCUSED LASER SCANNER ($\lambda = 1.5 \mu\text{m}$) (Response beyond the edges is due to edge illumination by scattered light).

ON OPTICAL MEASUREMENTS

We have observed that polycrystalline substrates/cells can exhibit different local surface profiles, in addition to random roughness, depending on the surface preparation technique utilized. Surface profiles are particularly pronounced for treatments involving chemical etching. These local profiles can lead to unpredictable scattering of a light beam, and hence give rise to erroneous measurements. Scattering is particularly important when measurements are made with a focussed beam. Scattering sources of particular significance are:

- (i) V-grooves formed due to an enhanced etch rate at G.B.s during chemical etching. V-grooves are also formed on thin poly silicon ribbons grown by solidification of a melt. This shape of the G.B. surface has been explained (in the case of metals) in terms of G.B. interfacial tension (5). Figure 18 shows a G.B. having a V-profile, in an as-grown RTR ribbon. When a focussed light beam is scanned over the G.B. with such a profile, scattering will result in a change of reflection coefficient as well as a change in the direction of light propagation (see Figure 19a). Consequently, photoresponse at a G.B. can be significantly different than that expected from a flat surface; in fact, over-compensation of the loss in photoresponse due to excess recombination at a G.B. may take place.
- (ii) Steps at G.B.s arising from differential etch rate for various grain orientations. The effects of light scattering at a step can easily be observed by examining the reflected light spot which displays a dark line as shown in figure 19b. Effects on light scattering are similar to that of a V-groove.
- (iii) Periodic surface perturbation. These are believed to be caused by coherent twins subjected to certain chemical etchants. The effect

FIGURE 18: PHOTOGRAPH SHOWING LOCALIZED V-PROFILE
AT G.B. IN AS-GROWN RTR RIDDON.
MAGNIFICATION: 100X

FIGURE 19: LIGHT SCATTERING AT TWO DIFFERENT SURFACE PROFILES
(a) V-GROOVE (b) STEP

of such a surface is similar to that of a grating. Figure 20 shows a laser line scan across a solar cell having a periodic ripple. It is seen that the defected region has the highest response and is believed to be the result of surface scattering. A photograph of the surface profile in this region is also shown.

Although the above arguments have been considered explicitly for light scanning, they apply to all optical techniques for small area measurements. To avoid these ambiguities due to light scattering, it is necessary to polish the surface of a polycrystalline silicon sample such that surface damage and profile variations, in particular at the grain boundaries, can be minimized. We have developed a polishing technique which yields a damage-free polished surface with grain-to-grain surface height variation, δ , less than $0.05 \mu\text{m}$. A method for monitoring surface damage due to polishing in order to optimize the polishing conditions is also described.

The problems associated with polishing polycrystalline silicon can be generalized as follows:

- (i) Both chemical and mechanical (using fine grit) polishing result in steps at the grain boundaries due to different removal rates for various grain orientations.
- (ii) Mechanical polishing results in surface damage, giving rise to a high surface recombination velocity (which has deleterious effects on solar cell performance and complicates the interpretation of measurement data).
- (iii) Chemical polishing/etching generally causes "grooving" at the grain boundaries due to the fact that the etch rate at grain boundaries is often higher than that of the grains.

From these considerations, we evolved a system to minimize surface damage and δ that utilizes a sequence of mechanical polish followed by chemical/mechanical

FIGURE 20: FLS CURRENT LINE SCAN ($\lambda = 0.6328 \mu\text{M}$) OF A RIBBON CELL

polish. The chemical/mechanical polishing should be done just long enough to remove the surface damage from mechanical polishing. Several mechanical and chemical/mechanical polishing procedures were investigated; the one that gave best results is described below.

5.1 PROCEDURE AND RESULTS

Polycrystalline silicon samples that were polished had sawn and etched surfaces. These wafers have considerable surface roughness and their grain structure is clearly visible, as shown in figure 21. Various grains show up due to variations in reflectivity caused by changing grain inclination with respect to the incident light. Wafers were first lapped with alumina powder (typical grit size $\sim 30\mu\text{m}$) using a felt pad* for about 30 minutes. The lapped sample exhibited a greyish appearance and no grains appeared under normal visual inspection. Heavy surface damage was evidenced by a lack of surface photovoltage signal due to high surface recombination velocity (1).

Samples were then polished with oil-based diamond grid (typical size $\sim 2\mu\text{m}$) while gradually reducing pressure from 5 psi to 2 psi and maintaining this value for 2 minutes. Diamond polishing removed much of the lapping damage, but there was still residual surface stress which had to be removed. This was done by a chemical/mechanical polish using Nalcoag slurry, type 2350**.

To optimize polishing conditions, surface photovoltage was used to monitor the degree of surface damage based on the fact that the signal developed across the sample is a function of surface recombination velocity (1).

* A laboratory type machine with single spindle and rocking arm was used for all polishing steps.

** Nalcoag is a colloidal silica slurry manufactured by Nalco Chemical Company.

FIGURE 21: PHOTOGRAPH OF A POLYCRYSTALLINE
WAFER BEFORE POLISHING.
SIZE: $2.5 \times 2.5 \text{ cm}^2$

Reduction in surface damage by chemical/mechanical polishing was compared by polishing samples for short intervals of time and measuring their photo-voltage responses. Light intensity, and the gap between top electrode and sample surface, were held constant throughout all measurements. Variation of photo-signal at 10 second intervals of polishing time is shown in figure 22. The solid circles show this signal variation. The decreased signal after 60 sec. of polish was felt to be caused by insufficient flow of Nalcoag during polishing since repeating the experiment on another wafer yielded the signal value shown by the triangle. Saturation of signal occurs after about 60 sec. of polishing, implying the surface to be free from damage.

In order to compare (qualitatively) the residual surface damage after lapping and diamond polishing with that of diamond polishing alone, the above sample (after Nalcoag polish) was given a diamond polish followed by repolishing with Nalcoag for 10 sec. intervals and remeasuring the SPV signal. These data are shown by squares in figure 22. Residual damage from diamond polishing alone was much less than when the sample was lapped prior to diamond polish. Furthermore, the signal saturation occurred after only 40 sec. of total polishing time. The two lines A and B in figure 22 indicate the signal levels obtained from two samples which were first Nalcoag polished and then etched using two different etchants; since the samples were not mechanically polished, these signal levels correspond to damage-free surfaces, lending support that the contention that saturation signal level implies a damage free surface.

The procedure was used to polish polycrystalline silicon wafers with negligible (or no) surface damage gives a smoothness, $\delta_{\max}$, of less than $0.05 \mu\text{m}$. This is clearly seen from figure 23 which is a surface profile trace of a polished Wacker Silso polycrystalline silicon wafer. A Nomarski photograph of a part of the polished surface is given in figure 24. Although the photographed region has many grain boundaries, only a few are visible in figure 24. A Dektak

FIGURE 22: AMPLITUDE OF SPV SIGNAL VS. POLISHING TIME FOR A WACKER SILSO POLYCRYSTALLINE SILICON WAFER. LIGHT INTENSITY AND OPTICAL BEAM SIZE WERE HELD CONSTANT ($\lambda = 1.0 \mu\text{m}$).

FIGURE 23: DEKTAK TRACE OF THE SURFACE PROFILE OF A POLISHED WACKER POLYCRYSTALLINE SILICON SAMPLE.

FIGURE 24

**NOMARSKI PHOTOGRAPH OF A
POLISHED POLY SAMPLE.
(ONLY A FEW G.B.'S ARE
VISIBLE) MAG. = 50X**

**DEKTAK TRACE TAKEN ALONG
THE DIRECTION OF ARROW**

trace (accompanying the photograph) across the most prominent grain shows the height variation to be $0.03 \mu\text{m}$. An interference photograph of a part of the surface, taken under sodium light ($\lambda = 0.513 \mu\text{m}$) is shown in figure 25.

The polishing procedure described above was established following several variations in mechanical and chemical/mechanical polishing sequences. Table 2 summarizes some essential features of these. It should be emphasized that procedures a, b, and c in table 2 lead to a steady state grain-to-grain height variation (i.e., δ does not change if the polishing is continued past an initial period of rapid variation). Results of chemically polishing the samples in two different etchants are also given in table 2 for comparison. These etchants are often used for silicon surface preparation.

We have also found Nalcoag polishing to be a very attractive technique for wafer thinning. Figure 26 shows a plot of thickness removed vs. polishing time for two pressures. It is seen that removal rates are comparable to that of lapping. In addition, Nalcoag polishing allows better control for these wafers. We have been able to parallel polish RTR silicon ribbons down to a thickness of $28.1 \mu\text{m}$ for the measurement of absorption coefficients at wavelengths down to $0.7 \mu\text{m}$ (6).

5.2 APPLICATIONS

The polishing of polycrystalline silicon is necessary for a variety of important electrical and optical characterization techniques. Some of these are listed below:

- (i) Focussed laser scanning to determine local variations in photo-response and to evaluate some effects of grain boundaries.
- (ii) Material thinning and polishing for measurement of optical constants such as reflection and absorption coefficients, and to

FIGURE 25: INTERFEROGRAM OF A POLISH SECTION
OF A POLYSILICON WAFER.
MAGNIFICATION = 10X

TABLE 2: SUMMARY OF THE RESULTS OF SOME OTHER POLISHING PROCEDURES

POLISHING METHOD	$\delta_{\max}$ μm	$\langle\delta\rangle$ μm	COMMENTS
a. Mechanical polish Final grit size = $0.05\ \mu\text{m}$ Pad: Micro-cloth	1.2	0.3	(i) Grain boundaries have smooth taper (ii) Severe surface damage indicated by very low SPV signal.
b. Lapping + Nalcoag Pressure 10 PSI Pressure 20 PSI	1.2 0.4	0.5 0.25	(i) δ attains steady-state value after about 4 min. of polish with Nalcoag. (ii) Lapping damage is not removed in 4 min. (iii) Grain boundaries show gentle taper (iv) Damage-free surface after 15 min. polish with Nalcoag. (v) Useful for sample thinning.
c. Lapping + Diamond	0.2	0.1	(i) Leaves shallow scratches. (ii) Residual surface damage.
d. Chemical Polish $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}$	4	1.5	
$\text{HNO}_3:\text{HF}:\text{Br}:\text{CH}_3\text{COOH}$	4	~ 2

FIGURE 26: PLOT OF THICKNESS REMOVED VS. POLISHING TIME DURING NALCOAG THINNING.

determine microscopic stresses by infrared birefringence.

- (iii) Planar defect characterization for delineating various types of defects using chemical etchants.
- (iv) Angle lapping for a variety of characterizations such as variation of defects in the bulk, junction depth measurements (at and away from grain boundaries), and a variety of other measurements (e.g. potential probing) which require signal pick-off from the surface.

This section will describe the physical characteristics (surface morphologies) and structural defects of ribbons.

6.1 SURFACE MORPHOLOGY

A detailed study of surface morphology of ribbons is important in two ways: (i) Optical characteristics such as reflection and surface scattering into the bulk, and solar cell P-N junction characteristics, depend on the surface properties of the substrates. Since ribbons are aimed at being low cost substrates for solar cells (and hence can not be given elaborate surface preparation), as-grown surface quality can play an important role. (ii) Surface morphology has been found to be closely related to surface defects (discussed later); hence, an understanding of growth conditions that determine a particular surface morphology is important.

Ribbon surfaces show several characteristic features. Well-grown ribbons exhibit a shiny surface with fine periodic undulations resembling a grating structure. The grating lines are normal to the growth direction. Figure 27 shows a photograph of the periodic surface relief. The pitch of the grating was determined to be $\sim 4.45 \mu\text{m}^*$. This was also confirmed by measuring the angular dispersion of the grating orders (in reflection) due to incidence of a visible HeNe laser beam. This surface relief is believed to be caused by periodic melt movement due to the combined effect of pulling and laser scanning. This surface condition often occurs when growth is carried out in an oxygen-free atmosphere (e.g. argon) and is consistently accompanied by desirable characteristics such as low dislocation density and high values of minority carrier diffusion length.

*A simple calculation of step periodicity due to pulling indicates that pitch of the grating should be $2.27 \mu\text{m}$ as compared to $4.45 \mu\text{m}$.

↑ GROWTH DIRECTION

G3695

FIGURE 27: PHOTOGRAPH OF A GRATING PATTERN SEEN
ON A RIBBON SURFACE

GRATING PERIOD - $1.5 \mu\text{m}$.

MAGNIFICATION = 400X

Growth in an inert atmosphere can, sometime, result in a greyish surface appearance, partially or fully covering the surface, as seen in figure 28a. A magnified view of a grey region, figure 28b, shows that it possesses an "orange-peel" structure with nodules projecting out of the surface. The shiny areas, figure 28c, exhibit a grating pattern (normal to growth direction) as described earlier. A close examination of the transition region (between grey and shiny) shows that this region consists of grating-like patterns, with grating lines parallel to the growth direction, figure 28d.

Very smooth surfaces, of mirror finish, are formed if the ribbons are grown in the presence of oxygen. A further discussion on the presence of oxygen will be given later (section 7). A cross-hatch pattern may be observed in certain sections of the ribbon. A photograph of such a section is shown in figure 29. The lines at an angle are due to slip during the growth.

From the general observations it appears that surface roughness is a consequence of turbulence in the melt during growth. However, the effect of turbulence is less when oxygen is present during growth. Furthermore, a periodic melt movement results in a periodic surface relief. It might be expected that such a movement of the melt would also introduce a periodic stress. We have seen that ribbons which did not exhibit any grating pattern on their as-grown surfaces (both smooth as well as rough), did show a grating pattern when etched for dislocations (using an anisotropic etch). Figure 30 shows a photograph of a sample which developed a grating pattern after dislocation etching. However, no microscopic stress could be observed under i.r. microscopic examination, implying perhaps low stress levels. Further investigations need to be carried out to assess the presence of periodic stress*.

* Significance of the concern for this stress (as explained later) is that it may be one of the dominant factors limiting minority carrier diffusion length in ribbons.

FIGURE 28a: PHOTOGRAPH OF A TRANSITION PART OF A RIBBON SHOWING REGIONS OF SHINY AND GREY APPEARANCE

FIGURE 28b: PHOTOGRAPH SHOWING THE APPEARANCE OF A GREY REGION.
MAGNIFICATION - 1000X

FIGURE 28c: PHOTOGRAPH OF A SHINY SELECTION OF THE RIBBON
GROWN IN ARGON.
MAGNIFICATION = 400X

← GROWTH DIRECTION

FIGURE 28d: PHOTOGRAPH OF A SECTION OF RIBBON SHOWING
TRANSITION BETWEEN GREY AND SHINY REGIONS.
MAGNIFICATION = 400X

FIGURE 29: PHOTOGRAPH SHOWING CROSS HATCH
(DUE TO SLIP) ON AS-GROWN RIBBONS.
MAGNIFICATION = 100X

FIGURE 30: PHOTOGRAPH OF A RIBBON SURFACE AFTER
DISLOCATION ETCH. NOTE THE GRATING
PATTERN REVEALED BY DISLOCATION ETCH.
MAGNIFICATION = 400X

6.2 DOMINANT ORIENTATIONS

Since RTR recrystallization depends on self seeding, it is expected that there will be some preferred orientations. The dominant orientations have been determined to be $\langle 110 \rangle$ and $\langle 100 \rangle$. These orientations may also be expected from the consideration that since the growth rates along various directions vary as:

$$\langle 100 \rangle > \langle 110 \rangle > \langle 111 \rangle,$$

fast growth rates will result in $\langle 110 \rangle$, $\langle 100 \rangle$ orientations.

6.3 DEFECTS IN RTR RIBBONS

Defect delineation was done using chemical etching and i.r. microscopic observation. Choice of these techniques was favored in view of their following advantages: (i) They are simple (ii) defects over large areas can be determined rapidly and (iii) in conjunction with step etching and/or angle polishing, they can be used very effectively to determine the propagation paths of the defects. The etchant used for defect delineation was "Wright" etch (7).

Figure 31 shows the etch pit configurations of a sample due to "Wright" etch. The orientation of the grain under examination was found to be $\langle 100 \rangle$. The etch pit figure for $\langle 100 \rangle$ slip dislocation is a square (four-fold symmetry plane). However, from figure 31 it is seen that in addition to square etch pit figures there are also several shallow pits. In this figure, it can also be seen that one of the etch pits (indicated by an arrow) ends up in another dislocation, implying that they form a dislocation tree. Figures 32a and 32b show surface dislocations terminating in one and two dislocation branches. These shallow etch pits were found to be either surface dislocation loops or a part of a dislocation network.

FIGURE 31a: PHOTOGRAPH OF DISLOCATION ETCHED RIBBON
SHOWING DIFFERENT ETCH PIT FIGURES.
MAGNIFICATION = 1000X

FIGURE 31b: PHOTOGRAPH SHOWING SURFACE DISLOCATION LOOPS
MAGNIFICATION = 1000X

FIGURE 32a:

FIGURE 32b:

PHOTOGRAPHS SHOWING SURFACE DISLOCATIONS TERMINATING
IN ONE (a) AND TWO (b) DISLOCATION BRANCHES.
MAGNIFICATION = 1000X

Several procedures were used to identify the bulk and surface dislocations (or dislocation networks).

- (1) Grain orientations were determined (by Laue X-ray or optical diffraction) and etch pit figures compared with those of the known etch figures of bulk dislocation in those orientations.
- (2) Step etching was used to determine the propagation path of dislocation below the surface. Figure 33 shows photographs of a sample taken successively after the following treatment: Figure 33a - after 10 minutes dislocation etch, Figure 33b - after 15 minute dislocation etch, Figure 33c - 15 minute dislocation etch followed by chemical/mechanical polish and 5 minute dislocation etch.

It is clear from figure 33c that many surface dislocations have merged together below the surface. Dark etch pits (square shape in this particular case) remain unchanged indicating their propagation normal to the surface.

- (3) The sample was angle lapped prior to defect etching. Figure 34 shows a photograph of etch pit figures. Dislocation loops and networks are clearly seen.

It should be emphasized that a distinction between surface and bulk dislocations has two-fold importance: (i) It appears that bulk and surface dislocations are formed by two different mechanisms which can be controlled independently, and (ii) influences of bulk and surface dislocations on the carrier transport (and hence solar cell performance) are different.

Our analysis has shown that bulk dislocations are strongly controlled by the temperature gradients (dynamic temperature profile due to laser and the auxiliary heaters) as seen by the ribbon; an excellent treatment of in situ stress distributions during the growth is given by Gurtler (8). Some experiments were

(a)

(b)

(c)

FIGURE 33: PHOTOGRAPHS SHOWING DEFECTS PROPAGATION PATHS BELOW THE SURFACE (SEE TEXT FOR EXPLANATIONS).
MAGNIFICATION - 400X

← GROWTH DIRECTION

FIGURE 34: PHOTOGRAPH OF DISLOCATION LOOPS AND NETWORKS SEEN ON ANGLE POLISHED (AND DISLOCATION ETCHED) RIBBON.
MAGNIFICATION - 1000X

carried out on regrowth of single crystal feedstock to determine the influence of temperature profiles. Since the feedstock is single crystal, the regrown ribbon can also be single crystal (of known orientation). Analyses of these ribbons have clearly indicated that bulk dislocations are controlled by the temperature gradients. (However, in polycrystalline growth, dislocations may be created/annihilated at the expense of other defects -- G.B.s and twins -- which serve as sinks for relieving stresses.)

The surface dislocations have been found to be related to surface morphology and are believed to be caused by melt turbulence and supercooling. The turbulence is believed to be a phenomenon similar to the Marangoni effect based on surface tension and convection flow (9). It is interesting to recognize that scanning is a source of periodic excitation; hence (within a range of laser intensity) effects on the surface will be periodic. However, beyond this linear range, violent melt conditions will prevail. This argument implies that surface morphology can be entirely controlled by laser power. Some of these patterns are shown in figure 35; growth conditions are indicated on the figures. These patterns were observed by viewing the (top) surface under an i.r. microscope (transmission mode). The bottom surface of the sample was polished.

Stacking faults are well revealed by defect etching. Stacking faults have been found mostly in ribbons grown in an excess oxygen ambient where they often occur in very high densities. It is believed that stacking faults are introduced by oxygen precipitation. This mechanism is suggested by the fact that (as discussed in Section 7) oxygen concentrations $\sim 10^{19}/\text{cm}^3$ have been measured in the ribbons grown in oxygen-containing ambients. Figure 36 shows a region containing stacking faults, revealed by dislocation etching. It has been observed that faulted regions are accompanied by strong residual stresses (see Section 7).

(a)

(b)

FIGURE 35: SURFACE TURBULANCE PROFILES VIEWED UNDER AN IR MICROSCOPE, FOR RIBBON GROWN IN DIFFERENT AMBIENTS.
(a) ARGON (b) Forming gas ($N_2 + H_2$)
MAGNIFICATION = 400X

FIGURE 35c: I.R. PHOTOGRAPH OF A PARTIALLY POLISHED RIBBON. SHOWING THE REGULAR FLOW PATTERN NEAR A G.B. (PHOTOGRAPHS TAKEN IN REFLECTION MODE).

$L_o = 20X$

FIGURE 35c: FLOW PATTERN ON THE SIDE OPPOSITE TO (35c) (UNPOLISHED) PHOTOGRAPH TAKEN IN TRANSMISSION MODE. MAGNIFICATION - 200X

REGION OF
STACKING FAULTS

G3698

FIGURE 36: PHOTOGRAPH SHOWING STACKING FAULTS
REVEALED BY DEFECT ETCHING.
MAGNIFICATION = 200X

RTR ribbons show a strong tendency for twinning. Twins can often be determined by a careful microscopic examination of as-grown surfaces. They can also be determined from the surface effects following anisotropic etching. These twins may be categorized into a number of groups according to their physical characteristics (which are also related to their photovoltaic responses).

- (a) Isolated Twins: These are large area twins, sometimes several mm wide and running along the length of the ribbon. Figure 37a shows a microphotograph of an as-grown twin boundary (notice the slip lines on either side of the boundary). Figure 37b shows a twin boundary seen after dislocation etching. An optical diffraction technique has been used to study the orientations of these twins. Twins in RTR ribbons have been found predominantly in (110). (In contrast Wacker Silso has twins predominantly in (111), with few (100) - (111).
- (b) Twin Bundles: There are multiple (parallel) twins spaced close to each other ($\sim 50 - 100 \mu\text{m}$), figure 38. Some of the twin bundles are decorated with dislocations, as seen in figure 50, whereas others are not. In either case they are accompanied by loss in photoresponse and diffusion length (more pronounced in the former case).
- (c) Twin Lamellae: Twin lamellae are cyclic (coherent) twins which show typical periodicity $\sim 3 - 4 \mu\text{m}$. Figure 39a is a photograph of twin lamellae as seen on as-grown surface. Cyclic twinned regions (in a solar cell) often show higher photoresponse as compared to that from the adjacent regions (Section 7). Yet, they show a considerable residual stress (figure 45). This paradox is resolved on the basis that cyclic twinned regions are accompanied by the absence of other

FIGURE 37a: PHOTOGRAPHS OF A SINGLE TWIN SEEN ON
AS-GROWN SURFACE.
MAGNIFICATION = 100X

FIGURE 37b: PHOTOGRAPH OF A TWIN BOUNDARY AFTER
DISLOCATION ETCHING THE SAMPLE.
MAGNIFICATION = 1000X

FIGURE 38: PHOTOGRAPH SHOWING TWIN BUNDLES
MAGNIFICATION = 100X

FIGURE 39a: PHOTOGRAPH SHOWING A REGION OF
COHERENT TWINS IN AN RTR RIBBON.
MAGNIFICATION = 400X

defects which tend to segregate in the neighboring region.

Figure 39b showing a region of cyclic twins after defect etching, supports this argument.

6.4 INFLUENCE OF ASYMMETRIC GROWTH

During RTR growth, laser heating is asymmetric i.e. one beam is focussed while the other is defocussed. It is, therefore, expected that surface morphologies of the two faces of the ribbon may differ. These differences are clearly observed (visually) on the ribbons and are often accompanied by variation in surface defects. Figure 40 shows i.r. photographs of two surfaces of a ribbon after dislocation etching. Clearly side A is nearly free from surface dislocations. The influence of the asymmetry (and surface defects) on cell performance is discussed further in Section 7.

FIGURE 39b: PHOTOGRAPH SHOWING SEGREGATION OF
DISLOCATIONS AWAY FROM TWIN LAMELLI.
MAGNIFICATION = 200X

(a)

Back side - up

Ribbon #

Photograph taken in
reflection

(b)

Front side

Photograph taken in
transmission

FIGURE 40: IR PICTURES OF A DISLOCATION ETCHED SAMPLE SHOWING VARIATION IN DISLOCATION DENSITIES DUE TO ASYMMETRIC GROWTH. (a) FOCUSED ON TOP SIDE (b) FOCUSED ON LOWER SIDE. MAGNIFICATION = 400X

In Section 6 we described surface morphologies and structural defects in RTR ribbons. In this section we will describe their effects on physical properties which are directly related to photovoltaic behaviour of the ribbon. For this report we will divide them into two categories viz, optical and electrical. Optical properties include reflection coefficient of the as-grown surface, and absorption coefficient of bulk. The electrical parameter of most importance is minority carrier diffusion length of as-grown material and the change (if any) in this parameter due to processing. We will also describe some effects of residual stress and the presence of oxygen during growth.

We have measured the reflection coefficient (diffuse reflectance) of as-grown ribbons as a function of wavelength, by an integrating sphere type of measurement. Figure 41 shows the variation of diffuse reflectance with wavelength. Specular reflectance was measured after polishing the sample using a stress-free polishing technique reported earlier. Due to the thinness of the ribbon (~ 8 mils) there is some reflection from the back-side in the long wavelength range. A novel approach was used to correct for this; an absorbing layer consisting of an alloyed metal was used on the back side. It can be shown that such a technique provides a refractive index gradient at the Si-metal interface, resulting in a nearly completely non-reflecting interface, with metal absorbing the transmitted light*.

Absorption coefficients were determined from transmission measurements. The samples were thinned (parallel polished) using a stress-free polishing technique, to a thickness of ~ 50 μm . A typical transmission curve is shown in figure 42. Interference effects at the long wavelength end are clearly seen indicating a good parallelism of the sample faces. From the

* Any residual reflected light, due to imperfect fabrication, will be absorbed in the second pass.

FIGURE 41: REFLECTION COEFFICIENTS FOR AS-GROWN AND POLISHED RIBBONS.

FIGURE 42: TRANSMISSION THROUGH A 28.1 μm THICK RIBBON.

transmission and reflection data of figures 41 and 42, we have calculated the absorption coefficient. Variation of absorption coefficient with wavelength is shown in figure 43. A comparison of the absorption coefficient for ribbon, with the stress-free single crystal absorption coefficient*, shows that ribbon has higher absorption near the band edge. This increase is believed to be due to residual stress in the ribbons.

Residual stresses were determined by the optical (I.r.) birefringence technique. Although no macroscopic stresses were detected, it was found that significant microscopic stresses exist in heavily faulted regions, G.B.s and at cyclic twins. To observe the birefringence, the samples were stress-free polished on both sides. Since this polishing results in grain-to-grain height variation of $< 0.05 \mu\text{m}$, there is very little ambiguity in the birefringence image due to surface scattering. Figure 44 shows a birefringence image in the vicinity of a G.B.. A reversal in the image contrast (figure 44b) upon change in the direction of $\vec{E}$ clearly indicates that the pattern is associated with stress. High residual stress levels have been found to exist in heavily faulted regions. Interestingly, stress variations have been found in the regions of cyclic twins, figure 45.

The presence of significant residual stress is expected to effect cell performance in two ways. Firstly, there is an increased band edge absorption leading to improved long wavelength photoresponse. Secondly, the residual stress is expected to lower minority carrier diffusion length. Both of these features are clearly seen when devices are fabricated in appropriate

*Data published by Runyan agrees well with our data on single crystal.

FIGURE 43:
ABSORPTION COEFFICIENTS FOR RTR RIBBON

(a)

(b)

FIGURE 44: PHOTOGRAPHS SHOWING INVERSION IN CONTRAST DUE
TO CHANGE IN $\vec{E}$.
MAGNIFICATION = 100X

Birefringence Pattern
Ribbon #1182
Polished on both sides
Magnification - 400X

Ribbon Sample 1182
Magnification = 200X

FIGURE 45: PHOTOGRAPH SHOWING TWIN LAMELLI AND ASSOCIATED STRESS.

regions. For example spectral response of a small area cell with a defect can show a higher long wavelength response as compared to a single crystal device of comparable diffusion length. Residual stress is believed to be responsible for low values of minority carrier diffusion length in RTR ribbons. This conclusion is based on the following observations:

- (i) Best short circuit current densities obtained using small area devices (which are very carefully processed to maintain identical surface finish, thickness and processed in the same run) are:

$$\begin{aligned} J_{SC} \text{ (Cz single crystal)} &= 25.4 \text{ mA/cm}^2 \\ J_{SC} \text{ (RTR)} &= 19.9 \text{ mA/cm}^2 \end{aligned}$$

- (ii) Highest diffusion lengths measured within a single grain (low dislocation densities) in ribbons grown from different feed-stocks (e.g. CVD, Cz, Fz) and different ambients are all the same ($\sim 60\mu\text{m}$).

These observations may also suggest that periodic ripple (or stress associated with it) may be, in part, responsible for limitations on achievable L values.

7.1 EFFECTS OF OXYGEN IN RTR RIBBONS

Oxygen in silicon has certain advantages, viz dislocation pinning, which makes the substrate less prone to process induced effects. A distinct advantage for ribbon growth is that, during melting, oxygen holds the melt in a quiescent state by forming a layer of an oxide (see Section 6 on surface morphology). It has, however, been found that very large amounts of oxygen can be incorporated into the lattice. Figure 46 compares the transmission spectra of the feed-stock (a Cz single crystal) with that of the recrystallized ribbon. It is seen that net oxygen content has increased significantly (to $\sim 10^{19}/\text{cm}^3$). Since this is much higher than the equilibrium concentration, it is believed that significant oxygen precipitation occurs. This process is perhaps related

FIGURE 46: TRANSMISSION SPECTRA OF MELTED AND UNMELTED FEEDSTOCK SHOWN OXYGEN ABSORPTION IN 9 μm BAND.

to a very high density of stacking faults observed in ribbons having high oxygen concentrations. Formations of stacking faults due to oxygen precipitation have been observed by other workers (10).

Another important effect of oxygen is its precipitation at G.B.s. Figure 47 shows a photograph of oxygen precipitated at a G.B., seen by i.r. microscopy. We have found that large precipitates can be seen only when the ribbons are annealed. It is believed that prior to annealing excess oxygen is dispersed as fine precipitates (including that at the G.B.s). Upon annealing (including other heat treatment that may be involved in cell fabrication), significant migration to defects and G.B.s takes place. Evidence of this has been seen in several ways:

- (a) Large broadening and appearance of a second absorption peak in the 9 μm band. Further studies need to be done at low temperatures.
- (b) G.B.s in oxygen grown samples show highly localized birefringence implying large stress at G.B.s.
- (c) On many occasions, normal handling resulted in a cleavage at a G.B. We have examined such G.B. planes under a microscope. Figure 48a shows a photograph of such a plane indicating a thin layer of (perhaps) oxide. Upon a short dip in dilute HF, this layer was dissolved. The resultant photograph of the clean G.B. plane is shown in figure 48b.
- (d) G.B.s in oxygen rich ribbons show high resistance across the boundary, as determined by a voltage pick-off probe. High oxygen concentrations were observed with Auger analysis done on a cleaved G.B.

It has been found that oxygen precipitation at a G.B, results in high resistance across the boundary. Although such an oxidation may be envisaged as a G.B. passivation technique, it has the disadvantage of leading to high resistance in series with the cell (see further discussion in Section 7.4).

FIGURE 47; I.R. BIREFRINGENCE PHOTOGRAPH
SHOWING OXYGEN PRECIPITATION
AT A G.B.
MAGNIFICATION = 400X

(a)

(b)

FIGURE 48: (a) PHOTOGRAPH SHOWING A THIN LAYER OF
OXIDE ON THE G.B. PLANE
(b) G.B. PLANE AFTER HF DIP
MAGNIFICATION = 100X

7.2 OXYGEN DEPLETION

When RTR growth of a feedstock containing oxygen (such as Cz) is carried out in an inert ambient, the regrown ribbon is depleted of oxygen (below the detection level).

7.3 DIFFUSION LENGTH

Minority carrier diffusion length was measured by surface photovoltage. In general, ribbons have low as-grown diffusion lengths, typically $15\mu\text{m}$ for ribbons grown in an oxygen-containing atmosphere and $\sim 25\mu\text{m}$ for ribbons grown in Argon. Longer diffusion lengths ($\sim 60\mu\text{m}$) have been observed in ribbons grown in a ($\text{N}_2 + \text{H}_2$) mixture. An improvement in diffusion length (in a majority of ribbons) has been found to occur due to phosphorus diffusion. The gettering mechanism is believed to be associated with oxygen migration as described earlier. Several observations support this view:

- (1) Significant gettering has been observed only in ribbons grown in oxygen-containing ambient.
- (2) There is no improvement in diffusion length in heavily faulted areas.
- (3) Ribbons with high as-grown diffusion lengths (such as grown in forming gas and Ar) do not show a gettering effect.

7.4 INFLUENCE OF DEFECTS ON PHOTOVOLTAIC BEHAVIOUR

Defects (including G.B.s) can profoundly influence the photovoltaic characteristics of ribbons. These effects may be divided into two categories:

- (i) bulk effects, manifested as a reduction in diffusion length and

(ii) junction effects (generation/recombination in the depletion region). These effects can be investigated utilizing a variety of experimental methods such as I-V characterization, diffusion length measurement, spectral response, and temperature dependence of cell parameters.

Figure 49 shows photographs of the photoresponse image of a ribbon cell (taken by a laser scanner with high contrast). The cell was scanned in parts. Photographs show predominantly right and left halves of the cell. A photograph of the cell is also given to show the metallization pattern. The photo-response image shows various dark segments corresponding to G.B.s and regions of high defect densities. (The dark regions correspond to a loss of about 10% in photo-current amplitude.) Two features of the image are of particular importance: (1) dark bands going across the cell. In order to relate the variations in photo-response to substrate structure, the cell was dislocation etched (following the removal of metallization). Figure 50 shows photographs of the structure revealed by dislocation etch in the region indicated by the circle in figure 49. It consists of a high density of stacking faults and twin bundles. (2) A missing section of the cell (in photo-image) in the lower right hand corner. This section is electrically isolated from the metallization pattern by a resistive grain boundary.

A quantitative evaluation of the influences of each type of defect and its density can be done using small area diodes such that each device covers only one type of defect. To pursue this novel approach we have fabricated arrays of 50 mil (diameter) diodes on RTR substrates (Wacker poly is also used for comparison).

PHOTOGRAPH OF A RIBBON CELL SHOWING METALLIZATION PATTERN.

FIGURE 49: LASER SCAN IMAGES OF PREDOMINANTLY RIGHT AND LEFT HALVES OF THE ABOVE CELL.

(a)

(b)

FIGURE 50: (a) PHOTOGRAPH OF THE CIRCLED AREA IN FIGURE 49,
AFTER DEFECT ETCHING.
(b) HIGHER MAGNIFICATION PHOTOGRAPH OF (a) SHOWING
TWIN BUNDLES.
MAGNIFICATION = 400X

Results of the investigation on large and small area cells may be briefly summarized as:

- (1) Isolated twin boundaries do not result in any significant photocurrent loss.
- (2) Twin bundles are accompanied by photocurrent loss ~10%. Figure 51 shows photoresponses of a diode (50 mil diameter) which has twin bundles as seen in figure 52.
- (3) Twin lamelli can have increased photoresponse as seen in figure 20.
- (4) Dislocation densities in the low $10^5/\text{cm}^2$ range contribute to loss in F.F. via excess leakage current. Higher densities of dislocations will reduce V_{OC} (via shunting) as well as I_{SC} (via loss in L).
- (5) Stacking faults (occurring in ribbon growth in oxygen rich ambients) severely deteriorate cell performance.
- (6) G.B.s cause lowering of V_{OC} via shunting.

7.5 INFLUENCE OF SURFACE DISLOCATIONS

We have also investigated the effects of surface defects on cell performance. A substrate with surface defects may be regarded as consisting of two regions, as shown in figure 53. The top region, containing the surface defects, is characterized by lower diffusion length (higher carrier recombination) as compared to the lower (bulk) region. The top region will influence the cell performance in two ways: (i) it will lower the effective bulk diffusion length - since the carriers to be collected by the junction have to flow across this region* and (ii) Increase the dark current via excess leakage.

* The effect has been analysed in a recent paper presented at the 14th IEEE Photovoltaic Specialists Conference in connection with bulk inhomogeneities in solar cells, reference (12).

(a)

FIGURE 51:
LASER SCANNED IMAGES
OF A 50 MIL DIODE

- (b) (a) ISOMETRIC
(b) Z-MODULATION
(c) LINE SCAN ALONG
THE ARROW IN (b).

(c)

FIGURE 52a: PHOTOGRAPH OF A 50 MIL DIODE WHOSE RESPONSE IS GIVEN IN FIGURE 51.

FIGURE 52b: PHOTOGRAPH OF THE DIODE IN (a) AFTER WRIGHT ETCH.

SURFACE DEFECTS REPRESENTING A
LAYER OF HIGH CARRIER RECOMBINATION

FIGURE 53: A MODEL OF SURFACE DEFECTS REPRESENTING THE SUBSTRATE TO BE COMPOSED OF TWO REGIONS OF DIFFERENT DIFFUSION LENGTHS AS SHOWN.

To determine their effects experimentally, a ribbon having surface defects was laser scribed into two sections. Cells were fabricated on both sections (in the same processing runs) such that the junctions on the two sections were formed on the opposite faces (faces with and without surface defects are referred to as A and B respectively). The parameters of these cells are given below:

TABLE 3
PARAMETERS OF CELL

	CELL I (Junction on A)	CELL II (Junction on B)
V_{OC}	550 mV	590 mV
I_{SC}	27.5 mA	30.6 mA
F.F.	.707	0.72
η	~11	12.8

Log I vs. V plots for the two cells are given in figure 54.

7.6 COMPARISON OF BASIC FEATURES OF LASER AND ELECTRON BEAM RECRYSTALLIZED RIBBONS

Many characteristics of laser and electron beam RTR-grown ribbons are expected to be the same. For example the surfaces of electron beam grown samples also show a grating structure of periodicity $\sim 2\mu\text{m}$ (as compared to 4.5 in laser grown), figure 27 as seen in Figure 55. The structural defects are similar to that of a laser grown ribbon as can be seen from Figure 56 which shows various sections containing different types of defects. Another similarity is in the fact that as-grown diffusion lengths of electron beam samples have been as high as $30\mu\text{m}$.

FIGURE 54: CHARACTERISTICS OF SOLAR CELLS FABRICATED ON OPPOSITE SIDES OF A RIBBON.

←GROWTH DIRECTION

FIGURE 55: NOMARSKI PHOTOGRAPH OF GRATING
PATTERN ON AN ELECTRON BEAM
GROWN SAMPLE $\Lambda \approx 2 \mu\text{m}$,
MAGNIFICATION = 400X

CVD UNMELTED

(a) CRYSTAL NUCLEATION
FROM CVD GRAINS
MAGNIFICATION = 200X

(b) SURFACE LOOPS
MAGNIFICATION = 1000X

FIGURE 56: PHOTOGRAPHS SHOWING VARIOUS DEFECTS IN AN ELECTRON BEAM GROWN RIBBON. (NOTICE THE SIMILARITIES WITH THOSE OF LASER RTR.)

(c) TWIN BUNDLES
MAGNIFICATION = 100X

(d) TWIN BUNDLES
MAGNIFICATION = 400X

FIGURE 56: (CONTINUATION)

8.0 THE INFLUENCE OF DEFECTS ON SOLAR CELL PARAMETERS - AN EXPERIMENTAL STUDY

Structural defects play an important role in determining the performance of a solar cell. An understanding of the nature and degree of influence due to various types of crystal defects is becoming increasingly important with the current trend to use polycrystalline sheets and cast ingots for solar cell applications (as a means of cost reduction). A theoretical assessment of the influence of defects on cell performance is hard to make, except in very simple cases, because the grown-in defects strongly interact with impurities and process-induced defects. Hence it is important that experimental techniques be used to determine such effects as losses in V_{OC} , I_{SC} and F.F. due to various defects in polycrystalline materials, and the mechanisms by which they degrade cell performance. This section describes experimental results on the degradation of solar cell parameters (V_{OC} , I_{SC} , and F.F.) due to various types of defects in polycrystalline silicon. These defects include dislocations, stacking faults, twins and other grain-boundaries.

8.1 EVALUATION TECHNIQUES

Our approach to determining the influence of structural defects on cell parameters is to analyze small area devices. Advantages of using small area devices are: (i) devices can be selected such that only one type of defect is predominant in that device, (ii) each device can be assumed to be macroscopically uniform and hence the terminal characteristics (V_{OC} , I_{SC}) have a simple relationship with material/device parameters, and (iii) effects due to metallization and series resistance can be ignored (to a first approximation).

Despite the above mentioned advantages, small area devices have a major drawback associated with the fact that due to a large perimeter/

area ratio they have considerable edge leakage. Such an edge leakage results in "shunting" of the device and, consequently, a lowering in open circuit voltage. The loss in V_{OC} depends on many factors such as type (p or n) and resistivity of the substrate, and diode fabrication technique. By careful fabrication and passivation of the diodes, the edge effects can be minimized. Figure 57 shows the dependence of V_{OC} on diode size for a p-type substrate ($\rho \approx 1 \Omega\text{-cm}$). The solid curve refers to devices made by progressively cleaving the edges of a large area device. The dotted line represents the V_{OC} values of devices fabricated by a process described later.

Edge effects also complicate device analysis, such as determination of carrier transport mechanisms in the presence of defects. However, two approaches can be used to circumvent this problem. Firstly, a relative comparison of device performance with and without a particular type of defect can be made. These data can be supplemented by other measurements to determine material/device parameters. Secondly, with a knowledge of "shunting" mechanisms due to edges, a computer program can be developed to isolate the edge effects. This report will follow the former approach. (Some work has also been done towards the latter approach.)

Arrays of small area solar cells (50 mil diameter p-n diodes) were fabricated on p-type polycrystalline silicon substrates (nominal $\rho \approx 1 \Omega\text{-cm}$) by phosphorus diffusion. The configuration of the diodes is shown in figure 58. Two types of polycrystalline silicon substrates were used; RTR ribbons and Wacker Silso. Single crystal Cz substrates were also used as controls.

Measurements made on diodes were aimed at isolating bulk effects (such as the influence on minority carrier diffusion length, L)

FIGURE 57: DEPENDENCE OF OPEN CIRCUIT VOLTAGE ON DIODE SIZE.

FIGURE 58: SCHEMATIC OF THE DIODE ARRAY CONFIGURATION.

from those due to junction effects (such as increased excess leakage current). These measurements included:

- (i) determination of minority carrier diffusion length in the base region
- (ii) I-V characteristics (dark and illuminated)
- (iii) Spectral response
- (iv) Laser scanning to determine variations in photo-response from different grains and at the G.B.s.

Following the above measurements, diodes were etched for defect delineation, and the types (and densities) of defects were determined.

8.2 STRUCTURAL DEFECTS

Detailed discussions of structural defects in RTR ribbons and Wacker Silso are given in Section 6. The main features related to this work may be summarized as follows:

- (a) RTR ribbons: (i) Dislocations in RTR ribbon may be categorized as bulk dislocations and surface dislocations
(ii) Dislocation densities (n_d) have a range of $\sim 10^5 - 10^6$ cm^{-2} . (iii) RTR ribbons have very low stacking fault (S.F.) densities ($n_{S.F.}$), except when grown in oxygen-rich ambients. (iv) Twinning occurs frequently. Twins have been categorized into -- isolated twins, twin bundles and twin lamellae. (v) Grain size is large*.
- (b) Wacker Silso: (i) low n_d ; only a few grains are decorated with dislocations (ii) low $n_{S.F.}$ (iii) frequent twinning (iv) small grain size -- the major photovoltaic loss is associated with G.B.s.

* Grain size at the edges of RTR ribbon is small (~ 0.1 mm); however grains become very large (typically ~ 1 cm wide and several inches long) a few mm away from the edges.

We have developed a simple process sequence to fabricate diodes on p-type substrates. This process involves four steps.

- (a) Damage-free polishing: Substrates are polished to a mirror finish following a technique described in detail in Section 5. Briefly, it involves lapping the substrate followed by chemical/mechanical polish using Nalcoag slurry. The chemical/mechanical polishing is done just long enough to remove the lapping damage thereby minimizing G.B. grooving and/or grain-to-grain height variations due to different removal rates for various grain orientations. Two major advantages of polishing are: (i) surface quality of all diodes is kept the same (ii) optical/electron beam characterization of G.B.s can be done unambiguously since local surface scattering is minimized.
- (b) Phosphorus diffusion: An unmasked PH_3 diffusion is carried out to achieve a diffusion depth of $\sim 0.5 \mu\text{m}$. The regions of unwanted diffusions are etched away during mesa etching.
- (c) Photoresist masking and mesa etching: Mesas are etched on the desired side through a photoresist mask to a depth of approximately $4 \mu\text{m}$. A chemical etchant for silicon was developed for this purpose which gives an excellent edge quality. The etchant has the following composition: 360 ml HF, 100 ml CH_3COOH and 20 ml HNO_3 . This etchant weakly delineates some defects (around mesas) which helps in selection of diodes for appropriate measurements to acquire desired data. Figure 59 shows a Nomarski photograph of a 50 mil diode fabricated on Wacker Silso which has some twins delineated by the

etchant. A similar picture of a diode on RTR ribbon, Figure 60, shows twins as well as dislocations in the etched region.

- (d) Aluminum deposition and alloying: A p^+ ohmic back contact is made by depositing $\sim 2000\text{\AA}$ of Al and alloying it at $800 - 900^\circ\text{C}$.

This step also serves another important purpose, viz formation of a thin oxide layer for passivation.

Cells fabricated by this process sequence show little edge leakage and the open circuit voltages of 50 mil diameter diodes on single crystal Cz wafers have a range of $\sim 560 - 580\text{ mV}$, under AM1 illumination.

8.4 RESULTS

Figures 61 and 62 show dependencies of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) on the number of grains per diode for an RTR ribbon (#1144-D). It should be emphasized that these data include the degradation of V_{OC} due to edge effects. However, on a comparison basis it is clear that grain boundaries contribute to junction shunting as well as loss in minority carrier diffusion length (which directly affects I_{SC}). Similar plots are shown for Wacker Silso in Figures 63 and 64. Data in figures 63 and 64 are indicated by three different symbols. Full open circles refer to data from diodes where the substrate region was dominated by twins. Partial open circles refer to diodes containing twins as well as grain boundaries, and the solid circles refer to diodes containing only grain boundaries. A comparison of figures 61 and 63, and figures 62 and 64 show:

- (a) V_{OC} 's of diodes on the RTR ribbon are higher than those of Wacker Silso (for same number of grains).
- (b) Both V_{OC} and I_{SC} have tighter distributions for RTR than for Wacker Silso. These can be explained on the basis of the

FIGURE 59: NOMARSKI PHOTOGRAPH OF A 50 MIL DIODE SHOWING DELINEATION OF TWINS (IN ETCHED REGION) DUE TO MESA ETCHING.

FIGURE 60: PHOTOGRAPH OF A DIODE SHOWING
DEFINITION OF DISLOCATIONS AND
TWINS DUE TO MESA ETCHING.

FIGURE 61: DEPENDENCE OF OPEN CIRCUIT VOLTAGE ON THE NUMBER OF GRAINS PER DIODE FOR RTR RIBBON.

FIGURE 62: DEPENDENCE OF SHORT CIRCUIT CURRENT ON NUMBER OF GRAINS PER DIODE (RTR RIBBON).

FIGURE 63: PLOT OF V_{OC} VS. NUMBER OF GRAINS FOR WACKER SILSO.

FIGURE 64: PLOT OF I_{SC} VS. NUMBER OF GRAINS FOR WACKER SIL50.

following substrate characteristics: (i) G.B.s in RTR ribbon constitute smaller misfit and hence less degradation of cell parameters as compared to those of Wacker Silso, and/or (ii) G.B.s in the RTR sample are "cleaner" (due to low impurity segregation) as compared to those in Wacker Silso.

- (c) Current densities in Wacker poly are higher than those in the RTR sample. The major reason for this was found to be that minority carrier diffusion lengths within the grains are larger than those of RTR (as measured by surface photovoltage). This feature can also be clearly seen from spectral responses of diodes, given in figure 65. Indicated on the figure are measured values of minority carrier diffusion lengths and a parameter, Y_{max} , which specifies response at the peak value for each curve.

- (d) Twins have much less influence on cell parameters.

Dependencies of V_{OC} and I_{SC} on dislocation density for an RTR ribbon are shown in figures 66 and 67. It has been shown earlier (Section 6) that dislocations in RTR ribbons are of two types -- surface dislocations and bulk dislocations. Data indicated by solid circles correspond to bulk dislocations and the open circles correspond to bulk plus surface dislocations. (To obtain these data we polished the samples so as to remove a region of surface dislocations in one case and retain them in the other.) It is clear that bulk dislocations are more effective in lowering V_{OC} and I_{SC} as compared to surface dislocations. Data on the influence of dislocations in Wacker Poly could not be determined because of relatively low densities of dislocations in these substrates.

Dependencies of fill factor on the number of grains per diode and dislocation density are shown in figures 68 and 69 respectively, for

FIGURE 65: COMPARISON OF SPECTRAL RESPONSES OF DIODES FABRICATED ON (1) WACKER POLY (W.P.) (2) SINGLE CRYSTAL (CZ) AND (3) RTR RIBBON.

FIGURE 66: PLOT OF OPEN CIRCUIT VOLTAGE VS. n_d (RTR RIBBON).

FIGURE 67: PLOT OF SHORT CIRCUIT CURRENT VS. DISLOCATION DENSITY (RTR RIBBON).

FIGURE 68: PLOT OF FILL FACTOR VS. NO. OF GRAINS PER DIODE (RTR RIBBON).

FIGURE 69: PLOT OF FILL FACTOR VS. DISLOCATION DENSITY (RTR RIBBON).

the RTR sample. Data do not include the dependence of cell parameters on stacking faults; (S.F.) this is due to the fact that RTR ribbon grown under conditions of this sample exhibit very low S.F. density. Under certain other growth conditions (oxygen rich ambients), ribbons possess high S.F. densities, and it is found that stacking faults are more effective than dislocations in degrading cell parameters.

We have also investigated local photo-current losses at twins and G.B.s. Some of these results may be summarized as:

- (I) Isolated twins have no observable effects on cell performance.
- (II) Twin bundles (coherent), in the presence of other defects/impurity precipitates are effective in lowering cell performance. (Increased local photo-currents in the regions of coherent twins have been found to be caused by periodic surface perturbations due to chemical etching used for surface preparation or during processing.) Figure 70 is a laser scan showing photocurrent loss at twin bundles.
- (III) G.B. Influence depends strongly on a number of factors:
 - (a) mismatch between the grains
 - (b) direction of grain boundary with respect to that of the junction
 - (c) impurity precipitation at the G.B.

Data presented in this section can be used to determine maximum values of defect densities which will yield high efficiency cells. Conversely, one can also predict performance of a large area cell fabricated on a substrate whose defect structure is known. For example, for an RTR ribbon of large grain size, with $n_d = 2 - 5 \times 10^5 \text{ cm}^{-2}$, the major loss is due to dislocations. From figures 66, 67, and 69 we can determine the cell parameter values to be:

FIGURE 70: LASER SCAN SHOWING PHOTOCURRENT LOSS AT TWIN BUNDLES.

$$V_{OC} \approx 590 \text{ mV (corrected for edge leakage loss)}$$

$$J_{SC} = 31 \text{ mA/cm}^2 \text{ (corrected for AR coating)}$$

$$F.F. = .74$$

$$\eta = 13.1\%$$

A cell (area 2 cm^2) fabricated on a RTR ribbon selected for the above requirements yielded the following data:

$$V_{OC} = 590 \text{ mV}$$

$$J_{SC} = 30.8$$

$$F.F. = .72$$

$$\eta = 12.8\%$$

9.0 PHOTOVOLTAIC LOSS-MECHANISMS DUE TO DEFECTS AND GRAIN BOUNDARIES IN POLYCRYSTALLINE SILICON

In previous sections we have described various structural defects in polycrystalline silicon, and their effects on solar cell parameters. This section describes a coherent approach to study mechanisms associated with defects/G.B.s which contribute to photovoltaic losses.

9.1 BASICS OF PHOTOVOLTAIC LOSS MECHANISMS

Photovoltaic losses in polycrystalline silicon can be evaluated in terms of electronic and physical characteristics of defects/G.B.s. Electronic effects are associated with localized states introduced in the forbidden gap by discontinuities in the periodic lattice potential. Upon fabrication of a solar cell, electronic effects can influence the cell performance in several ways. Conceptually these are separated into bulk effects and junction effects. Bulk effects of defects/G.B.s arise because of the significantly increased number of recombination sites available. Minority carriers diffusing to defects/G.B.s have a high probability of recombination, with the result that the photocurrent arriving at the solar cell junction is reduced. Consequently the effective lifetime of a carrier can be lower than in a single crystal sample.

Junction effects are due to "interface states" which alter the barrier height and can lead to significantly higher generation-recombination currents near defects/G.B.s. Other carrier transport mechanisms such as tunneling can also occur. The over-all effect is to lower the solar cells open-circuit voltage.

Electronic effects described above depend strongly on the physical characteristics of defects/G.B.s (which may be altered by the processes required for cell fabrication). Physical characteristics of interest include:

types of defects, G.B. misfit, impurity segregation at a defect/G.B., residual stress etc. (11). Cell processing steps can cause such photovoltaic effects as defect-defect and defect-impurity interactions leading to strong changes in photovoltaic (P.V.) losses. Knowledge of these effects can be important in designing processing sequences for fabrication of high quality cells.

Overall characteristics of polycrystalline cells may be described in terms of diode equations with due consideration to various carrier transport mechanisms. Accordingly we may write (assuming superposition):

$$I - I_L = I_0 \quad (1)$$

where I is the diode current, I_d and I_L are dark and light generated currents respectively. I_d can be written as (neglecting series resistance effects)

$$I_d = I_{01} e^{qv/kT} + I_{02} e^{qv/nkT} + k_1 N_t e^{BV_j} + V/R_{SH} \quad (2)$$

The four terms in the right hand side of equation 2 are the following components, respectively: injection, space charge recombination, tunneling, and shunting currents. Expressions for various quantities in equations 1 and 2 can easily be found in literature, e.g. see (12).

9.2 EXPERIMENTAL MEASUREMENTS

We have studied several aspects of photovoltaic (P.V.) loss mechanisms in cells fabricated on two types of polycrystalline substrates, viz. RTR ribbons and Wacker Silso. Arrays of small area solar cells (50 mil diameter mesas) were fabricated on p-type polished substrates by a process described in Section 8. Measurements made on the cells include determination of bulk minority carrier diffusion length (L) and I-V characterization (dark and illuminated).

Selected diodes were light scanned with a two-wavelength laser scanner to determine: (a) local variations in L and (b) recombination in the vicinity of the depletion region.

Following these measurements the devices were dislocation etched and densities of defects and G.B.s determined in each diode. Dependences of cell parameter (V_{OC} , I_{SC} , F.F.) and L on the density of defects/G.B.s were determined.

Other physical characteristics such as residual stresses and impurity segregation (in particular oxygen) at G.B.s were also determined. Their implication on P.V. losses were analyzed.

9.2.1 BULK EFFECTS

Bulk losses were determined in terms of minority carrier diffusion length. This parameter determines the short circuit current obtainable from the cell. Figure 71 shows dependence of L on the density of G.B.s (in this case plotted as number of grains per diode; diode area equals 1.26 mm^2). Data in figure 71 are shown by two symbols. Open circles represent data from diodes fabricated on Wacker Poly (W.P.) and solid dots represent those of RTR ribbons*. Certain important features in figure 71 are: (i) No effort has been made to characterize G.B.s, such as individual grain orientations (although we have established that some orientations are dominant in each of the substrates). Correspondingly, scatter in the data may be expected due to varying degrees of influence from different G.B.s. (ii) The G.B. effect on L in RTR and Wacker substrates agrees fairly well. Consequently we have drawn a single curve indicative of average variation. (iii) The diodes represented in figure 71 were low in other defects such as dislocations and stacking faults.

* The data for RTR ribbons in figure 71 are obtained from diodes located close to the ribbon edge in order to get samples with appreciable numbers of grains. The grain size becomes very large a few millimeters away from the ribbon edge.

FIGURE 71: DEPENDENCE OF DIFFUSION LENGTH ON THE DENSITY OF GRAIN BOUNDARIES.

Dependence of L on dislocation density (for RTR ribbons) has been reported earlier (2). Dependencies of cell parameters on defect/G.B. density are discussed in Section 8.

We have also determined the dependence of short circuit current (under AM1 illumination) on diffusion length. This dependence is shown in figure 72. The data presented are from diodes on RTR ribbons as well as W.P. However, no distinction in type of defect/G.B. is made. Clearly the curve is universal (independent of the source responsible for the loss). It should be pointed out that the curve in figure 72 is independent of the cell size if current density is used as a dependent parameter i.e. using $J_{SC} = I_{SC}/A$, where $A = 1.266$ for the diodes. We have verified this on large area cells.

9.2.2 JUNCTION EFFECTS

Junction effects are determined by comparing the I-V characteristics of diodes having different densities of G.B.s/defects. Figure 73 shows the dark I-V characteristics of diodes on W.P. which have different number of grains/diode. Curve (a) corresponds to a diode containing three grains; curves (b) and (c) correspond to diodes having 11 and 22 grains respectively. The cell parameters (V_{OC} , I_{SC}) for AM1 illumination are: Diode (a) $V_{OC} = 536$ mV, $I_{SC} = 0.304$ mA; Diode (b): $V_{OC} = 500$ mV, $I_{SC} = 0.256$ mA; Diode (c): $V_{OC} = 480$ mV, $I_{SC} = 0.232$ mA. These parameters clearly indicate degradation in cell performance with increase in grain density. Various current transport mechanisms can be determined by analysing the I-V curves to identify particular components of equation 2. However analysis is complex (in particular with the added effect of edge leakage). Here we will only emphasize that increase in grain density is contributing to increase in dark current.

Figure 74 shows similar plots for diodes on RTR substrates. Curves a and b are for diodes on the same grains but having dislocation density, n_d , of

FIGURE 72: DEPENDENCE OF SHORT CIRCUIT CURRENT (UNDER AM1 ILLUMINATION) ON DIFFUSION LENGTH.

FIGURE 73: DARK $I-V$ CHARACTERISTICS OF VARIOUS DIODES WITH DIFFERENT GRAIN DENSITIES (WACKER SILSO). SEE TEXT FOR DIODE PARAMETERS.

FIGURE 74: DARK I-V CHARACTERISTICS OF VARIOUS DIODES FABRICATED ON RTR RIBBON. SEE TEXT FOR DIODE PARAMETERS.

$2 \times 10^5 \text{ cm}^{-2}$ and $1 \times 10^6 \text{ cm}^{-2}$ respectively. Curve (c) corresponds to diode containing 22 grains. The cell parameters for the diodes are; (a) $V_{OC} = 561 \text{ mV}$, $I_{SC} = .251 \text{ mA}$, F.F. = 0.78 (b) $V_{OC} = 535 \text{ mV}$, $I_{SC} = 0.21$, F.F. = 0.68 and (c) $V_{OC} = 520 \text{ mV}$, $I_{SC} = 0.2$, F.F. = 0.75.

9.3 LIGHT INDUCED CURRENT (LIC) TECHNIQUES FOR LOSS EVALUATION

Bulk and junction effects can be directly seen from photoresponse studies. It has been shown earlier, that photoresponse (short circuit current) of a cell due to long wavelength excitation is proportional to the diffusion length (3). By using a long wavelength focussed laser scanner one can determine local variations in diffusion length due to the presence of defects/G.B.s. Furthermore, recombination in the vicinity of the depletion region can also be evaluated if short wavelength excitation is used.

As an example, figure 75 shows Nomarski photographs of three selected diodes which lie on the G.B. between two grains. Individual grains vary significantly in their dislocation densities*. Photoresponse scans of one of the diodes (shown in figure 75) taken with a focussed laser scanner at wavelengths of $1.15 \mu\text{m}$ and $0.6328 \mu\text{m}$, are shown in figures 76a and 76b, respectively. It is clear from figure 76a that region B of the scanned diode has a diffusion length $L_B \approx 1/2 L_A$. Diffusion length measured on diodes located entirely within grains A and B were found to be $48 \mu\text{m}$ respectively. Average diffusion length of the scanned diode was found to be $27 \mu\text{m}$. The long wavelength scan also shows that G.B.s are very effective for carrier recombination. Figure 76b shows that both dislocations and the G.B. are effective recombination centers for carriers generated close to depletion region (hence contributing to recombination currents).

*Dislocations in the etched region (away from mesas) can be seen in the Nomarski photographs of figure 75. Defects are delineated mildly (shallow) by the etchant used for defining mesas and help in selecting diodes for appropriate measurements.

(a)

REGION
A

(b)

REGION
B

(c)

FIGURE 75: NOMARSKI PHOTOGRAPHS OF THREE SELECTED DIODES WHICH LIE ON A GRAIN BOUNDARY BETWEEN TWO GRAINS.

FIGURE 76: PHOTORESPONSE OF ONE OF THE DIODES (FIGURE 75b) TAKEN WITH A FOCUSED LASER SCANNER AT WAVELENGTHS OF (a) $1.15 \mu\text{m}$ AND (b) $0.6328 \mu\text{m}$.

(a)

(b)

(c)

FIGURE 77: LIC SCANS SHOWING ENHANCED PHOTORESPONSE AT A G.B. NODE.

Cell parameters for the diodes in figure 75 are also given. These show qualitatively, the degradation effects as the area of diode covering grain B increases.

We have also made measurements of photo-current loss due to various types of boundaries such as twin boundaries, low and high angle G.B.s. Two interesting features were observed during these investigations: (i) it was found that certain regions of large area cells fabricated in a conventional manner (unpolished surface) showed that regions containing twin lamelli resulted in increased local photoresponse, see Section 5, figure 20. (ii) Increased photoresponse was also observed in certain regions of G.B.s, in particular, at nodes joining several G.B.s. Figure 77a shows the laser scanned image (current mode) of a 50 mil diode which has enhanced response at a G.B. The scan was terminated just past the region of enhanced response. Figure 77b shows a magnified line scan across this region. Figure 77c shows, in perspective, that the region of enhanced response corresponds to a G.B. node. It should be pointed out that the sample was polished to a mirror finish following a polishing sequence described in Section 5. Hence, the response is not due to surface scattering. Probable reasons are: (i) the G.B. nodal region is low in defect density (defect annihilation at the G.B.) (ii) impurity segregation at the node may cause it to be p+ resulting in a shallower junction.

9.4 INFLUENCE OF PHYSICAL CHARACTERISTICS OF DEFECTS/G.B.s IN P.V. RESPONSE

In this section we describe influences of some physical characteristics of defects/G.B.s on P.V. loss/gain. These include: residual stresses, enhanced diffusion along G.B.s and impurity segregation (in particular that of oxygen). Furthermore, we will indicate some effects of inhomogeneities in polycrystalline cells (caused by G.B.s, defect segregation, and grain orientation effects).

Residual stresses occur in most polycrystalline materials. These are, in general, characteristic of material growth and are related to such factors as thermal gradients during growth, and annealing conditions. Residual stresses can be particularly important in the case of sheet silicon growth at high speeds. Residual stresses may be either macroscopic, as is generally found in silicon sheets (causing warpage), or microscopic, such as localized near G.B.s. Microscopic stresses can be observed by optical ("infra red") birefringence, as described in Section 7. Microscopic stresses may also be caused by impurity segregation at defects/G.B.s. The effect of residual stress is to lower the band gap (band broadening) which can influence P.V. characteristics in two ways: (i) increase band edge absorption resulting in increased photocurrent and (ii) lowering attainable V_{OC} .

The disorder present at a G.B. can also result in appreciably enhanced diffusion rates for dopants or impurities. If high temperature diffusion is utilized for junction formation, a non-planar junction can result. Figure 78 shows enhanced diffusion of phosphorus into G.B.s of a p-type Wacker Silso poly substrate. This sample was polished prior to diffusion to avoid any steps or grooves at the G.B.s. After diffusion, the sample was angle lapped and stained. The junction depth (away from G.B.s) is $0.5 \mu\text{m}$. Enhanced G.B. diffusion will influence carrier collection. For example it will have detrimental effect for holes generated within the N^+ region. However, a major advantage could be obtained if a deep diffusion occurs along G.B.s extending several diffusion lengths into the base region, resulting in improved carrier collection from the base.

FIGURE 78: ENHANCED DIFFUSION OF PHOSPHORUS
INTO G.B.s OF A P-TYPE WACKER SILSO
POLY SUBSTRATE.
MAGNIFICATION = 1000X

When polycrystalline silicon is formed, impurity segregation at a G.B. can be significantly different than that in the bulk Si (grain) regions. For example, the grain boundary may incorporate a higher level of active impurities (which diffuse slightly during cool-down), giving a p^+ region in the p-type base, Figure 79a. When a junction is formed on such a substrate, the p^+ region will cause an alteration in the barrier height, figure 79b, accompanied by an increase in generation-recombination (G.R.) currents. In the extreme case, tunneling can occur across the N+P+ barrier.

Segregation of impurities at G.B.s could also improve overall P.V. performance. For example, segregation can make G.R. currents at the G.B. higher, but at the same time, this can reduce the level of impurities within the bulk (grains), making them to have lower G.R. currents.

An ideal situation should be attained if oxygen were selectively segregated at grain boundaries, producing a thin SiO_2 layer on either side of each G.B. as shown in figure 80. This would effectively isolate each grain, allowing much more efficient cells to be produced. We have investigated this hypothesis further by examining G.B. effects in ribbons grown in oxygen-rich ambients. It was found, indeed, that G.B.s become highly resistive. Figure 81 shows traces taken with a voltage pick-off probe comparing G.B. resistance in oxygen rich substrate with that of Wacker poly.

From the previous discussions it is clear that polycrystalline cells can have strong variations in local photoresponses due to such effects as: G.B. losses, non-uniform defect densities, and variation in the photovoltaic properties of different grain orientations. These inhomogeneities can degrade total cell

FIGURE 79: SOME DISTORTED BARRIER CONFIGURATIONS DUE TO IMPURITY SEGREGATION (OR MIGRATION) AT G.B.s.

FIGURE 80: SCHEMATIC SHOWING G.B. PASSIVATION
DUE TO SEGREGATION OF OXYGEN.

FIGURE 81: VOLTAGE PICK-OFF SHOWING G.B. RESISTANCE IN VARIOUS SUBSTRATES.

performance. This degradation mechanism may be viewed as similar to that of a parallel string of cells of varying characteristics (with a difference that internal carrier transport can also take place within a polycrystalline cell). Influences of inhomogeneities are similar to those described earlier for single crystal cells, resulting in loss in F.F. and V_{OC} (13).

Impurity migration can also be induced during thermal processes such as phosphorus diffusion (as a standard solar cell processing step) leading to gettering effects by defects/ambients, to cause increases in minority carrier diffusion length. Oxygen precipitation at G.B.s was determined to be a responsible mechanism for the gettering.

This report describes various measurement techniques that we have further developed and employed to study photovoltaic mechanisms in polycrystalline silicon substrates and solar cells. These measurement techniques include (in addition to standard I-V characterization): (a) surface photovoltage to measure minority carrier diffusion length for substrate/cell characterization and solar cell process control. (b) The current phase-shift technique for determination of lifetime. (c) A two-wavelength laser scanner (d) An automatic spectral response station (e) A voltage pick-off probe. It was found that all of these measurements require a very flat, stress-free surface in order to yield unambiguous results. Consequently it was necessary to develop a polishing sequence which gives a stress-free high quality surface polish with maximum grain-to-grain height variation $\delta_{\max} < 0.05 \mu\text{m}$. As a by-product of this polishing process, a method for monitoring polishing damage in semiconductor wafers was also developed (Appendix 1). Furthermore, it was recognized that measurements on polycrystalline substrates/cells should be done with caution since inhomogeneity effects inherent in polycrystalline silicon may invalidate conditions of the measurement. Appendix 2 describes these considerations for measurement of average diffusion length.

Various studies were carried out to: (a) Analyze structural defects in RTR ribbons and Wacker Silso. (b) Determine the influences of defects and G.B.s on solar cell parameters and (c) formulate a coherent approach to determining photovoltaic loss mechanisms in polycrystalline silicon substrates/cells.

It is found that defects in RTR sheets may be categorized into two groups: (a) surface defects and (b) bulk defects. Surface defects are associated with turbulent (Marangoni) effects during growth, experienced when using very highly focussed laser beams. Surface defects were determined to be dislocation loops and networks. It is shown that surface defects result in high carrier

recombination velocity at the surface and, hence, reduce solar cell performance. Under optimum growth conditions ribbons exhibit periodic surface undulations with grating pitch $\Lambda = 4.5 \mu\text{m}$. In contrast, electron beam grown ribbons have $\Lambda \approx 2 \mu\text{m}$. Formation of surface gratings is believed to be due to periodic temperature variations associated with periodic scanning and pulling.

Major bulk defects were found to be dislocations (for oxygen-free substrates) and stacking faults (for oxygen rich substrates). Dislocation densities are typically in the low to mid 10^5 cm^{-3} range. Significant variations in dislocation densities within a ribbon have been observed. Dislocations are strongly controlled by thermal profiles during growth, and it was found that average dislocation densities within a ribbon depend on growth ambients. Dislocations influence the cell parameters via increased dark current and reduction in minority carrier diffusion length.

High densities of stacking faults, typically $\sim 10^3 \text{ cm}^{-1}$, have been found to occur in oxygen-rich ribbons. Oxygen precipitation due to annealing was found to take place in some ribbons which were grown in an oxygen-rich ambient. It was found that stacking faults are very effective in degrading cell performance.

Twinning occurs very frequently in RTR ribbons. Twins were categorized into three groups depending on their physical characteristics and local photocurrent losses associated with them. These are: (a) isolated twins, (b) twin bundles and (c) twin lamellae.

Small area diode techniques were used to determine the influences of type and density of defects on solar cell parameters. Dependences of V_{OC} , I_{SC} and F.F. on grain and dislocation densities have been determined for RTR ribbons and Wacker Poly; some comparisons, based on limited numbers of samples, are:

- (a) V_{OC} 's of diodes on RTR ribbon are higher than those of Wacker Silso (for same number of grains).

- (b) Both V_{OC} and I_{SC} have tighter distributions for RTR than for Wacker Silso. These can be explained on the basis of the following substrate characteristics: (i) G.B.s in RTR ribbon constitute smaller misfit and hence less degradation of cell parameters as compared to those of Wacker Silso, and/or (ii) G.B.s in the RTR sample are "cleaner" (due to low impurity segregation) as compared to those in Wacker Silso.
- (c) Current densities in Wacker poly are higher than those in RTR. The major reason for this was found to be that minority carrier diffusion lengths within the grains of Wacker poly are larger than those of RTR.
- (d) Twins have much less influence on cell parameters than G.B.s.

Photovoltaic loss-mechanisms are divided into two groups: electronic and physical. Electronic mechanisms are further separated into bulk effects (resulting in changes in L) and junction effects (characterized by changes in dark I - V characteristics). A study of loss-mechanisms has shown:

- (a) Minority carrier diffusion length, L , depends strongly on grain and dislocation densities. These dependencies have been experimentally determined.
- (b) It is found that defects/G.B.s lead to increase in dark current. A major contribution to dark current is to space charge recombination; tunneling currents associated with defects/G.B.s have been observed.
- (c) Evaluation of local photocurrent losses due to twins and G.B.s have shown:
 - (i) Isolated twins have no observable effects on cell performance.
 - (ii) Twin bundles (coherent), in the presence of other defects/impurities precipitates are effective in lowering cell performance.

(Increased local photo-currents in the regions of coherent twins have been found to be caused by periodic surface perturbations due to chemical etching used for surface preparation or during processing.)

- (iii) G.B. influence depends strongly on a number of factors:
- (a) mismatch between the grains
 - (b) direction of grain boundary with respect to that of the junction
 - (c) impurity precipitation at the G.B.

It is shown that defect-defect and defect-impurity interactions can strongly influence the photovoltaic behavior of cells. A knowledge of these is important to the design of processing sequence for high efficiency cells.

Further work on defect/G.B. characterization and their influence on photovoltaic mechanisms will be carried out as outlined in the statement of work for the follow-on contract. (See Appendix II).

11.0 TECHNICAL PRESENTATIONS AND PAPERS RESULTING FROM CURRENT PROGRAM

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APPENDIX 1

**A RAPID NON-DESTRUCTIVE TECHNIQUE FOR
MONITORING POLISHING DAMAGE IN
SEMICONDUCTOR WAFERS**

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**A RAPID NON-DESTRUCTIVE TECHNIQUE FOR
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ABSTRACT

A rapid non-destructive (optical) technique, which can be used to monitor directly the chemical polishing/etching time required for removal of lapping (or sawing) damage in semiconductor wafers, is described. This technique utilizes dependence of the amplitude of surface photovoltage signal on the residual surface stress to determine the "end-point" of chemical polishing/etching. It is shown that this technique is very sensitive and well suited for large scale polishing facilities.

A RAPID NON-DESTRUCTIVE TECHNIQUE FOR
MONITORING POLISHING DAMAGE IN SEMICONDUCTOR WAFERS

Semiconductor wafers which are either sawn or mechanically polished possess surface stresses (damage) which must be removed prior to device fabrication, by either chemical polish or etching. The extent of damage depends on the type of saw (e.g. wheel or wire) and the polishing conditions (e.g. grit material, grit size, pad material etc.). At present there exists no definitive simple procedure which can be used to determine how deep the damage has propagated. Hence, in most cases, to remove the damaged region an empirically determined thickness is removed (which may be more than is actually needed). This constitutes both material loss as well as the added cost of longer polishing/etching times.

Several techniques have been used in the past to arrive at empirical values of damage depth. These include: (i) measurement of excess density of oxidation induced stacking faults on wafers from which surface layers of different thicknesses have been etched away and (ii) lowering in fracture strength as a result of surface stress. These techniques are, in addition to being destructive, quite cumbersome, time-consuming and insensitive. This paper describes a rapid, non-destructive (optical) technique which can be used, directly, to monitor the chemical polishing/etching time required to remove the damaged surface layer. This technique is highly sensitive, and can be used on flat or uneven surfaces.

The proposed technique is based on the fact that when a semiconductor surface is illuminated with light, a voltage signal (surface photovoltage (SPV)) is developed across the sample. The amplitude of the SPV, V , depends on several parameters and may be written as (1):

$$V \propto \frac{I_0 (1-R) \alpha L}{(1+\alpha L)(S+D/L)} \quad (1)$$

Where I_0 is the incident light intensity, R and α are reflection and absorption coefficients respectively. D , L and S represent diffusivity, minority carrier diffusion length and the surface recombination velocity, respectively. In relationship (1), it is assumed that the incident light is monochromatic. S is the parameter which depends on the magnitude of surface damage (introduced by mechanical polishing). Since, during polishing all parameters except S remain constant, the change in SPV, ΔV , will reflect the contribution due to change in surface damage only (1).

An experimental set-up to monitor surface damage is shown schematically in Figure 1. Light from a collimated source (e.g. microscope light) is filtered ($\lambda = 1.0 \mu\text{m}$), chopped and focussed on the sample. Chopped light permits capacitive coupling of the SPV signal, obviating the need for fabricating metal contacts on the sample. An electrode arrangement used for capacitive coupling of the signal is also shown in Figure 1. It consists of a metal electrode which also serves as a vacuum chuck and a top (spring-loaded) transparent electrode. The top electrode consists of a glass plate coated with a layer of indium-tin-oxide. A thick layer of a transparent insulator such as Ta_2O_5 is deposited on the ITO. When a sample, for which surface damage has to be monitored, is interposed between the two electrodes, a reproducibly uniform gap is maintained between the sample surface and the top electrode. This ensures a constant coupling coefficient between the sample and the electrode. The amplitude of the photo-signal is measured with a synchronous detection system, including a lock-in amplifier.

A sawn or mechanically polished wafer will show an unmeasurably low signal (when placed in the electrode structure). As the damaged layer is reduced, either by chemical polishing or etching, the sample will show an increase in photo-signal.

The increase in photosignal will continue until all the damage is removed and, hence, the signal will saturate. The thickness to be removed is determined by this condition. Figures 2 and 3 show typical signal variations from silicon samples, as a function of surface layer thickness removed by chemical polish/etching; the sample surfaces were prepared differently prior to final chemical polish/etching. Figure 2 is for a sample which was mechanically polished with a 25 μm alumina grit. The sample was then etched in an acidic solution consisting of $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}$ (1:1:5) for short time intervals, and the photosignal was measured following each etching step. A constant time lag between etching and measurement was utilized in order to allow the surfaces to stabilize. Surface stabilization was also confirmed by lack of any significant drift in the SPV signal. Saturation of the signal, in Figure 2, occurs when a surface layer of approximately 0.6 mils was removed. This implies that lattice damage produced by a 25 μm grit polish was approximately 0.6 mils. Figure 3 shows signals from a group of wire sawn silicon wafers which were etched (using a KOH solution) to remove surface layers of different thicknesses. It is clear that wire saw damage was about 0.8 mils deep.

This technique can also be used to monitor polishing damage in polycrystalline wafers. Such a monitoring scheme is particularly important in order to prepare stress-free optically polished surfaces of polycrystalline samples. It is well known that excessive chemical etching/polishing can generate deep V-grooves and/or steps at grain boundaries due to different etch rates of various grain orientations. It is, therefore, difficult to make meaningful electro-optical measurements (such as evaluations of grain boundary properties by a focussed laser beam). Using this monitoring technique, we have been able to polish polycrystalline silicon (Wacker Silso) wafers with a maximum grain-to-grain surface variation of less than 0.05 μm (and with no residual surface stress) (3).

The experimental plots shown in Figures 2 and 3 were made using a small, 5 mm optical beam. By using a large optical beam one can increase sensitivity by an order of magnitude. As an example, Figure 4 shows a comparison of signal variation as a function of thickness removed from the surface, for two different beam sizes. The diameters of the small and large beams were approximately 5 mm and 10 mm respectively. The sample was a wire sawn 3 inch diameter silicon wafer (similar to the one used for Figure 3) and was etched in steps in the acidic etchant described earlier. A similarity between Figure 3 and that of the curve for small beam in Figure 4 is clearly evident although the etchants used were different.

In conclusion, we have presented a rapid, non-destructive technique for monitoring polishing damage in semiconductor wafers. Although this technique is valuable in a variety of applications for monitoring surface stress, its use is simple and convenient for monitoring polishing damage. In practice, one may simply compare the signal amplitude from a test wafer with a predetermined value from that of a stress-free sample to determine whether all the lattice damaged has been removed.

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FIGURE CAPTIONS

Figure 1. Schematic of an experimental set-up for monitoring surface damage.

Figure 2. Variation of photo signal as a function of a surface layer thickness removed (sample was mechanically polished with 25 mm alumina grit prior to etching).

Figure 3. Photo signal for wire-sawn samples which were etched for different times to remove different thicknesses from the surface.

Figure 4. Variation of photo signal as a function of thickness of surface layer removed: (a) small beam; (b) large beam. The starting sample was a wire-sawn wafer.

FIGURE 1. SCHEMATIC OF AN EXPERIMENTAL SET-UP FOR MONITORING SURFACE DAMAGE.

FIGURE 2.

G5940

VARIATION OF PHOTO SIGNAL AS A FUNCTION OF A SURFACE LAYER THICKNESS REMOVED (SAMPLE WAS MECHANICALLY POLISHED WITH 25 mm ALUMINA GRIT PRIOR TO ETCHING)

FIGURE 3. PHOTO SIGNAL FOR WIRE-SAWN SAMPLES WHICH WERE ETCHED FOR DIFFERENT TIMES TO REMOVE DIFFERENT THICKNESSES FROM THE SURFACE

FIGURE 4. THICKNESS ETCHED FROM ONE SIDE (IN MILS) G5941

VARIATION OF PHOTO SIGNAL AS A FUNCTION OF THICKNESS OF SURFACE LAYER REMOVED: (a) SMALL BEAM; (b) LARGE BEAM. THE STARTING SAMPLE WAS A WIRE-SAWN WAFER

APPENDIX II

MEASUREMENTS OF MINORITY CARRIER DIFFUSION LENGTH IN POLYCRYSTALLINE SOLAR CELLS

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Measurements made on polycrystalline solar cells show that short circuit currents (I_{SC}) do not bear expected relationship with minority carrier diffusion lengths (L) measured by a surface photovoltage type of technique. Several possible explanations for this discrepancy have been investigated. These include inhomogeneity effects due to grain boundaries, light level effects associated with defects, and non-uniformities in the bulk along the direction of light propagation. An alternative method, based on IR induced current, has been developed for measurement of L .

INTRODUCTION

Minority carrier diffusion length is an important parameter which is related to both the material purity as well as device performance. In particular, for polycrystalline silicon, it is known that structural defects such as dislocations, stacking faults and grain boundaries (G.B.'s) lower the carrier diffusion length in the bulk (which can indirectly degrade junction characteristics). They also influence junction characteristics directly via shunting and series resistance effects. A knowledge of each of the influences is essential to evaluate the potential of polycrystalline cells and to develop techniques to minimize these effects. Consequently, a technique which can independently measure the bulk diffusion length is valuable.

Several techniques are known for the measurement of minority carrier diffusion length (L) in single crystalline (uniform) semiconductors. A technique well-suited for solar cells is based on steady-state surface photovoltage (SPV) used for unprocessed wafers (1-3). Measurements made by this technique show excellent correlation with cell parameters, in agreement with theory. This technique has been extended to polycrystalline silicon substrates or cells to measure L within a grain by using an optical beam smaller than the grain size (4,5). However, extension of this technique to determine average diffusion length, $\langle L \rangle$, over a large area in polycrystalline materials, must be done with caution because the basic inhomogeneous nature of polycrystalline material may invalidate the assumptions of the technique. Our experience with such measurements has shown that measured values of $\langle L \rangle$ (in a large area polycrystalline cell) often do not agree with solar

cell performance such as short circuit current. We have, therefore, carried out investigations on polycrystalline substrates/cells which have different defect structures and G.B. characteristics, with a two-fold aim: (i) to determine such conditions under which the measured results are valid and (ii) to develop an alternate technique which can be used to measure $\langle L \rangle$ in polycrystalline cells/substrate. A number of other techniques have been used to verify the results -- these include long wavelength laser scanning, correlation with cell parameters and spectral response.

MEASUREMENTS BY SPV TECHNIQUE

The principle of the SPV technique for measurement of L is described well in the literature (1-4). Main features of this technique may be summarized for completeness as follows. The substrate/cell is illuminated by nearly monochromatic (filtered) chopped light. The light intensity (photons/sec) at the solar cell surface is determined by a calibrated reference detector and the photo-response of the cell is measured using a lock-in amplifier. The procedure for determining L consists of measuring light intensity I_λ incident at the solar cell surface required to maintain a constant photo-signal at each wavelength of illumination. A plot of $I_\lambda(1-R)$ vs α^{-1} is made (R and α are the reflection and absorption coefficients respectively). Such a plot for a uniform cell is a straight line whose intercept with the α^{-1} axis gives the diffusion length. Measurements on unprocessed wafers can be made using capacitive coupling of the photovoltage signal. Measurements on cells can be made using either open circuit photovoltage (OCPV) or short circuit photocurrent (SCPC) as the signal.

To determine the spatial variations in L a small optical beam ($\sim 1\text{mm}$) is used. Figure 1a shows measured values of diffusion length in a 1×2 cm cell fabricated on an RTR ribbon (grown in oxygen rich ambient). A long wavelength laser line scan, across the cell, in the direction of the arrow showing variation in L is given in figure 1b (the amplitude of the line scan, at any point, is proportional to the local value of L). An average value of L on the right hand side of the cell, $\langle L \rangle_{\text{RHS}}$, was determined by illuminating this area of the cell during measurement, to be $31 \mu\text{m}$; similarly $\langle L \rangle_{\text{LHS}}$ was found to be $\sim 41 \mu\text{m}$. When the whole cell was illuminated during measurement we obtained $\langle L \rangle = 36 \mu\text{m}$ which agrees well the cell's I_{SC} . The example shows that the SPV type of measurement indeed gives correct value of $\langle L \rangle$, in this case.

There are other cases, where $\langle L \rangle$ measurements do not agree with J_{SC} values. A critical examination of such cells showed that they had either one or both of the following features: (a) Rapid spatial variations in L - it was determined empirically using small spot size laser scanning and variable beam size OCPV that if the variation in diffusion length exceeded 10% over the illuminated area, erroneous results would be obtained. It was also found that the measured value of

L is higher than $L_{\text{(actual)}}$ if d^2L/d^2X is positive (local diffusion length well) and $L_{\text{(measured)}} < L_{\text{(actual)}}$ if d^2L/d^2X is negative (local diffusion length peak). The physical mechanism responsible for the incorrectness of the measured $\langle L \rangle$ value is believed to be as follows: carriers generated in any region of the cell/substrate by the illuminating monochromatic light traverse laterally into adjacent regions of different diffusion length. This process results in a photosignal which has a wavelength dependence different from the one given by theory. Under strong non-uniformities the I vs α^{-1} plot may significantly deviate from a straight line. (b) Residual stress present in the material. Presence of residual stress is sometimes directly indicated by the curvature of I vs α^{-1} plot (such a curvature can also be shown if the material has in-depth variations in L). To confirm the presence of residual stress, the cells/substrates were polished and stress determined by i.r. optical birefringence. Figure 2a shows an optical birefringence photograph of a region of Wacker Silso having residual stress. The corresponding photograph of this region (taken with i.r.) is shown in figure 2b. The dominant effect of residual stress is expected to be associated with changes in absorption coefficient. For small stresses the measured values of L appear higher than actual values (unless appropriate corrections are made). However, for large stresses I vs α^{-1} plot becomes a concave curve.

Examples described above may be referred to as lateral inhomogeneities following a convention described previously for single crystal cells/substrates (6). The sources of lateral variations in L are: grains varying in orientation and/or defect structure (and density), grain-boundaries, and residual stress. Our experimental data has shown that if G.B. regions have little or no stress and no decoration by other defects, correct values of $\langle L \rangle$ are given by SPV technique (7). This condition is met by large size columnar grains in Wacker poly and much of the recent RTR material.

To confirm the validity of the SPV type of technique in the presence of a G.B. (where G.B. only acts as a region of high recombination) we cleaved a silicon (100 oriented) sample and made small beam SPV measurements on it at different distances away from the edge. Figure 3 shows the plots thus obtained. It is clear from the straight line plot as well as from progressive lowering in L values that such a measurement is valid.

Another difficulty in making meaningful measurements was found to be with some sheet grown material which routinely exhibited low measured values of diffusion length (when measured both on the substrate as well as after cell fabrication). Analysis of the material showed that such sheets have surface dislocations which constitute a region of high recombination. However, interestingly these defects seem to have light dependent influence such that at high light intensities saturation effects occur. This type of non-uniformity may be referred to as in-depth inhomogeneity (again following the convention in ref. 6). Effects of in-depth non-uniformities are also expected to occur when

grain boundaries run either parallel or at shallow angles to the surface (or junction). Light intensity effects were also observed in other samples which showed reduction in L with light intensity. Figure 4 shows I vs. α^{-1} plots for two cells, one having low diffusion length and the other fairly high, at two different light intensities (initial values). It is seen that the measured value, L_2 at higher intensities ($I_2 \approx 10 I_1$) is smaller than L_1 . Although no further experiments were carried out to identify the origin of this effect, it is believed to be related to the changes in fermi level upon illumination with respect to the defect levels within the band gap. Light intensity effects are also easily observed when an additional unchopped (i.e. d.c.) bias light is used during measurements on the cell.

From the previous discussions it is clear that non-uniformities in polycrystalline substrates can result in errors in measurement of diffusion length by SPV type of technique. Significant errors can occur if lateral non-uniformities give rise to a rapid variation in L . Errors can also occur with in-depth non-uniformities if the sample shows light intensity dependence of L . However, these effects may be eliminated by carrying out the measurement with simultaneous illumination by a d.c. bias light.

When the sample can be approximated as uniform we can get a good correlation between I_{SC} and L measured by SPV type technique. Figure 5 shows I_{SC} vs. L plot for small area solar cells (50 mil diameter) fabricated on various types of RTR substrates and Wacker Silso diffusion lengths were measured by OCPV/SCPC technique.

SHORT CIRCUIT CURRENT TECHNIQUE

From the previous discussion we see that an incomplete knowledge of polycrystalline substrate/cell may result in incorrect values of L as measured by SPV type of measurement. The major problem seems to arise due to use of variable wavelength illumination, which has a different contribution from various regions (due to internal carrier transport).

An alternate scheme for determination of L is to measure short circuit current density, J_{SC} , of a cell for a monochromatic long wavelength illumination. It can be shown that for long wavelength illumination

$$J_{SC} = q \phi (1-R) \alpha L$$

Where q is the electronic charge, ϕ is incident photon flux, and R is the reflection coefficient. Importance of long wavelength lies in the fact that for the above equation to be valid, $1/\alpha J L$ at the wavelength of illumination. Another consideration for selection of the wavelength of operation is to minimize variations in absorption coefficient due to stress in different samples. It has been shown

earlier that the presence of defects and residual stresses causes increased band edge absorption (6). To avoid ambiguity due to stress effects wavelength of illumination, $\lambda \leq 1 \mu\text{m}$.

We have verified the use of the monochromatic illumination technique both for large area as well as small area cells. Figure 6 shows the relation between J_{SC} (under AM1 conditions) with the signal due to monochromatic (narrow band, $\lambda = 0.95 \mu\text{m}$) excitation for 2 cm^2 cells fabricated on RTR ribbons. Figure 7 is a similar plot for small area diodes (area = 1.26 mm^2) fabricated on RTR ribbons.

A simple approach in using the short circuit current technique is to employ a signal from a standard cell of known diffusion length as a reference directly in terms of L .

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FIGURE 1a: SKETCH OF THE CELL SHOWING VARIOUS G.B.'S AND MEASURED VALUES OF L.

FIGURE 1b: LONG WAVELENGTH LASER SCAN ALONG THE DIRECTION OF ARROW IN FIGURE 1a.

FIGURE 2a: IR BIREFRINGENCE IMAGE OF A POLY-CRYSTALLINE SAMPLE SHOWING RESIDUAL STRESS.

FIGURE 2b: IR PHOTOGRAPH OF THE REGION IN FIGURE 2a SHOWING VARIOUS GRAINS.

FIGURE 3: $I(1-R)$ vs α^{-1}
PLOTS TAKEN ON
A CLEAVED SAMPLE
VARIOUS DISTANCES
AWAY FROM THE
EDGE.

FIGURE 4: $I(1-R)$ vs α^{-1} PLOTS FOR TWO CELLS HAVING
LIGHT INTENSITY DEPENDENT DIFFUSION LENGTHS.

FIGURE 5:
PLOT OF I_{SC} VS L FOR
SMALL DIODES (50 MIL
DIAMETER). DIFFUSION
LENGTHS WERE MEASURED
BY OCPV

FIGURE 6:
LOW LEVEL IR RESPONSE
VS AM1 PERFORMANCE
FOR 2 cm^2 CELLS.

FIGURE 7: SHORT CIRCUIT CURRENT (AM1) VS IR SIGNAL FOR SMALL AREA DIODES.

APPENDIX II

STATEMENT OF WORK

"Photovoltaic Mechanisms in Polycrystalline Thin Film Silicon Solar Cells"

1.0 OBJECTIVES

The objectives of the proposed work include: (1) the development of surface preparation techniques to aid in the interpretation of grain boundary data; (2) the characterization of grain boundaries in terms of chemical, physical, electrical and optical analyses and correlations to solar cell performance; (3) the identification of the effects of intragrain crystal defects; and (4) the determination of the effects of solar cell processing on grain boundary parameters and bulk defects.

2.0 SCOPE OF WORK

In order to fulfill the above-stated objectives, the Subcontractor shall perform the following four (4) research tasks:

2.1 TASK 1: Physical and Electrical Characterization of Defects

- (a) Characterize crystallographic defects in Motorola RTR material, Wacker "Silso" material and other polycrystalline silicon samples supplied by SERI/PVAS using the following techniques:
 - (i) x-ray and SEM analysis to identify the angle of misfit between adjacent grains;
 - (ii) optical birefringence (using an I-R microscope) to determine grain boundary stress;
 - (iii) dislocation etching;
 - (iv) TEM analysis;
 - (v) EBIC and Light Induced Current (LIC); and
 - (vi) grain boundary voltage pick-off.
- (b) Correlate the physical and electronic behavior of the grain boundaries.
- (c) Investigate grain boundary precipitation by use of I-R microscopy.

2.2 TASK 2: Correlation of Defects to Solar Cell Performance

- (a) Fabricate small area solar cells on the materials specified in Task 1.
- (b) Measure dark and illuminated I-V characteristics of the solar cells as a function of temperature and illumination.

- (c) By suitable etching techniques, characterize and categorize the defect structure in the small area cells.
- (d) Determine by the above analysis the dominant carrier transport mechanisms near and across the grain boundaries and other defects.
- (e) Correlate to solar cell performance.

2.3 TASK 3: Processing Effects

- (a) Determine the effects of solar cell processing on grain boundary parameters and bulk defects by:
 - (i) examining variations in processing conditions;
 - (ii) selective diffusion into grain boundaries; and
 - (iii) changes in the structural composition of the substrates such as lattice stresses, alteration of interface states and annihilation of defects.
- (b) Identify the dominant process(es) responsible for improvements in diffusion length and in solar cell performance.

2.4 TASK 4: Theoretical Studies

Perform theoretical modelling of the analytical techniques in order to relate measured parameters to grain boundary parameters.

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