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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE THIN FILM
SOLAR CELLS

Quarterly Technical Progress Report No. 3 for April 1—June 30, 1979

By
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ABSTRACT

The "vertical" junction effect in polysilicon solar cells (due to dopant penetration along grain boundaries) is investigated using a cylindrical grain model. The model shows that for small grain radii the short circuit current can increase above the single crystal value if the grain boundaries collect carriers and that the short-circuit current approaches the single crystal value as the grain size increases. The spatial dependence of the dark I-V characteristic is investigated by fabricating small diodes on a polysilicon wafer. Dark I-V characteristics are measured and illuminated characteristics are projected for each of the diodes. The diode characteristics are given together with SEM micrographs of the diodes and the effect of areal inhomogeneity is investigated. The relative orientations of adjacent crystal grains and the nature of the boundaries between grains are studied by x-ray diffraction, optical microscopy and SEM methods. Orientation data is presented along with electron channelling patterns obtained from individual grains. A conclusion is drawn on the origin of "sinuous" grain boundaries.

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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List of Symbols

- J_{SC} - Short-circuit current density
- I_{SC} - Short-current current
- r_o - Grain radius
- α - Absorption coefficient
- n - Minority carrier density
- D_n - Electron diffusivity
- V_r - Recombination velocity at grain boundary ($r=r_o$)
- q - Electron charge (coulombs)
- k - Absolute temperature
- η - Quantum yield
- F_o - Incident photon flux at the junction ($z=0$)
- L_n - Minority carrier diffusion length
- J_D - Dark diode current density
- J_{SCO} - Generation current from the junction space-charge region.
- J_{QNO} - Generation current from the quasi-neutral regions.
- n_{sc} - Diode quality factor (space-charge region)
- V_{OC} - Open circuit-voltage

I. INTRODUCTION

This report summarizes the progress achieved during the third quarter of a program 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 summarizes the theoretical modeling effort. Section III details the experimental measurements, both electrical and structural, and the development of measurement techniques. Finally, the conclusions are presented in Section IV and a summary of the results to date is given in Section V.

II. THEORETICAL MODELING

It has been experimentally observed that certain grain boundaries in polycrystalline silicon solar cells exhibit an increased photoresponse as compared to adjacent grains. It appears that the collecting volume around these boundaries is greater than normal due to the formation of a "vertical" junction at these boundaries because of dopant diffusion deep into the silicon.^{1/} This effect is being investigated using the cylindrical grain model, previously reported, where an individual silicon grain is approximated as a right circular cylinder.^{2/}

An upper estimate of the increase in short circuit current density, J_{sc} , due to carrier collection at the grain boundary can be found by evaluating the flux of minority carriers into the

boundary ($r=r_0$) and assuming that all of these carriers are collected as current. In this case the depth of the vertical junction exceeds the depth of light penetration (hence the minority carrier generation depth) into the silicon (i.e. the vertical junction depth exceeds the extinction length, $1/\alpha$). If the grain boundary behaves as a depletion region then the minority carrier density, $n(r,z)$, is zero at the boundary ($n(r_0,z)=0$). Alternatively the "recombination" velocity, V_r , at the boundary is infinite. The flux of minority carriers into the boundary is given by:

$$(1) \quad J_{SC}^{GB}(r_0, z) = -qD_n \frac{\partial}{\partial r} n(r_0, z)$$

The total current flowing into the boundary, $I_{SC}^{GB}(r_0)$ is found by integrating $J_{SC}^{GB}(r_0, z)$ over the cylinder walls. The contribution of the grain boundary current to the quantum yield (number of electrons collected per absorbed photon) of the grain is:

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

For the special case $V_z = 0$ (no recombination at the back surface $z = z_0$), $\delta_1 z_0 > 5$, and $\alpha z_0 > 10$, the quantum yield is:

$$(3) \quad \eta^{GB} = \frac{4}{\pi} \sum_{i=1}^{\infty} \frac{1}{\delta_i (\delta_i + \alpha)}$$

where:

$$(4) \quad \delta_i^2 = \frac{1}{L_n^2} + \frac{\gamma_i^2}{r_0^2}$$

L_n is the minority carrier diffusion length 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). The quantum yield due to carriers collected at the front junction is:^{2/}

$$(5) \quad \eta^F = \sum_{i=1}^{\infty} \frac{4}{\gamma_i^2 \left(1 + \frac{\delta_i}{\alpha}\right)}$$

The quantum yield of the grain is found by adding the contributions from the cylinder walls (grain boundaries) and the front surface junction (equations (3) and (5) respectively).

$$\eta^T = \eta^{GB} + \eta^F$$

$$(6) \quad \eta^T = \sum_{i=1}^{\infty} \left[\frac{4}{r_0^2 \delta_i (\delta_i + \alpha)} + \frac{4}{\gamma_i^2 \left(1 + \frac{\delta_i}{\alpha}\right)} \right]$$

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

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

Figure 1 shows a plot of the quantum yield versus r_0/L_n for the following three cases with the condition $\alpha L_n = 1$:

- (1) Carriers recombine at the grain boundary with an infinite recombination velocity ($\eta^T = \eta^F$, eg. (5)).
- (2) Carriers reaching the grain boundary are collected as current (i.e. the grain boundary is enclosed in a depletion region, $\eta^T = \eta^{GB} + \eta^F$, eg. (6)).
- (3) $r_0 \rightarrow \infty$ (i.e. single crystal, eg. (7)).

Figure 1. Quantum Yield Versus r_o/L_n for Various Boundary Conditions

Cases (1) and (2) were evaluated numerically by summing the first 20 terms of equation (5) and (6) respectively. The convergence of both series is rapid and the contributions of the remaining terms in the series is negligible. Figure 1 shows that for small grain radii the quantum yield can increase above the single crystal value if the grain boundaries collect carriers (case 2) while the converse is true for boundaries which act as recombination centers (case 1). However, both cases approach the single crystal value as the grain size increases, as expected.

The results again show that neither recombination nor collection of minority carriers at grain boundaries will have much influence on the short circuit current if the radius of the grains exceed $8 L_n$. Since most of the current from silicon solar cells is produced from light having wavelengths less than 900nm where $\alpha=380 \text{ cm}^{-1}$, the equation $\alpha L_n=1$ will be satisfied for $L_n=26\mu\text{m}$. Thus, for grain radii exceeding 200 μm , which is easily the case for the cast polysilicon studied here, the determining influence on the short circuit current density will be the minority carrier diffusion length within a grain.

III. MEASUREMENTS

Spatial Dependence of I-V Characteristics

The spatial dependence of the dark I-V characteristics within a polycrystalline wafer is being investigated in an

effort to understand the effect of grain boundaries on the measured diode characteristics. Diodes were fabricated on a thin polysilicon wafer by diffusing phosphorus into small circular areas (0.32 cm diameter) and then forming evaporated metal contacts. The dark current was separated into two components - one originating from recombination within the space-charge region - and the other from recombination in the quasi-neutral regions using a previously described method:^{3/}

$$J_n = J_{SCO}^D \left[\exp (qV/n_{SC} kT) - 1 \right] + J_{QNO}^D \left[\exp (qV/kT) - 1 \right]$$

The dark I-V characteristics of five of the diodes (within the same wafer) are summarized in Table 1 together with a 16.0% AMI single crystal cell. (Other diodes on the wafer have similar characteristics) The last column in Table 1 shows the voltage where the current contributions from the space-charge region and the quasi-neutral regions are equal (denoted by V_E).

TABLE 1

Dark I-V Characteristics of Polysilicon Diodes

Diode	J_{SCO} (ma/cm ²)	J_{QNO} (ma/cm ²)	n_{sc}	V_E (mV)
D-8	1.08×10^{-3}	3.65×10^{-9}	2.43	550
E-7	1.67×10^{-4}	2.43×10^{-9}	2.00	582
E-8	1.40×10^{-4}	1.34×10^{-9}	1.83	660
F-5	6.80×10^{-5}	1.65×10^{-9}	1.81	615
F-6	3.26×10^{-3}	7.02×10^{-9}	3.05	498
Single Crystal Cell	5.40×10^{-4}	3.71×10^{-9}	2.67	490
"Effective"	6.22×10^{-4}	5.29×10^{-9}	2.35	528

The dark I-V characteristics of the polysilicon diodes are again dominated by the space-charge component as previously seen in polysilicon solar cells.^{2/}

In order to interpret the effect of the dark I-V characteristics of the individual diodes on solar cell efficiency, illuminated solar cell characteristics are generated by assuming a short-circuit current density for each of the diodes and then applying the shifting approximation. The shifting approximation states that the illuminated solar cell I-V characteristic is the dark I-V characteristic shifted by the short circuit current:^{4/}

$$(8) \quad J(V) = J_D(V) - J_{SC}$$

The projected illuminated characteristics of the diodes are shown in Table 2 along with a single crystal cell (calculated using eg. 8).

TABLE 2
Illuminated I-V Characteristics

Diode	J_{SC} (ma/cm ²)	V_{OC} (mV)	V_{mp} (mV)	P_{max} ($\frac{mW}{cm^2}$)	F.F.
D-8	30	587	489	13.2	.750
E-7	30	585	490	13.5	.769
E-8	30	570	490	12.8	.749
F-5	30	588	500	13.6	.771
F-6	30	578	487	13.3	.767
Single Crystal	30	586	512	14.3	.813
Effective	30	582	489	13.3	.762

Although the dark I-V characteristics of the five diodes vary considerably, Table 2 shows that the illuminated characteristics do not. The fill factors for all of the diodes are reasonably high and the largest maximum power variation between diodes is 0.8 mW/cm^2 .

The degradation in solar cell performance due to areal inhomogeneity is investigated by adding the five diodes dark I-V characteristics in parallel using an equal weighting factor (1/5) for each diode.^{5/} The resulting "effective" diode dark I-V characteristics are shown in Table 1 while the illuminated characteristics are given in Table 2. The illuminated characteristics of the "effective" diode are not degraded significantly due to any variation in the dark characteristics of the five diodes and its' maximum power is equal to the average power of the five diodes. Hence it appears that, because of the widely varying diode quality factors and reverse currents (J_{SC0} in particular), that the overall characteristics of the "effective" diode are not dominated by areal inhomogeneity. Areal inhomogeneity is most often observed in the form of shunts which may be due to phosphorus dopant penetration along particular grain boundaries to the back of the solar cell.

In an effort to relate the structural and electrical characteristics of the diodes, the front contacts were etched away and then SEM micrographs were taken. Figure 2 shows SEM micrographs of diodes E-7 and E-8 while Figure 3 shows the SEM micrographs of diodes F-5 and F-6. All of the micrographs were taken at a magnification of 37x. There is no clear in-

Figure 2. Diodes E-7 and E-8

Figure 3. Diodes F-5 and F-6

dication that the electrical performances of a given diode can be inferred from the appearance of the silicon surface. Diodes E-7, E-8, and F-6 all contain numerous grain boundaries, while diode F-5 is composed mostly of twin planes. Diode F-5 is the best of the five diodes, electrically, and this may be another indication of the relative electrical inactivity of twin planes. Further structural investigation is continuing.

Deep Level Transient Spectroscopy (DLTS)

(H.C. Lin, C.D. Wang)

The closed-system cryogenic refrigerator unit for the DLTS system was installed this quarter. A stage has been constructed to fit the cryogenic system so that samples three quarters of an inch square can be cooled to temperatures of four degrees absolute in seventy-five minutes. The sample temperature can be maintained at any intermediate temperature indefinitely. Probes are mounted so that electrical measurements of the sample are possible at these temperatures. Figure 4 shows a schematic of the system with all the components identified.

With the completion of the sample holder, DLTS measurements are being made. Preliminary measurements conducted on a conventional junction diode indicate that the system is working. During the next quarter, systematic DLTS measurements will be made on polysilicon solar cells.

DLTS SYSTEM WITH A LOCK-IN AMPLIFIER

Figure 4

Structural Studies

(R. W. Armstrong, M.E. Taylor, Jr.)

For cast polysilicon material, the relative orientations of adjacent crystal grains and the nature of the boundaries between grains have been studied by X-ray diffraction, optical microscopy, and scanning electron microscopy (SEM) methods. The structural information will be applied to determining models of the positions of atoms at the interfaces between grains and, consequently, to understanding the diffusional properties and electronic character of individual boundaries within polysilicon solar cells.

Figure 5 shows a longitudinally cut cast polycrystalline silicon section. In this longitudinal section, a main portion of the volume is shown to be taken-up by grain 1 which envelops grain 2. (The envelopment of grain 2 by grain 1 was confirmed by serial sectioning of the casting.) Also, the boundary between grains 1 and 2 appears straight along segment AB and CD in Figure 5.

The relative orientations of grains 1 and 2 are shown superimposed in the stereographic projection in Figure 6. The vertical axis of the casting is the direction on the northern extremum of the vertical diameter of the boundary great circle. The grains have a common direction of the form $\langle 101 \rangle$ as shown in the second quadrant of Figure 6. In the plane of the form $\{101\}$ common to both grains, the $[111]_1$ direction in grain 1 is coincident with the $[\bar{1}10]_2$ direction of grain 2 (i.e. $[\bar{1}10]_2$).

The relative orientations of these grains may have been produced by several stages of twinning occurring between the grains

Figure 5. Optical Micrograph and Tracing of a Longitudinally - Cut Cast Polysilicon Section

at the initial stages of the grain nucleation process. Ellis has reported this observation for cast germanium material.^{6/} More recently, Kressel, C'Aiello, Levin, Robinson, and McFarlane have reported special orientation relationships between polycrystal grains formed within silicon ribbon material produced by the edge-defined-growth (EFG) process.^{7/} A common direction of the form $\langle 101 \rangle$ was found also for the misorientation of adjacent grains, and this appears to have been the preferred direction of crystal solidification. Also in Figure 6 the final direction of crystal solidification for grain 1 is near to the direction $[0\bar{1}\bar{1}]$ as compared with $[0\bar{1}\bar{0}]$ direction for grain 2.

From serial sections, the straight segment of boundary CD (Figure 5) was found to match the coincident orientations of the $(\bar{1}10)_2$ plane being parallel to the $(111)_1$ plane. For segment AB, a nearly coincident orientation of the $(111)_2$ plane being parallel to the $(\bar{1}\bar{1}2)_1$ plane was found. The preference of the boundary interfaces to follow apparent low energy orientations such as these may have contributed to the envelopment of grain 2 by grain 1.

Near the top of the wafer shown in the optical micrograph in Figure 5, there appears a "sinuous" grain boundary. Scanning photoresponse measurements have revealed that regions containing "sinuous" grain boundaries show an increased photoresponse in comparison to the rest of the cell. The origin of "sinuous" boundaries is attributed to the incorporation of excess solute into such boundaries during the solidification process.

The relative orientations of grains have been determined most recently by obtaining electron channelling patterns.^{8,9/} The channelling pattern is derived from electron scattering processes within a layer of material approximately 600 Å deep from the surface and is sensitively dependent on the structural perfection of this layer. These patterns, when checked against known reference orientations, allow the determination of grain orientations directly in the scanning electron microscope (SEM) at specimen locations where other SEM measurements are to be made (such as EBIC).

Figure 7A and 7B show electron channelling patterns (estimated 8° field of view) obtained from grains 1 and 2 (shown in Figure 5) respectively. The channelling patterns were obtained by orienting the grains at angles determined by the X-ray diffraction measurements. Figure 7A is the characteristic pattern for a direction of the form $\langle 111 \rangle$ while Figure 7B is the characteristic pattern for a direction of the form $\langle 100 \rangle$. These orientations have been confirmed by the X-ray measurements. Figure 8A is a SEM micrograph (30x magnification) of the grain boundary between grains 1 and 3 (shown in Figure 5) and Figure 8B is the electron channelling pattern obtained at the same location. From the X-ray orientation measurements and the individual channelling patterns obtained on each grain, the orientation of grain 1 is closest to a direction of the form $\langle 111 \rangle$ and grain 3 is closest to a direction of the form $\langle 110 \rangle$.

Figure 7A. Electron Channelling $\langle 111 \rangle$

Figure 7B. Electron Channelling $\langle 100 \rangle$

Figure 8A. SEM Micrograph Showing Boundary Between Grains 1 and 3

Figure 8B. Electron Channelling Pattern of the Same Region shown in Figure 8A

Optical Scanning System

All of the equipment needed to construct the optical scanner is in house and presently being assembled. The circuitry needed to interface the precision scanning tables and measurement apparatus with a PDP 11/03 minicomputer is designed and assembly is near completion. The minicomputer will be used to control the positioning tables in a step-and-repeat mode by accessing individual points within the cell, taking a measurement, and either plotting the data or storing it for later analysis.

IV. CONCLUSIONS

1. The effect of enhanced current collection at grain boundaries, due to dopant penetration into the boundary creating a "vertical" junction, was investigated using the cylindrical grain model previously reported. The results show that for grain sizes exceeding a few tenths of a millimeter, the minority carrier lifetime in a grain essentially determines the short-circuit photoresponse and neither collection nor recombination of minority carriers at the grain boundary will have a substantial effect.

2. The spatial dependence of the dark I-V characteristics within a polysilicon wafer was investigated by fabricating small diodes on the wafer and then measuring their dark I-V characteristics. Illuminated I-V characteristics were generated by assuming a short-circuit current density and then using the shifting approximation. The dark current of the diodes was dominated by recombination within the space-charge region well past the one-sun maximum power point and although the dark I-V characteristics of the diodes varied considerably, the illuminated characteristics did not vary greatly. Additionally, the degradation of cell performance due to areal inhomogeneity was not observed for these diodes.

3. The relative orientations of adjacent crystal grains in cast silicon have been determined by X-ray diffraction. Electron channelling patterns of individual grains were obtained and the results were confirmed by the X-ray orientation measurements. The crystal structure exhibits a $\langle 110 \rangle$ preferred growth direction. Also the preference of boundary interfaces between grains to be crystallographic planes can act to limit the growth of individual crystals. Finally, the origin of "sinuous" boundaries is attributed to the incorporation of excess solute into such boundaries during the solidification process.

V. SUMMARY OF RESULTS TO DATE

Measurement techniques used to date include standard measurements such as dark and light I-V characteristics, I_{sc} - V_{oc} and spectral response. Additionally the spatial dependence of I_{sc} has been investigated using a laser scanner and a fine light spot. The relative orientations of adjacent crystal grains and the nature of the boundaries between grains have been studied by X-ray diffraction, optical microscopy, and scanning electron microscopy (SEM) methods. Theoretical modeling, so far, has been primarily used to investigate the effect of grain size and grain boundary recombination on the short-circuit current and to investigate the "vertical" junction effect.

The major effects seen to date which limit the photovoltaic conversion efficiency in polysilicon solar cells are summarized below:

Short-Circuit Current - Laser and fine light spot scanning has shown both increases and decreases in I_{sc} near grain boundaries. Other boundaries, in particular twin boundaries, exhibit no change in I_{sc} . Theoretical modeling has shown that for grain radii exceeding a few tenths of a millimeter - which is the case for the polycrystalline silicon investigated in this program - the minority carrier lifetime in the grain determines the short-circuit current response.

Fill Factor and V_{oc} - The dark current of the polysilicon solar cells studied here is generally dominated by recombination within the space-charge region well past the one-sun maximum power point.

This has the effect of lowering the output power via the fill factor and the open circuit voltage. It is presently uncertain as to whether space-charge recombination dominates in the grains or at grain boundaries.

Lowering of the fill factor and V_{oc} because of ohmic shunts is also observed. This is believed to be caused by dopant penetration along grain boundaries to the back contact, thereby shunting the junction.

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