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PHOTOVOLTAIC MECHANISMS IN
POLYCRYSTALLINE THIN FILM
SOLAR CELLS

Quarterly Technical Progress Report No. 2

January 1, 1979 - March 31, 1979

Solarex Corporation
1335 Piccard Drive
Rockville, Maryland 20850

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H. C. Lin and R. W. Armstrong at the
University of Maryland

Sponsored by DOE Division of Solar Energy
Photovoltaics Program Office

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ABSTRACT

The effect of grain size on short circuit current density was investigated by approximating individual silicon grains as right circular cylinders and solving the diffusion equation within the base region. This model confirms the previous results that for grain radii exceeding a few tenths of a millimeter, the minority carrier lifetime in the grain essentially determines the short-circuit current response of the cell. The dark I-V characteristics of some polycrystalline solar cells were measured and compared with single crystal cells. The dark current of the polycrystalline cells is dominated by recombination within the space-charge region well past the one sun maximum power point. This has the effect of lowering the cells output power and open circuit voltage. Single crystal cells are dominated by recombination within the quasi-neutral regions at the one sun maximum power point and, consequently, the fill factor and open circuit voltage are greater. Additionally, some preliminary measurements of the spatial dependence of diffusion length were made, Laue X-ray diffraction study of crystal orientations was performed and some SEM micrographs of polycrystalline wafers were taken.

DESCRIPTION OF PROJECT

This study is designed to increase the understanding of the mechanisms in thin film polycrystalline silicon solar cells that limit the photovoltaic conversion efficiency under solar illumination conditions. Theoretical models will be generated to relate the photovoltaic conversion efficiency to the chemical, physical, and electrical characteristics of polycrystalline thin film solar cells; and measurement techniques will be developed to test and update the proposed models. Finally, theoretical and experimental investigations of grain boundary effects will be conducted.

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I. INTRODUCTION

This report summarizes the progress achieved during the second quarter of a program undertaken by the Solarex Corporation and its subcontractor, the University of Maryland, that is designed to increase the understanding of the mechanisms in thin film polycrystalline silicon solar cells that limit the photovoltaic conversion efficiency under solar illumination conditions. Section II is a summary of the theoretical modeling effort. Section III details the experimental measurements made during the quarter and discusses the results. Finally, the conclusions are presented in Section IV.

II. THEORETICAL MODELING

The effect of grain size on short circuit current density, J_{sc} , and the quantum yield, η , is being evaluated by approximating an individual silicon grain as a right circular cylinder. The silicon grain is assumed to be cylindrically symmetric. Consequently, the minority carrier density, n , is a function of r and z only ($n = n(r, z)$). The minority carrier density is found by solving the diffusion equation within the cylinder which is bounded by the n^+p junction ($z = 0$), the pp^+ junction ($z = z_0$) and the grain boundary ($r = r_0$). The diffusion equation is applicable up to the edge of the depletion region (which lies within the p region). The minority carrier optical generation

rate is given by $g = F_0 \alpha e^{-\alpha z}$ where F_0 is the incident photon flux at the junction ($z = 0$) and α is the absorption coefficient. The minority carrier recombination rate in the bulk is given by $n(r, Z)/\tau_n$ where τ_n is the minority carrier bulk lifetime. The diffusion equation is:

$$(1) \quad D_n \nabla^2 n(r, Z) + F_0 \alpha e^{-\alpha z} = n(r, z)/\tau_n$$

The boundary conditions are: $n(r, 0) = 0$ (all carriers are collected at the junction), $D_n \partial/\partial z n(r, z_0) = -v_z n(r, z_0)$ (minority carriers recombine at the pp^+ junction with a recombination velocity v_z), and $D_n \partial/\partial r n(r_0, z) = -v_r n(r_0, z)$ (minority carriers recombine at the grain boundary with a recombination velocity v_r). Once the boundary value problem for $n(r, z)$ is solved, the short circuit current density is given by:

$$(2) \quad J_{sc}(r) = -q D_n \partial/\partial z n(r, 0)$$

Finally, the short circuit current, I_{sc} , is found by integrating $J_{sc}(r)$ over the grain surface and the quantum yield (number of electrons collected per absorbed photon) is given by:

$$(3) \quad \eta = \frac{I_{sc}}{q(\pi r_0^2 F_0)}$$

For the special case $v_z = 0$ (no recombination at the back surface $z = z_0$) and $v_r = \infty$ (infinite recombination velocity at the grain boundary) the quantum yield is:

$$(4) \quad \eta = 4\alpha \sum_{i=1}^{\infty} \frac{\delta_i \tanh(\delta_i z_0) - \alpha + \alpha e^{-\alpha z_0}}{\gamma_i^2 (\delta_i^2 - \alpha^2)}$$

where:

$$(5) \quad \delta_i^2 = 1/L_n^2 + \gamma_i^2/r_0^2$$

and γ_i are the roots of $J_0(\gamma_i) = 0$ ($J_0(x)$ is the Bessel function of the first kind of order zero). For $\delta_i z_0 \geq 5$ and $\alpha z_0 \geq 10$, which is easily satisfied for the polycrystalline cells being studied, the quantum yield is:

$$(6) \quad \eta = \sum_{i=1}^{\infty} \frac{4}{\gamma_i^2 (1 + \delta_i/\alpha)}.$$

In the limit as the grain radius approaches infinity (i.e. single crystal) then:

$$(7) \quad \eta_{\max} = \lim_{r_0 \rightarrow \infty} \eta = \frac{\alpha L_n}{\alpha L_n + 1}$$

The optical generation rate of minority carriers in the bulk silicon decreases exponentially with depth from the surface ($g = F_0 \alpha e^{-\alpha z}$). Therefore, after reaching a depth of $z = \alpha^{-1}$ (commonly called the extinction length), almost two thirds of the minority carriers have already been generated within the bulk. Additionally, the majority of carriers which reach the junction come from within a distance $z = L_n$ of the junction. For $L_n > \alpha^{-1}$ most of the generated carriers will be collected at the junction, while for $L_n < \alpha^{-1}$ most of the carriers will never reach the junction. Thus $L_n = \alpha^{-1}$ ($\alpha L_n = 1$) represents an effective transition point between the two regions.

Figure 1 is a plot of the ratio $\eta/\eta_{\max}$ versus r_o/L_n for $\alpha L_n = 1$, where η was calculated by summing the first 20 terms of the infinite series in equation (6). Convergence is quite rapid and the contribution of the remaining terms in the series is negligible. The ratio $\eta/\eta_{\max}$ was calculated as a function of r_o/L_n for $\alpha L_n = 1$ with $L_n = 10, 25, 50, 100$, and 150 microns and these curves were found to be identical to three significant figures. Comparing $\eta/\eta_{\max}$ in Figure 1 with J_1/J_L^T (the ratio of the short circuit current density collected from the grain to the current density collected when there is no grain boundary) calculated from a more simple model shows surprisingly good agreement between the two models (within 0.5%).¹ These results again show that recombination at grain boundaries will have little influence on the collected current if the radius of the grains exceed $8L_n$. Since most of the current from silicon solar cells is produced from light having wavelengths less than 900 nm where $\alpha = 380 \text{ cm}^{-1}$, the equation $\alpha L_n = 1$ will be satisfied for $L_n \leq 26 \text{ } \mu\text{m}$. Thus, for grain radii exceeding $200 \text{ } \mu\text{m}$, the determining influence on the short circuit current density will be the minority carrier diffusion length within a grain.

The preceding analysis considered only the limiting case of infinite recombination at the grain boundaries ($v_r = \infty$) and no recombination at the back surface ($\nabla_z = 0$), while the grain model incorporates these as variables. Hence, we can investigate the effects of finite recombination velocities, grain size, and minority carrier lifetime on the short circuit current.

Figure 1. $\eta/\eta_{\max}$ versus r_o/L_n

III. MEASUREMENTS

Spatial Dependence of Minority Carrier Diffusion Length

Preliminary measurements of the spatial dependence of I_{sc} versus wavelength in a polycrystalline solar cell are being made using a Nikon microscope with a mechanical stage to position a fine monochromatic beam of light onto the sample and using a picoammeter to measure I_{sc} . Initially, some difficulty was encountered in measuring the short circuit current because the shunt resistance of the cells affected the zero stability of the picoammeter. Polycrystalline cells having large shunt resistances (12-27 k Ω) were found to be suitable for stable measurements.

The quantum yield of the polycrystalline sample is measured using a standard cell (single crystal) as a reference since η as a function of position and intensity is essentially constant for a single crystal cell. Therefore, after accounting for differences in reflectance:

$$(8) \quad \eta_{\text{sample}} = \frac{I_{\text{sample}}}{I_{\text{standard}}} \eta_{\text{standard}}$$

The minority carrier diffusion length in the p-type base is then determined from quantum yield measurements of the cell at various wavelengths using the formula:²

$$(9) \quad \eta = \frac{\alpha L_n}{\alpha L_n + 1}$$

where η is obtained from equation (8) and has been corrected for reflectance (i.e. η is the true internal quantum yield).

Rewriting equation (9):

$$\eta^{-1} = (1/L_n)\alpha^{-1} + 1$$

If η^{-1} versus α^{-1} is plotted and a straight line is fitted to the data then a reciprocal of the slope will yield L_n . In order to minimize the effects of the emitter region, long wavelength monochromatic light is used for the measurements.

Figure 2 illustrates the results of two spectral response measurements made within a polycrystalline cell along with the spectral response of a standard (single crystal) cell. Measurements were made in the wavelength range of 780-880 nanometers. One measurement shows the spectral response in a grain center, while the other measurement was taken at a boundary of the same grain. This boundary exhibits enhanced spectral response. This enhancement may be due to phosphorus diffusion along the grain boundary into the silicon thereby creating a "vertical" junction.¹

Current-Voltage (I-V) Characteristics

The dark I-V characteristics of polycrystalline solar cells are being measured and compared with single crystal cells. At first inspection, the major difference between the polycrystalline and the single crystal I-V characteristics is that the diode quality factor, n , is greater for the polycrystalline cells. The dark I-V characteristics of a 13.6% AM1 single crystal cell and a 11.9% AM1 polycrystalline cell are shown in Figure 3 and Figure 4, respectively. To eliminate the effect

Figure 2. η^{-1} versus $\alpha^{-1} (\mu)$

of series resistance the curves were generated by measuring $I_{sc} - V_{oc}$ at voltages above 400 mv and dark I-V below 400 mv.

The dark current, I_D , has two components - one originating from recombination within the space charge region - and the other from recombination in the quasi-neutral regions:³

$$(10) I_D = I_{SCO}^D \left[\exp(qv/n_{sc}kT) - 1 \right] + I_{QNO}^D \left[\exp(qv/kT) - 1 \right]$$

where the first term is the component arising from the space charge region and the second term is the current component arising from the quasi-neutral regions (I_{QNO}^D is the saturation current). The parameters I_{SCO}^D , I_{QNO}^D , and n_{sc} were determined graphically using a previously described method and are shown in Table 1.^{4,5}

TABLE 1

Dark I-V Characteristics of Single Crystal
and Polycrystalline Solar Cells

Cell	AM1 Efficiency	I_{SCO}^D (ma)	I_{QNO}^D (ma)	n_{sc}
Single Crystal	13.6%	2.47×10^{-3}	7.24×10^{-8}	2.95
Polycrystalline	11.9%	6.02×10^{-3}	3.97×10^{-8}	2.52

The two components comprising the dark current are shown with the experimentally measured I-V curve in Figure 3 and Figure 4.

The dark current of the single crystal cell is dominated by the quasi-neutral region at the one sun maximum power point,

Figure 4. Polycrystalline Dark I-V (11.9% AM1)

while the dark current of the polycrystalline cell is dominated by the space-charge region well past the one sun maximum power point. The fact that the dark I-V characteristics are dominated by the space-charge component is generally true for all the polycrystalline cells studied so far and has the effect of lowering the fill factor, the open circuit voltage, and the resultant conversion efficiency of the solar cells. Further investigations are under way to determine the relationships that may exist between polycrystalline cell efficiency and the injection mechanisms.

Deep Level Transient Spectroscopy (H. C. Lin)

DLTS effects have been successfully observed and some preliminary measurements have been made. After the system is fully calibrated, exhaustive measurements will be made on polycrystalline solar cells. The DLTS technique will be used to determine defect concentrations, energy levels, capture cross-sections and emission rates in and around the space-charge region. These measurements will provide very useful information on the various recombination processes in the space charge region which tend to dominate the dark I-V characteristics of the polycrystalline cells we have studied.

Structural Studies (R. W. Armstrong)

Good resolution SEM pictures of surface etching features on polycrystalline wafers have been obtained both at deeply grooved grain boundaries and at clusters of etch pits. Figure 5A, 5B, and 5C are SEM micrographs at magnifications of 50X, 350X, and 1750X respectively of a region exhibiting twin and grain boundaries. Figure 6A, 6B, and 6C are SEM micrographs at

magnifications of 50X, 350X, and 1750X, respectively, of a region containing sinuous or degenerate grain boundaries. Both regions exhibit grooves at the grain boundaries and etch pits. The etch pits in both figures 5C and 6C resemble triangular inverted pyramids which suggests the presence of the (111) crystal plane. Additionally, some of these etch pits appear to contain precipitates and further analysis will be performed to determine the actual composition of the precipitates.

The orientation of crystal axes for individual grains within a polycrystalline wafer is being determined by the Laue X-ray back reflection method. For the polycrystalline wafer previously examined by SEM the crystal orientations within regions of sinuous boundaries and pitted grain volumes will be compared with crystal orientations which are free from these effects. Additionally, the orientation of the boundary interfaces will be determined.

Two preliminary Laue X-ray diffraction pictures were taken within a polycrystalline wafer. The first picture was obtained from X-radiation normally incident on a single grain included within sinuous grain boundaries. The growth direction of this grain is closest to the (111) axis. The second picture was obtained from X-radiation normally incident on a single grain in an area showing twin interfaces or pairs of twin interfaces in nearly all grains. The growth direction of this grain is closest to the (011) axis. Work is continuing to determine how these particular crystal orientations are related to the various types of grain boundaries.

Figure 5A. Grooves and Etch Pits at Twin Boundaries and Grain Boundaries

Figure 6A. Grooves at Grain Boundaries and Clusters of Etch Pits

Figure 5B. Etch Pits at Boundaries and at Individual Sites

Figure 6B. Grooves at Grain Boundaries and Individual Etch Pits

Figure 5C. Precipitates at Some Etch Pits

Figure 6. Precipitates at Some Etch Pits

The X-ray measurements will be employed, also, to produce Schulz and Berg-Barrett X-ray topographs of the exposed crystal surfaces.⁶ Such topographs, which can be matched on a point-by-point basis with the internal microstructure of individual grains, can be utilized in conjunction with the scanning photoresponse measurements to give structural information relating directly to the photovoltaic properties of the cells. In particular, the X-ray topographs give detailed information about the internal crystal strains produced by dislocations, segregated solutes, precipitates, and grain boundaries.

IV. CONCLUSIONS

1) A theoretical model which approximates an individual silicon grain as a right circular cylinder was generated. This model confirms the previous result that for grain radii exceeding a few tenths of a millimeter, the minority carrier lifetime in the grain essentially determines the short-circuit current response of the cell.

2) The dark current of the polycrystalline cells studied is dominated by recombination within the space-charge region well past the one sun maximum power point. This has the effect of lowering the cells output power and open circuit voltage. Single crystal cells, on the other hand, are dominated by recombination within the quasi-neutral regions at the one sun maximum power point. Consequently, the fill factor and open circuit voltages are greater.

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