301
11-7-80
JLP

On 2026

MASTER

DSE-4042-T37

**PHYSICAL MODELS OF THIN FILM POLYCRYSTALLINE SOLAR CELLS
BASED ON MEASURED GRAIN-BOUNDARY AND ELECTRONIC-
PARAMETER PROPERTIES**

Quarterly Report

By
F. A. Lindholm
J. G. Fossum
P. A. Holloway
A. Neugroschel

December 1979

Work Performed Under Contract No. EG-77-C-01-4042

College of Engineering
University of Florida
Gainesville, Florida

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$6.00
Microfiche \$3.50

PHYSICAL MODELS OF THIN FILM POLYCRYSTALLINE SOLAR CELLS BASED
ON MEASURED GRAIN-BOUNDARY AND ELECTRONIC-PARAMETER PROPERTIES

Quarterly Report

December 1979

Prepared for the
SOLAR ENERGY RESEARCH INSTITUTE

Contract No. XS-9-8275-1

Program Manager: Fredrik A. Lindholm

Principal Investigators: F. A. Lindholm, J. G. Fossum, P. A. Holloway, and
A. Neugroschel

Graduate Students: D. Lee, J. A. Mazer, P. Russell, and R. Sundaresan
College of Engineering
UNIVERSITY OF FLORIDA
Gainesville, Florida 32611

This report summarizes the technical findings obtained at the University of Florida during the first quarter under support by SERI contract XS-9-8275-1. The contract began September 15, 1979; funding became available on November 6, 1979.

In Section 1 of this report, we describe the program objectives. Section 2 briefly summarizes that part of the program for which most progress was made during the quarter: the development of theory for grain-boundary and intra-grain recombination in polysilicon pn-junction solar cells. Subsequent sections provide details.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States, nor any agency thereof, nor any of their employees, makes any warranty, express or implicit, or assumes any legal liability or responsibility, for any third party's use, or the results of such use of any information, apparatus, product or process described in this report, or represents that its use by such third party would not infringe privately owned rights.

TABLE OF CONTENTS

	page
1. Program objectives.....	1
2. Summary/overview.....	3
3. Introduction.....	4
4. Grain-boundary model.....	6
5. Effects of a grain boundary adjacent to a quasi-neutral region.....	11
6. Effects of a grain boundary within the junction space-charge..... region	16
7. Discussion.....	19
8. Acknowledgements.....	21
9. References.....	22
10. Figure captions and Figures.....	24
11. Conclusions and Recommendations for future work.....	34

1. PROGRAM OBJECTIVES

The research seeks the following: to identify and characterize the basic photovoltaic mechanisms that govern the conversion efficiency of polycrystalline thin-film solar cells; to experimentally determine the electronic parameters related to these photovoltaic mechanisms; and to relate these mechanisms and parameters to the conversion efficiency through theoretical physical models developed for engineering design. These objectives are all intimately related. The emphasis of our work is now on polysilicon, although it is building a foundation of understanding useful for similar research in the future on other thin-film materials.

The following photovoltaic mechanisms are particularly important of polycrystalline cells and are under study: grain-boundary effects, including the effects on carrier recombination and the contributions to low shunt or high series resistances; positional dependencies of material and structural parameters in directions both normal and parallel (areal inhomogeneity) to the illuminated surface; and dependence of the photovoltaic mechanisms and their associated parameters on illumination level.

Much of our research now concentrates on (characterizing grain-boundary and intra-grain) recombination and its effects on solar-cell performance. But we also work on photovoltaic mechanisms associated with heavy-doping concentrations, which are relevant to thin-film polycrystalline cells for four reasons. First, one of the goals of the SERI program and our work is to obtain an understanding of grain-boundary recombination that will enable its suppression so that high efficiency can be achieved. In highly efficient polycrystalline cells the structure and the material parameters will be such that many of the same photovoltaic mechanisms that limit the obtainable efficiency of single-crystal silicon cells will also limit the obtainable efficiency of polycrystalline silicon cells. Thus we conduct studies to determine the

relative importance to cell performance of Auger recombination, surface recombination velocity, and bandgap narrowing in the heavily doped regions of p-n junction single-crystal silicon solar cells. Second, these studies also relate to characterizing the recombination current at a grain boundary surface passivated by the diffusion of dopant impurities down the grain boundary such that a pn or a high-low junction surrounds the grain boundary. Third, if high levels of base doping concentration or profiled base doping concentrations are used, then the effects of heavy doping within a grain become important. Fourth, bandgap narrowing and distorted energy bands can occur in the grain boundaries of polycrystalline materials, introduced by the random atomic potential associated with dangling bonds.

2. SUMMARY/OVERVIEW

Our work toward obtaining a fundamental description of these recombination currents has consisted of both theoretical and experimental studies. In the theoretical studies, which this report describes, we built upon the foundations laid by earlier workers including Card and Yang, Kazmerski, and Seager and Castner. The results of these earlier workers contained many useful concepts and experimental data. Our aim was to supplement this previous work by emphasizing physical insight and providing justification for the assumptions and approximations used, and, most importantly, to provide theoretical models whose predictions could be tested by comparison with experimental data on the recombination currents.

Our theoretical analysis reveals that, in general, the description of intra-grain and grain-boundary recombination in a polysilicon solar cell requires the solution of a nonlinear three-dimensional boundary-value problem. At this stage of the research, we have stopped short of attempting a general solution of this problem, but, rather, have considered cases of practical interest for which this problem becomes greatly simplified and analytically tractable. For these cases, we solve the resulting linear three-dimensional boundary-value problem, and describe the relationships among the effective minority-carrier lifetime, the actual lifetime, and the effective grain-boundary surface recombination velocity. Current-voltage characteristics measured on non-illuminated p-n junction cells fabricated on both bulk and thin-film polysilicon are consistent with our analysis. Furthermore, the measurements made on p-n junctions fabricated on bulk (Wacker) polysilicon, when interpreted by our analysis, yield estimates of important parameters characterizing the grain boundaries and their influence on carrier recombination.

3. INTRODUCTION

Solar cells fabricated on polycrystalline silicon, either bulk [1] or thin-film [2], can potentially be cost-effective when used in terrestrial photovoltaic energy-conversion systems. To achieve this goal, the polysilicon cell efficiency must be increased considerably from its present values. A severe limitation to the cell efficiency is due to the grain boundaries and their influence on carrier recombination. To remove this limitation, an understanding of the fundamental physics underlying the effects of the grain boundaries on cell performance is helpful.

In this paper we discuss this fundamental physics, and, based on it, we develop models for recombination currents in polysilicon pn-junction solar cells. Several analytic approximations, suggested by physical insight, are used and checked ultimately for self-consistency with the results of the analysis. The models are defined such that their parameters can be related directly to measurements, and the models are hence useful in interpreting experimental results. They also can be used to study, in a systematic way, cell-design modifications to improve the efficiency, e.g., grain-boundary passivation techniques.

The development of these physical solar-cell models begins with the definition of a fundamental model for the grain boundary itself. In particular, this grain-boundary model relates carrier recombination through grain-boundary "surface" states to the excitation, i.e., the separation of the electron and hole quasi-Fermi levels. This fundamental model is then applied to the portions of the grain boundary within the quasi-neutral and pn-junction space-charge regions of the cell. The general result of these applications is that the description of intra-grain and grain-boundary recombination in a polysilicon solar cell requires the solution of a boundary-value problem which is nonlinear and three-dimensional. A primary emphasis in this paper is placed on approximations that make this problem tractable to analysis.

In quasi-neutral regions, the effective surface recombination velocity for minority carriers at the edge of a grain-boundary space-charge region is, in general, dependent on the excitation. There are, however, cases of practical interest for which the boundary-value problem is tractable, i.e., for which the effective recombination velocity is constant. For these cases, we solve the three-dimensional boundary-value problem, and describe the relationships among the effective minority-carrier lifetime, the actual lifetime, and the effective grain-boundary surface recombination velocity.

Analysis of the two-dimensional carrier flow problem in the pn-junction space-charge region near a grain boundary yields an $\exp(qV/2kT)$ dependence for the grain-boundary recombination current (V is the cell forward bias). The reciprocal slope factor of exactly two results from quasi-equilibrium and steady-state conditions at the grain boundary.

Current-voltage characteristics measured on non-illuminated pn-junction cells fabricated on both bulk and thin-film polysilicon are consistent with our analysis. The analysis, and the physical insight it provides, are thus useful in studying the influence of the fundamental physical mechanisms on the performance of polysilicon solar cells. A description of open-circuit voltage is obtained by assuming that the current in the illuminated cell is approximated well by the dark current shifted by the short-circuit current. The description of short-circuit current is made possible by the determination of the effective grain-boundary surface recombination velocity in our analysis.

4. GRAIN-BOUNDARY MODEL

We begin our analysis by developing a model that describes carrier recombination at the grain boundary resulting from excitation, i.e., light or junction bias. Our work discussed in this section supplements previous work [3], [4] by emphasizing physical insight, and by providing justification for the assumptions and approximations on which the model is based. In later sections, this grain-boundary model enables the formulation of the boundary-value problems that define the grain-boundary and intra-grain recombination currents in pn-junction polysilicon solar cells.

A. Thermal Equilibrium

To provide a basis for non-equilibrium analysis, we first consider the grain boundary in thermal equilibrium [5]. The electron energy-band diagram in the vicinity of a grain boundary, for p-type grains, is shown in Figure 1. We have assumed that the grain-boundary width is much smaller than the space-charge-region width, w_{SCRO}^{GB} . This allows us to treat the grain boundary as a surface, characterized, in part, by distributions of donor, $N_{ST}^D(E)$, and acceptor, $N_{ST}^A(E)$, surface states within the bandgap.

Depending on the location of the Fermi level E_F , a net charge density Q_{GB} exists on these states:

$$Q_{GB} = q \int_0^{E_g} N_{ST}^D(E) [1 - f(E, E_F)] dE - q \int_0^{E_g} N_{ST}^A(E) f(E, E_F) dE, \quad (1)$$

where $f(E, E_F)$ is the Fermi-Dirac distribution function. In (1), E_F is determined by the doping level N_{AA} :

$$[E_F - E_V]_{x > w_{SCRO}^{GB}} \approx kT \ln \left(\frac{N_V}{N_{AA}} \right), \quad (2)$$

where N_v is the effective density of states at the valence-band edge.

Typically, in polycrystalline silicon, the nature of $N_{ST}^D(E)$ and $N_{ST}^A(E)$ is such that Q_{GB} is positive for p-type grains [5]. This causes the electron energy bands to bend downward, as pictured in Figure 1. The resulting grain-boundary potential barrier height, ϕ_{BO} , is obtained from the neutrality condition,

$$\frac{Q_{GB}}{2} + Q_{SCR} = 0, \quad (3)$$

where Q_{SCR} is the space charge density on either side of the grain boundary. In writing (3), we have assumed that the energy bands are symmetrical with respect to the grain-boundary surface. This assumption requires that the adjacent grains have identical material parameters (N_{AA} , etc.). Typical values of ϕ_{BO} [5], [6] are such that the hole and electron densities near the grain-boundary surface are much less than N_{AA} . This assures the validity of the depletion-approximation solution of Poisson's equation, which gives

$$Q_{SCR} \approx -qN_{AA}W_{SCRO}^{GB} \approx -(2q\epsilon_{Si}N_{AA}\phi_{BO})^{1/2}. \quad (4)$$

The simultaneous solution of (1) - (4), with the relationship,

$$E_F = q\phi_{BO} + [E_F - E_v]_{x > W_{SCRO}^{GB}}, \quad (5)$$

evident in Figure 1, describes the equilibrium barrier height:

$$\phi_{BO} = \phi_{BO}[N_{AA}, N_{ST}^D(E), N_{ST}^A(E)] \quad (6)$$

B. Non-Equilibrium

We now discuss the effects of excitation on the energy-band picture in Figure 1. Consider the quasi-neutral portion of the grain ($x > W_{SCRO}^{GB}$). For low-level injection ($P \approx N_{AA}$), the hole quasi-Fermi level E_{FP} remains fixed relative to the valence-band edge, while the electron quasi-Fermi level E_{FN} rises

above E_{FP} . To extend the non-equilibrium energy-band picture into the grain-boundary space-charge region, we consider two limiting cases. In the first, the parameters characterizing the grain-boundary region are such that the recombination occurring there reduces the excess electron density to nearly zero at the edge of the space-charge region, as shown in Figure 2. The band picture within the space-charge region is virtually unaltered from that in equilibrium.

In the second case, the grain-boundary recombination rates are small enough that both E_{FN} and E_{FP} are nearly flat and that their separation is nearly constant across the space-charge region, as illustrated in Figure 3. This non-equilibrium condition in the space-charge region results in a change of the charge on the grain-boundary surface states. To describe this change, assume initially that the barrier height remains at its equilibrium value as the excitation is applied. Then, as E_{FN} moves above E_{FP} , the electron density $N(0)$ increases, which leads to an increase in the net electron capture rate of the surface states. Ultimately, in the steady state then, the number of electrons occupying the surface states is larger than that in equilibrium. Thus, Q_{GB} and the barrier height ϕ_B are smaller than their equilibrium values, which means that the hole density $P(0)$ has increased.

The separation of E_{FN} and E_{FP} shown in Figure 3 implies a net hole-electron recombination rate at the grain-boundary surface. To make a detailed quantitative analysis of this recombination rate tractable, and to provide physical insight, we approximate the distribution of grain-boundary surface states by a monoenergetic (E_T) density (N_{ST} per unit area) of recombination centers near midgap ($E_T \approx E_g/2$). This assumption is consistent with the experimental observations that, in polysilicon, the grain-boundary surface-state distribution peaks near midgap [6].

The grain-boundary model based on this assumption and on the quasi-equilibrium assumption of flat quasi-Fermi levels, i.e.,

$$P(x)N(x) \equiv n_i^2 \exp\left(\frac{E_{FN} - E_{FP}}{kT}\right) \approx \text{constant} \quad (7)$$

for $0 \leq x \leq W_{SCR}^{GB}$, is illustrated in Figure 4. Using this model, we shall derive an expression for the hole-electron recombination rate U_S at the grain-boundary surface, and we shall check the results for self-consistency with the quasi-equilibrium assumption.

The thermal recombination-generation process at the grain boundary is described in the Shockley-Read-Hall theory [7]. With $E_T \approx E_g/2$, the net rate (per unit area) of hole-electron-pair recombination through the centers is

$$U_S \approx \frac{P(0)N(0) - n_i^2}{\frac{P(0) + n_i}{v_{th}^n \sigma_n N_{ST}} + \frac{N(0) + n_i}{v_{th}^p \sigma_p N_{ST}}} \quad (8)$$

where v_{th}^p and v_{th}^n are the hole and electron thermal velocities, and σ_p and σ_n are the hole and electron capture cross-sections. Based on our discussion of non-equilibrium as depicted in Figure 4, we assume that

$$P(0), N(0) \gg n_i \quad (9)$$

We demonstrate later that the excitation necessary to validate the inequalities in (9) is common for typical solar-cell operation. These inequalities simplify (8) to

$$U_S \approx \frac{P(0)N(0)}{\frac{P(0)}{S_n} + \frac{N(0)}{S_p}} \quad (10)$$

in which we have defined the hole and electron grain-boundary (surface) recombination velocities,

$$S_p \equiv v_{th}^p \sigma_p N_{ST} \quad (11)$$

and

$$S_n \equiv v_{th}^n \sigma_n N_{ST} \quad (12)$$

The grain-boundary recombination rate as given in (10) is not definitively specified since $P(0)$ and $N(0)$ are unknown. Only the product, $P(0)N(0)$, related

to the excitation by (7), is known at this stage of the analysis. To specify $P(0)$ and $N(0)$, we use the following argument. Since (a) the excitation provides substantial numbers of holes and electrons at the grain-boundary surface, and (b) no physical constraints are imposed on ϕ_B , in contrast, for example, to the presence of constraints on the barrier height of a pn junction, we assume that the surface states will fill or empty, and thereby alter ϕ_B , until the condition which most enhances the tendency toward equilibrium is reached. That is, for any non-equilibrium, steady-state condition, with sufficient excitation, $P(0)$ and $N(0)$ will have attained the values that maximize U_S . Combining (7) and (10) implies that U_S reaches a maximum value when

$$S_p P(0) = S_n N(0) \quad (13)$$

The relationship between $P(0)$ and $N(0)$ in (13), which implies equal hole and electron capture rates of the centers [7], allows us to completely specify the grain-boundary recombination in terms of the excitation. If we combine (7) and (13), we obtain

$$P(0) = \left(\frac{S_n}{S_p} \right)^{1/2} n_i \exp \left(\frac{E_{FN} - E_{FP}}{2kT} \right) \quad (14)$$

and

$$N(0) = \left(\frac{S_p}{S_n} \right)^{1/2} n_i \exp \left(\frac{E_{FN} - E_{FP}}{2kT} \right) \quad (15)$$

Inserting (14) and (15) into (10) yields

$$U_S = \frac{1}{2} (S_p S_n)^{1/2} n_i \exp \left(\frac{E_{FN} - E_{FP}}{2kT} \right) \quad (16)$$

The sufficient-excitation conditions given in (9), on which the validity of (16) is partly based, are now completely specified by (14) and (15). The conditions typically require that $(E_{FN} - E_{FP})$ be greater than about $4kT$. Later, when we use (16) to characterize the recombination currents in polysilicon solar cells, we shall be able to assess when this requirement is met.

As we mentioned earlier, $\phi_B < \phi_{B0}$. Using the grain-boundary model we have developed, we can describe ϕ_B in terms of the excitation. Consider the case in

which low-level injection prevails in the quasi-neutral (p-type) grain adjacent to the grain boundary:

$$P(W_{SCR}^{GB}) \approx N_{AA} \quad (17)$$

Because of the assumption of quasi-equilibrium in the grain-boundary space-charge region (Figure 4),

$$P(W_{SCR}^{GB}) \approx P(0) \exp\left(\frac{q\phi_B}{kT}\right) \quad (18)$$

Combining (14), (17), and (18), we obtain

$$\phi_B \approx \frac{kT}{q} \ln \left[\left(\frac{S_P}{S_n} \right)^{1/2} \frac{N_{AA}}{n_1} \right] - \frac{E_{FN} - E_{FP}}{2q} \quad (19)$$

Equation (19) describes how ϕ_B decreases with increasing excitation. Note that it does not reduce to $\phi_B = \phi_{B0}$ when $(E_{FN} - E_{FP}) = 0$. The reason for this is that (19) is valid only for the sufficient-excitation conditions described by (9), (14), and (15).

5. EFFECTS OF A GRAIN BOUNDARY ADJACENT TO A QUASI-NEUTRAL REGION

Having developed a model [Equation (16)] that describes the recombination at a grain boundary adjacent to a quasi-neutral region in terms of the excitation, we now apply it to a pn-junction polysilicon solar cell. In general, we want to characterize an illuminated solar cell that is forward-biased by the voltage developed across its load. Based on previous demonstrations of the applicability of the superposition principle to silicon solar cells [8]-[10], we assume that the current in the illuminated cell is approximated well by the current in the non-illuminated cell under forward bias shifted by the short-circuit photocurrent. Thus, the solar-cell characterization problem simplifies to separate characterizations of the dark current and the short-circuit current.

We focus attention on the dark current-voltage characteristic of the polysilicon solar cell. In this section, we limit consideration to that portion of the current influenced by the grain boundary adjacent to a quasi-neutral region, for example, the quasi-neutral base region. This current consists of two components: (a) the current

I_{GB}^B supporting recombination at the grain-boundary surface; and (b) the current I_{QN}^B supporting recombination within the quasi-neutral base of the adjacent grain. These currents are illustrated in Figure 5, in which we have assumed columnar grains perpendicular to the plane of the pn junction.

The grain-boundary model developed in Section II will serve as the basis for the description of $I_{GB}^B(V)$ and $I_{QN}^B(V)$, or, from a more general viewpoint, for the specification of the boundary condition for minority carriers in the quasi-neutral base at the edge of the grain-boundary space-charge region. We shall thereby completely describe the effects of the grain boundary on the minority-carrier transport in the base. A similar description for the emitter follows from the analogous application of the grain-boundary model.

Using (16), and referring to Figures 4 and 5, we express the grain-boundary recombination current density ($J_{GB}^B \equiv dI_{GB}^B/dA_{GB}$ where A_{GB} is the grain-boundary area) as

$$\begin{aligned} J_{GB}^B &\equiv -J_P(0) \equiv J_N(0) \\ &= \frac{q}{4}(S_p S_n)^{1/2} n_i \exp\left(\frac{E_{FN} - E_{FP}}{2kT}\right) \end{aligned} \quad (20)$$

In (20), J_P and J_N are the hole and electron current densities, which, at $x = 0$, are equal in magnitude but opposite in direction for the assumed steady-state condition. Note that J_{GB}^B in (20) accounts for one-half of the total grain-boundary recombination current.

From (7), evaluated at $x = w_{SCR}^{GB}$, we rewrite (20) as

$$J_N(0) = \frac{q}{4}(S_p S_n)^{1/2} [P(w_{SCR}^{GB})N(w_{SCR}^{GB})]^{1/2} \quad (21)$$

If we assume low-level injection in the quasi-neutral base region, (17) applies.

Furthermore, since typically N_{ST}/w_{SCR}^{GB} is much greater than the average recombination center density in the grain-boundary space-charge region [6], we can neglect recombination in the space-charge region; i.e.,

$$U_S \gg \int_0^{w_{SCR}^{GB}} U dx, \quad (22)$$

where U is the recombination rate per unit volume. Then, from (21),

$$J_N(W_{SCR}^{GB}) \approx \frac{q}{4} (S_p S_n)^{1/2} N_{AA}^{1/2} [N(W_{SCR}^{GB})]^{1/2}. \quad (23)$$

The electron (minority-carrier) current density at the edge of the grain-boundary space-charge region can be expressed in terms of an effective electron surface recombination velocity:

$$J_N(W_{SCR}^{GB}) \equiv q S_{n(eff)}^{GB} N(W_{SCR}^{GB}) \quad (24)$$

Combining (23) and (24), we obtain

$$S_{n(eff)}^{GB} = \frac{1}{4} (S_p S_n)^{1/2} N_{AA}^{1/2} [N(W_{SCR}^{GB})]^{-1/2}. \quad (25)$$

Equations (23)-(25) describe the main result of this section: a nonlinear boundary condition for minority carriers at the edge of the grain-boundary space-charge region. It implies that, generally, the solution of the (three-dimensional) carrier-transport problem in the quasi-neutral grain regions is complicated. We discuss this solution later.

A simplification occurs in the analysis for high levels of carrier injection, such that, because of quasi-neutrality,

$$P(W_{SCR}^{GB}) \approx N(W_{SCR}^{GB}) \quad (26)$$

For this case, (21), (22), (24), and (26) yield

$$S_{n(eff)}^{GB} = \frac{(S_p S_n)^{1/2}}{4} \quad (\text{high injection}) \quad (27)$$

and the boundary condition is linear.

Our analysis is based on the assumption of quasi-equilibrium (flat quasi-Fermi levels) in the grain-boundary space-charge region, expressed in (7) and illustrated in Figure 4. We now check the result (23) for self-consistency with this assumption.

Since $P(x) > N(x)$, as implied by our analysis and Figure 4, the validity of the quasi-equilibrium assumption is threatened most by a possible significant gradient of E_{FN} necessary to support a substantial grain-boundary recombination current:

$$J_N = \mu_n N \frac{dE_{FN}}{dx} \quad (28)$$

This possibility is illustrated in Figure 6. The validity of the quasi-equilibrium assumption demands that

$$\Delta E_{FN} \equiv \int_0^{w_{SCR}^{GB}} dE_{FN} = \int_0^{w_{SCR}^{GB}} \frac{J_N dx}{\mu_n N} \ll qV_B, \quad (29)$$

where qV_B is the separation of E_{FN} and E_{FP} at the edge of the space-charge region:

$$qV_B \equiv [E_{FN} - E_{FP}]_x = w_{SCR}^{GB}. \quad (30)$$

Because of the assumed inequality in (22), J_N is nearly constant in the space-charge region, and is given by (23). Therefore, because $N(w_{SCR}^{GB}) < N(x)$, the inequality in (29) is valid if

$$\frac{J_N(w_{SCR}^{GB}) w_{SCR}^{GB}}{\mu_n N(w_{SCR}^{GB})} \ll qV_B. \quad (31)$$

Using (23) and (30), we rewrite (31) as

$$(S_p S_n)^{1/2} \ll \frac{4\mu_n n_i}{w_{SCR}^{GB} N_{AA}} V_B \exp\left(\frac{qV_B}{2kT}\right) \equiv S_{QE}. \quad (32)$$

Thus, (32) defines an upper limit, S_{QE} , for the grain-boundary ambipolar surface recombination velocity, $(S_p S_n)^{1/2}$, above which the quasi-equilibrium assumption is invalid. Note that S_{QE} increases with the excitation V_B , thereby expanding the range of validity of quasi-equilibrium.

Typically, for polysilicon cells operated under normal conditions, (32) is satisfied. For example, with $N_{AA} = 10^{16} \text{ cm}^{-3}$, $V_B = 0.5V$, and $w_{SCR}^{GB} \sim 0.1 \mu\text{m}$, we find $S_{QE} \sim 5 \times 10^6 \text{ cm/sec}$. Even in high-angle grain boundaries, where N_{ST} is high, $(S_p S_n)^{1/2}$ is considerably smaller than this value of S_{QE} [3], [4].

In this section, we have shown that minority-carrier transport in the quasi-neutral portion of a grain is, in general, subject to a nonlinear boundary condition at the grain boundaries; that is, the surface recombination velocity given in (25) is dependent on the injection level. This result is based on the assumption of quasi-equilibrium in the grain-boundary space-charge region, which

is assured by the inequality expressed in (32). For this case, the general three-dimensional boundary-value problem for carrier transport in the grain is difficult to solve.

If (32) is not valid, or if $S_{n(\text{eff})}^{\text{GB}}$ is much larger than the diffusion velocity characterizing carrier flow in the quasi-neutral grain to the grain boundary, the boundary-value problem and the related grain-boundary model can be simpler. To develop this model, assume that $S_{n(\text{eff})}^{\text{GB}}$ is so high that excess carrier densities cannot be sustained in the grain-boundary space-charge region; i.e., $(E_{\text{FN}} - E_{\text{FP}}) \approx 0$ and $\phi_B \approx \phi_{B0}$. This is equivalent to assuming that

$$S_{n(\text{eff})}^{\text{GB}} \rightarrow \infty, \quad (33)$$

which results in a linear boundary condition, $N(W_{\text{SCR}}^{\text{GB}}) \approx 0$. The physics underlying this model was previously discussed in connection with the band diagram of Figure 2.

When (33) adequately characterizes the grain boundaries, or when $S_{n(\text{eff})}^{\text{GB}}$ is constant, the three-dimensional minority-carrier transport within a grain can be described by Shockley's filament theory [11]. For example, consider the square-faced filament, or grain, pictured in Figure 7, defined by four lateral surfaces, or grain boundaries. If we think of this filament as that portion of a columnar grain (perpendicular to the plane of the junction) within the quasi-neutral base region of the n^+p polysilicon diode in Figure 5, the solution of the three-dimensional electron continuity equation is obtained directly from Shockley's analysis.

If we assume that the filament (grain) length (base width) W_B is longer than the electron diffusion length L_n , then the total electron current injected into the filament (grain) is [11]

$$I_G^B = d_G^2 \left[\frac{q n_i^2}{N_{\text{AA}}} \left(\frac{D_n}{\tau_{n(\text{eff})}} \right)^{1/2} \exp\left(\frac{qV}{kT}\right) \right] \quad (34)$$

In (34), d_G is the grain size, D_n is the electron diffusion coefficient, and $\tau_{n(\text{eff})}$ is the effective electron lifetime as derived by Shockley [11], which accounts for electron recombination both within the grain (I_{QN}^B) and at the grain

boundaries (I_{GB}^B) as illustrated in Figure 5:

$$\frac{1}{\tau_{n(\text{eff})}} = \frac{1}{\tau_n} + 2 D_n b_0^2, \quad (35)$$

where

$$b_0 \tan(b_0 \frac{d_G}{2}) = \frac{S_{n(\text{eff})}^{GB}}{D_n}. \quad (36)$$

In (35), τ_n is the actual electron lifetime within the grain, and b_0 is a coefficient resulting from the solution of the boundary-value problem and given by the transcendental equation (36).

Note that when (33) applies, $b_0 = \pi/d_G$, and

$$\begin{aligned} \frac{1}{\tau_{n(\text{eff})}} &= \frac{1}{\tau_n} + \frac{2\pi^2 D_n}{d_G^2} \\ &= \frac{1}{\tau_n} \left(1 + 2\pi^2 \frac{L_n^2}{d_G^2} \right). \end{aligned} \quad (37)$$

The combination of (34) and (37) describes electron recombination in the base region of a forward-biased n^+p polysilicon diode as a function of grain size for this case. As d_G decreases, $\tau_{n(\text{eff})}$ decreases, and the current density I_G^B/d_G^2 increases. For d_G large, $\tau_{n(\text{eff})} \approx \tau_n$, and I_{QN}^B dominates; for d_G small, $\tau_{n(\text{eff})} \approx d_G^2/2\pi^2 D_n$, and I_{GB}^B dominates.

In Figure 8, we have plotted the dependence of $\tau_{n(\text{eff})}$ on d_G , as given by (37), for three representative values of τ_n (and $L_n = \sqrt{D_n \tau_n}$). We have assumed that $D_n = 25 \text{ cm}^2/\text{sec}$ and that changes in D_n due to changes in N_{AA} are of only secondary importance. Note in (34) that the electron recombination current depends on $1/N_{AA}$ in addition to the likely dependence implicit in $\tau_{n(\text{eff})}(N_{AA})$ resulting from $\tau_n(N_{AA})$.

6. EFFECTS OF A GRAIN BOUNDARY WITHIN THE JUNCTION SPACE-CHARGE REGION

In this section, we discuss the application of the grain-boundary model developed in Section II, i.e., (16), to that portion of the grain boundary within

the pn-junction space-charge region illustrated in Figure 9 for columnar grains. Consider the junction space-charge region away from the grain boundary. When the junction is forward-biased, this region is characterized by: (a) substantial densities of holes and electrons; (b) large gradients (y-direction) of these densities resulting in large carrier diffusion tendencies; (c) a large electric field E_y resulting in large carrier drift tendencies that nearly balance the diffusion tendencies; and consequently, (d) nearly flat hole and electron quasi-Fermi levels. If the majority-carrier quasi-Fermi levels are nearly flat across the quasi-neutral regions to the contacts (e.g., if ohmic drops are negligible), then, in the junction space-charge region,

$$E_{FN} - E_{FP} \approx qV \quad (38)$$

The presence of a grain boundary in the junction space-charge region distorts this characterization by introducing an x-component of electric field. This component, which arises from the charge on the grain-boundary surface states, produces a two-dimensional boundary-value problem. The solution of this problem would describe the two-dimensional flow of holes and electrons to the grain-boundary surface where they recombine, as illustrated in Figure 9.

The recombination current density at the grain boundary, J_{GB}^{SCR} , can be determined without having to solve this two-dimensional boundary-value problem completely provided certain conditions prevail. These conditions are that P and N are large enough and $|\bar{J}_P|$ and $|\bar{J}_N|$ are small enough that $|\nabla E_{FP}|$ and $|\nabla E_{FN}|$ are sufficiently small to assure the validity of the quasi-equilibrium approximation expressed in (38). We assume these conditions prevail and later check the results they yield for self-consistency.

We therefore can use (38) in (16) to obtain

$$J_{GB}^{SCR} = \frac{qU_S}{2} = \frac{q}{4}(S_p S_n)^{1/2} n_i \exp\left(\frac{qV}{2kT}\right) \quad (39)$$

The reciprocal slope factor of exactly two is a direct result of the grain-boundary

physics described in this paper. It should not be confused with the result of the Sah-Noyce-Shockley analysis of pn-junction space-charge-region recombination [12], in which the reciprocal slope factor is voltage-dependent and has a value between one and two depending on the parameters characterizing the dominant recombination-generation center. In our analysis, the value of exactly two occurs because of quasi-equilibrium and the steady-state condition of maximum U_S at the grain boundary. Using different, but equivalent, reasoning, Henry, et al. [13] obtained the $\exp(qV/2kT)$ dependence for surface recombination in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterojunctions.

A thorough check of (39) for self-consistency with the quasi-equilibrium assumption (38) is more difficult than the self-consistency check of (23) described in Section III because of the two-dimensionality of the present problem. However, a worst-case check of (39) can be made by focusing attention on the two planes defined by the edges of the junction space-charge region. At these planes, the y-dependence of the carrier flow disappears, and the analysis reduces, in form, to the one-dimensional treatment of Section III.

Thus, in analogy to (31), the following inequalities describe the conditions for which quasi-equilibrium exists at the base and emitter edges, respectively, of the junction space-charge region in the vicinity of a grain boundary:

$$\frac{J_{GB}^{SCR, GB}}{\mu_n N_{GB}^{(W_{SCR}^{GB})}} \ll qV \quad ; \quad (40)$$

$$\frac{J_{GB}^{SCR, GB}}{\mu_p P_{GB}^{(W_{SCRE}^{GB})}} \ll qV \quad . \quad (41)$$

In (41), W_{SCRE}^{GB} is the grain boundary space-charge-region width adjacent to the (n^+) quasi-neutral emitter as indicated in Figure 9. These inequalities represent worst-case conditions since they involve minority carriers at planes where their quasi-Fermi level gradients (x-direction) are maximum.

Using (39), (40) and (41) become

$$(S_p S_n)^{1/2} \ll \frac{4\mu_p n_i}{W_{GB} N_{AA}} V \exp\left(\frac{qV}{2kT}\right) \quad (42)$$

and

$$(S_p S_n)^{1/2} \ll \frac{4\mu_p n_i}{W_{GB} N_{DD}} V \exp\left(\frac{qV}{2kT}\right) \quad (43)$$

In (43), N_{DD} is the net donor doping density at the emitter edge of the junction space-charge region. We assume that N_{DD} is low enough that n_i in (43) is well approximated by the intrinsic carrier density in pure silicon. If both of these worst-case conditions are satisfied, the quasi-equilibrium assumption is valid and (39) describes J_{GB}^{SCR} adequately. Note that in writing (42) and (43), as well as (32), we have implicitly assumed that $(S_p S_n)^{1/2}$ is constant everywhere along the grain boundary.

7. DISCUSSION

The main objectives of this paper have been to describe the physics controlling recombination in polysilicon pn-junction solar cells and to develop models characterizing this recombination whose parameters can be related directly to experiment. A model describing recombination through grain-boundary surface states was developed from an understanding of the important physical mechanisms. This understanding suggested several analytic approximations which simplified the modeling and which were later checked for self-consistency with the results of the analysis.

Assuming columnar grains, we then applied the grain-boundary model to those portions of the grain boundary adjacent to quasi-neutral regions. The general result of this application is a nonlinear boundary condition (effective surface recombination velocity) for minority carriers in the quasi-neutral region at the edge of the grain-boundary space-charge region. Thus, the description of intra-grain and grain-boundary recombination in a polysilicon solar cell requires,

in general, the solution of a boundary-value problem which is nonlinear and three-dimensional.

There are cases of practical interest for which this boundary-value problem is analytically tractable. If, for example, high-injection conditions exist at the edge of the grain-boundary space-charge region, the effective surface recombination velocity is constant, and the boundary-value problem is linear. The problem is also linear when the effective surface recombination velocity is high enough to prevent accumulation of excess carriers at the edge of the grain-boundary space-charge region. For this case, the grain-boundary barrier height remains at its equilibrium value, and the grain boundary is characterized by an infinite effective surface recombination velocity.

If the effective grain-boundary surface recombination velocity is constant, Shockley's filament theory [11] can be used to solve the three-dimensional boundary-value problem and to describe the intra-grain and grain-boundary recombination current in the non-illuminated cell. This theory defines the effective minority-carrier lifetime in a grain in terms of the actual lifetime and the effective surface recombination velocity.

We next applied the grain-boundary model to the portion of the grain boundary within the junction space-charge region. Careful attention was given to the two-dimensionality of the carrier flow problem in this region, and from it came an $\exp(qV/2kT)$ dependence for the grain-boundary recombination current. We emphasize that the reciprocal slope factor of exactly two results from the quasi-equilibrium and steady-state conditions at the grain boundary, and it should not be confused with the results of the Sah-Noyce-Shockley analysis [12] nor with the consequences of high-level injection in a quasi-neutral region [14].

Recent experimental results are consistent with our theoretically based prediction of an $\exp(qV/2kT)$ component of recombination current in polysilicon pn-junction solar cells. Current-voltage characteristics measured in non-illuminated

cells fabricated on bulk [15] and thin-film [16] polycrystalline silicon have shown the $\exp(qV/2kT)$ dependence. Such data, when interpreted by our theory, can yield an evaluation of the important grain-boundary parameter, $(S_p S_n)^{1/2}$, the ambipolar surface recombination velocity.

Our analysis of the dark current-voltage characteristic of polysilicon pn-junction solar cells, and the physical insight it provides, reveal how the fundamental physical mechanisms influence the cell conversion efficiency. If we assume that the current in the illuminated cell is approximately the current in the non-illuminated cell shifted by the short-circuit current I_{SC} [8]-[10], then, once I_{SC} is determined, the cell efficiency, and in particular the open-circuit voltage V_{OC} , follow from the dark current-voltage analysis. Limited experimental evidence of the validity of this current-shifting approximation for polysilicon pn-junction cells has been reported [16].

The determination of I_{SC} in polysilicon cells is also aided by our dark current-voltage analysis. The effective grain-boundary surface recombination velocity defined in Section III provides the necessary boundary conditions to solve the three-dimensional boundary-value problem in the quasi-neutral portions of the grains. The solutions obtained for $V = 0$ yield the components of I_{SC} generated in the quasi-neutral regions. The component of I_{SC} resulting from carrier generation in the junction space-charge region can be adequately estimated by neglecting the loss of any photo-generated carriers at the grain boundary [17]. This loss will indeed be negligible if the x-component of electric field is much less than the y-component near the grain boundary in the junction space-charge region (see Figure 9).

8. ACKNOWLEDGEMENTS

We thank C. Feldman for providing thin-film polysilicon devices and data characterizing these devices; and H.P.D. Lanyon, and C. T. Sah for helpful discussions.

9. REFERENCES

1. J. Lindmayer, "Characteristics of Semicrystalline Silicon Solar Cells," Record of 13th IEEE Photovoltaic Specialists Conf., 78CH1319-3, 1978.
2. T. L. Chu, S. S. Chu, E. D. Stokes, C. L. Lin, and R. Abderrassoul, "Thin Film Polycrystalline Silicon Solar Cells," Record of 13th IEEE Photovoltaic Specialists Conf., 78CH1319-3, 1978.
3. H. C. Card and E. S. Yang, "Electric Processes at Grain Boundaries in Polycrystalline Semiconductors Under Optical Illumination," IEEE Trans. Electron Devices, vol. ED-24, pp. 397-402, April 1977.
4. L. L. Kazmerski, "The Effects of Grain Boundary and Interface Recombination on the Performance of Thin-Film Solar Cells," Solid-State Electron., vol. 21, pp. 1545-1550, Nov./Dec. 1978.
5. C. H. Seager and T. G. Castner, "Zero-Bias Resistance of Grain Boundaries in Neutron Transmutation Doped Polycrystalline Silicon," Record of 13th IEEE Photovoltaic Specialists Conf., 78CH1319-3, 1978.
6. C. H. Seager, "Barrier Heights and Passivation of Grain Boundaries in Polycrystalline Silicon," Photovoltaic Material and Device Measurements Workshop--Focus on Polycrystalline Thin Film Cells (SERI/TP-49-185), Arlington, VA, June 1979.
7. W. Shockley and W. T. Read, Jr., "Statistics of the Recombination of Holes and Electrons," Phys. Rev., vol. 87, p. 835, Sept. 1952;
R. N. Hall, "Electron-Hole Recombination in Germanium," Phys. Rev., vol. 87, p. 387, July 1952.
8. F. A. Lindholm, J. G. Fossum, and E. L. Burgess, "Application of the Superposition Principle to Solar-Cell Analysis," IEEE Trans. Electron Devices, vol. ED-26, pp. 165-171, March 1979.
9. N. G. Tarr and D. L. Pulfrey, "An Investigation of Dark Current and Photocurrent Superposition in Photovoltaic Devices," Solid-State Electron., vol. 22, pp. 265-270, March 1979.
10. N. G. Tarr and D. L. Pulfrey, "The Superposition Principle for Homojunction Solar Cells," IEEE Trans. Electron Devices, this issue.
11. W. Shockley, Electrons and Holes in Semiconductors, Princeton, NJ: Van Nostrand, 1950.
12. C. T. Sah, R. N. Noyce, and W. Shockley, "Carrier Generation and Recombination in P-N Junctions and P-N Junction Characteristics," Proc. IRE, vol. 45, pp. 1228-1243, Sept. 1957.
13. C. H. Henry, R. A. Logan, and F. R. Merritt, "The Effect of Surface Recombination on Current in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ Heterojunctions," J. Appl. Phys., vol. 49, pp. 3530-3542, June 1978.
14. J. R. Hauser, "Bipolar Transistors," in Fundamentals of Silicon Integrated Device Technology, edited by R. M. Burger and R. P. Donovan, Englewood Cliffs, NJ: Prentice-Hall, 1968.

15. J. A. Mazer, A. Neugroschel, and P. E. Russell, "Experimental Study of Passivation of Grain-Boundary Recombination Current in p-n Junction Polysilicon Solar Cells," submitted for publication in Appl. Phys. Lett. .
16. C. Feldman, private communication, 1979.
17. C. Lanza and H. J. Hovel, "Efficiency Calculations for Thin-Film Polycrystalline Semiconductor Schottky Barrier Solar Cells," IEEE Trans. Electron Devices, vol. ED-24, pp. 392-396, April 1977.

10. FIGURE CAPTIONS AND FIGURES

- Figure 1. Electron energy-band diagram near a grain boundary in thermal equilibrium.
- Figure 2. Non-equilibrium energy-band diagram for a grain boundary characterized by very high recombination rates.
- Figure 3. Non-equilibrium energy-band diagram for a grain boundary characterized by quasi-equilibrium.
- Figure 4. Non-equilibrium energy-band diagram for a grain boundary characterized by quasi-equilibrium and a monoenergetic density of surface states. Holes and electrons flow to the grain-boundary surface where they recombine.
- Figure 5. Portion of an n^+p polysilicon solar cell (no illumination). For assumed columnar grains, the grain-boundary (I_{GB}^B) and intra-grain (I_{QN}^B) base recombination currents are shown.
- Figure 6. Non-equilibrium energy-band diagram near a grain boundary showing a possible breakdown of quasi-equilibrium.
- Figure 7. Filament representing the quasi-neutral base region of a columnar grain in an n^+p polysilicon diode.
- Figure 8. Effective electron lifetime in the filament (grain) shown in Figure 7 versus d_G and τ_n with $S_{n(eff)}^{GB} \rightarrow \infty$ ($D_n = 25 \text{ cm}^2/\text{sec}$).
- Figure 9. Portion of a grain boundary (columnar grains) in the forward-biased n^+p -junction space-charge region (no illumination). Holes and electrons flow, in two dimensions, to the grain-boundary surface where they recombine.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

11. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The great majority of our present and future work relating to this contract deals with the influence of grain boundaries on polysilicon solar-cell performance, although some effort will be given to writing of results we have already obtained concerning heavy doping effects in silicon. The theoretical modeling described above of recombination currents associated with grain boundaries and the capabilities we have established for measuring these currents and determining the morphology and electrical activity of the grain boundaries will provide the foundation for much of our future research studies.

Part of our research will treat various methods of grain-boundary passivation. We will study the passivation resulting from both shallow-level dopants such as phosphorous and boron, and also from hydrogen. In the experimental portion of this study we plan to: (a) use the methods developed during the preceding contract for determining by electrical measurements the recombination current associated with grain boundaries; (b) measure the segregation coefficients for the surface and grain boundaries of silicon; (c) measure grain-boundary diffusion coefficients of dopants in silicon; and (d) determine by measurements the degree of validity of the shifting approximation for various types of polysilicon having many grain boundaries. From a theoretical standpoint, we plan to use the experimental findings above to calculate dopant concentration profiles associated with grain boundaries, and study the effects of p-n and high-low junction formation down grain boundaries and the dopant segregation to the grain boundaries and consequent alteration of the electrical activity of the grain-boundary surface states.

Questions remain concerning the theoretical modeling described in this report of intra-grain and grain-boundary recombination currents. We will try to place some of the approximations (delineated in Section 7) used in the modeling on a firmer physical foundation, and to replace certain approximations with better ones, when possible. We will also try to treat in a more general

way the three-dimensional boundary-value problem, including its nonlinearities, that describes carrier recombination within a grain and at grain boundaries. Experimental and theoretical attention will move toward the special case of carrier recombination and generation in thin films of polysilicon, and to methods of increasing the performance of solar cells made of such material despite the presence of electrically active grain boundaries.

Throughout our studies we plan to integrate theory with experiment.