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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE THIN-FILM
SILICON SOLAR CELLS

Summary Report for May 31, 1979—January 31, 1980

By
David Redfield

February 1980

Work Performed Under Contract No. AC01-79ET23108

RCA Laboratories
Princeton, New Jersey

U.S. Department of Energy

Solar Energy

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For the Period May 31, 1979 to January 31, 1980

DAVID REDFIELD

FEBRUARY 1980

RCA LABORATORIES
PRINCETON, NJ 08540

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ABSTRACT

Fundamental limitations on the performance of Si solar cells are shown to be quite different from those that have been conventionally invoked. Particularly for heavy-doping effects, the usual models are shown to be invalid and a new method is devised for calculating the reverse saturation current of a heavily doped device in which nearly all minority carriers reach the junction (viz., good blue-response). Calculations by the new method show: (i) increased doping above 10^{18} cm^{-3} does not improve the open-circuit voltage as has been thought, and (ii) previous estimates of bandgap narrowing in diffused cells are much too high because of the neglect of Auger recombination effects. Also of importance are the effects of doping gradients and their relation to the properties of the front surface of a diffused-junction cell; experiments are clarifying some of these relations. These experiments have led to a new, simple method of separating the internal optoelectronic properties of a solar cell (or optical detector) from the reflectance properties of the front surface. This method thus provides a direct means of evaluating the effectiveness of antireflection coatings on such devices.

SECTION I

INTRODUCTION

A. CONTRACT OBJECTIVE

The objectives of this contract are: to develop theoretical models of those solar-cell properties that can lead to fundamental limitations in their efficiency; to analyze specifically heavy-doping effects and doping-gradient effects; to optimize solar-cell designs by use of these models; and to apply these models to anticipated grain-boundary effects in polycrystalline thin-film cells.

B. BACKGROUND OF THIS PROGRAM

It is well known that Si solar cells have never achieved the highest efficiencies that were theoretically predicted, but the explanations for observed limitations are still being sought. Experiments show that the major discrepancy between theory and observation occurs in V_{oc} , although attempts to increase V_{oc} by increased base doping generally also cause the values of I_{sc} to diminish [1,2]. There is a broad consensus that these limitations are due, in large part, to effects associated with heavy doping (HD) in the front regions; but the mechanisms by which HD produces these effects are in dispute. Since a better understanding of these mechanisms should improve our ability to maximize solar-cell efficiency, the present work seeks to clarify the mechanisms that may cause fundamental limitations in that efficiency. Moreover, it is generally thought that in polycrystalline materials the grain boundaries form regions of HD, so that some of the same phenomena are likely to influence polycrystalline solar cells.

A major problem arises from the number and variety of HD effects that may occur. These include:

- (1) The need to use Fermi-Dirac statistics governing majority carriers at degenerate doping levels.
- (2) Change in the crystal lattice constant with a resulting change in the electron energy gap E_g .

1. P. A. Iles and S. I. Soclof, Proc. 11th IEEE Photovoltaic Specialists Conf. (IEEE, New York, 1975), p. 19.
2. H. Fischer and W. Pschunder, Ref. 1., p. 25.

- (3) Modification of the density of electronic states as a function of energy. This may take the form of impurity bands or energy band-tails (or both).
- (4) Many-body effects among the majority carriers that cause bandgap narrowing (BGN).
- (5) Alteration of electrostatic field energy due to screening, also with a resulting BGN.
- (6) Possible creation of crystalline defects or impurity precipitates that might drastically shorten minority carrier lifetimes.
- (7) Intrinsic limitations on the lifetime due to Auger recombination processes which generally dominate in HD regimes.

Only Abram, Lees, and Wilson have attempted to deal with most of these effects [3]. Their results were somewhat ambiguous because of both the complexity of the subject and the underdeveloped state of some of the theories. The present work is designed to deal only with those effects that can be treated with some confidence. For example, effect (2) has been shown to be insignificant [4] and is ruled out here.

The principal disagreements over what effects limit V_{oc} are transformed into discussions of the reverse saturation current density J_o of a p-n junction since

$$V_{oc} = \frac{kT}{q} \left(\ln \frac{J_L}{J_o} + 1 \right) \quad (1)$$

and J_L , the light generated current, is easily measured. The analysis of J_o customarily uses the simple diffusion-theory expression which can be written as

$$J_{op} = q \left(\frac{n_i^2}{N_D} \right) \left(\frac{D_p}{\tau_p} \right)^{1/2} \quad (2)$$

where J_{op} is just the hole contribution from the n-type diffused layer of a typical n+/p solar cell, N_D is the doping concentration in the diffused layer, n_i is the intrinsic carrier concentration, and D_p and τ_p are respectively, the diffusion coefficient and the lifetime for holes in the n-type material. It

3. R. A. Abram, G. J. Lees, and B. L. H. Wilson, Adv. Phys. 27, 799 (1978).
4. D. Redfield, Appl. Phys. Lett. 33, 531 (1978).

is important to note for the subsequent discussion that the first factor in parentheses in Eq. (2) is an approximation for the equilibrium minority carrier concentration in the n-region, p_{no} , while the second factor in parentheses represents the rate at which minority carriers are generated in the dark and delivered by diffusion to the junction (with dimensions of a velocity).

Because Eq. (2) has been used so widely in the interpretation of performance limitations on Si solar cells and transistor emitters, its implications should be clearly noted. First, from its inverse dependence on doping density have come numerous efforts to reduce J_o by increasing the doping in the base region [1,2]. These experimental efforts always fail for doping levels $\gtrsim 10^{18} \text{ cm}^{-3}$, hence, for the HD regimes. Second, the dependence of J_o on n_i^2 in Eq. (2) has led to the expectation that any mechanism that could cause BGN would increase n_i and, therefore, J_o .

Thus, the most common interpretation for the limitations on V_{oc} is that J_o is larger than expected because of an increase in n_i caused by energy bandgap narrowing due to heavy doping in the n-region (with the mechanism unspecified). In this model, the entire responsibility for "excess" J_o is placed on the dark minority carrier contribution, and no role is given to the rate factor in Eq. (2). An example given in the most widely cited paper using this model takes a junction depth of $x_j = 0.25 \text{ } \mu\text{m}$ and a surface concentration of the diffused region of $N_D = 2 \times 10^{20} \text{ cm}^{-3}$ (both typical of good solar cells) and infers from observed values of V_{oc} that the Si bandgap shrinks by an average of 0.23 eV over the diffused layer [5]. The great nonuniformity of the diffused dopant concentration was not treated there.

That type of analysis has recently been disputed on several grounds. To begin with, the basic model of the p-n junction on which Eq. (2) is based has been shown to need serious revision because of the doping gradients as well as HD in Si solar cells [6]. Furthermore, the very short lifetimes τ_p associated with Auger recombination in HD material may have as important an influence on J_o as does the minority carrier concentration [4]. The work in this present program is directed toward clarifying these issues.

5. F. A. Lindholm et al., Proc. 12th IEEE Photovoltaic Specialists Conf. (IEEE, New York, 1976), p. 1. The gap shrinkage given in this paper is 0.17 eV, but has since been modified by F. A. Lindholm to the 0.23-eV value to take degeneracy into account.
6. D. Redfield, Appl. Phys. Lett. 35, 182 (1979).

SECTION II

THEORY OF HEAVY-DOPING EFFECTS

A. THE IMPORTANCE OF AUGER PROCESSES

It has recently been shown with high reliability [7] that in crystalline Si the minority carrier lifetime becomes dominated by Auger recombination processes when the doping levels exceed $\sim 10^{18} \text{ cm}^{-3}$. Therefore, more than half of the diffused region of a typical solar cell (having properties mentioned in Section I and shown in Fig. 1) will have the lifetime dominated by Auger recombination which has the behavior

$$\tau_p^{-1} \approx \tau_{pA}^{-1} = C_n N_D^2 \quad (3)$$

Fig. 1. Doping profile that is typical of diffused Si solar cells and is used for calculations here.

7. J. Dziewior and W. Schmid, Appl. Phys. Lett. 31, 346 (1977).

where $C_n = 2.8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ for n-type Si [7]. Under these conditions the rate factor in Eq. (2) becomes

$$\left(\frac{D_p}{\tau_p} \right)^{1/2} = N_D \sqrt{D_p C_n}.$$

Substituting this into Eq. (2) we obtain the modified form applicable to HD regimes

$$J_o = q n_i^2 \sqrt{D_p C_n}. \quad (4)$$

This simple result has a major difference from Eq. (2): the dependence of J_o on N_D has vanished. Thus, once the HD regime has been reached, there should no longer be the expectation that increased doping should reduce J_o . This offers a direct explanation for the results cited from Refs. 1,2 in which HD attempts failed above levels of $\sim 10^{18} \text{ cm}^{-3}$. Moreover, there is no longer any quantitative basis on which to relate doping levels to BGN through the values of n_i^2 and observed values of J_o . In short, all analyses of HD effects based on Eq. (2) are necessarily invalid in precisely the range of dopings that is of primary interest.

These objections to the use of Eq. (2) for HD effects are unrelated to other problems with its use. For one thing, these objections apply to cases of uniform doping. So, the additional problems caused by the strong doping gradients, to be discussed in Section III, in typical diffused solar cells have no bearing on the present argument. Still another difficulty with Eq. (2) is that it is valid only for classical statistics which do not describe very heavy dopings ($\gtrsim 10^{19} \text{ cm}^{-3}$ for Si). The Auger-dominated regime, however, sets in below the degenerate regime, so the degeneracy problem is also separable from the present argument. In fact, even if Eq. (2) is modified to account for degenerate statistics, the Auger lifetime would still cause a near-cancellation of the dependence on doping. Calculations, whose results are given below, in which Fermi-Dirac statistics are used in an alternative method of evaluating J_o , show that cancellation.

The foregoing arguments summarize a central result of this work: the invalidity of Eq. (2) for the analysis of HD effects. It must be noted, however, that Eq. (4) also suffers from the two non-Auger problems mentioned in the last paragraph. It is still a version of simple diffusion-theory transport that neglects effects of doping gradients, and it is not directly applicable to

degenerately doped materials. Thus, there is still a need for some alternative method of calculating J_0 that is applicable in HD regimes in that it incorporates Auger-recombination effects, effects of doping gradients and Fermi-Dirac statistics. Such a method is developed in Sec. II.C and applied to solar-cell properties.

B. EFFECTS OF DOPING GRADIENTS

In typical diffused solar cells the doping profiles are similar to that shown in Fig. 1, so there are very strong doping gradients in the diffused region. Since these gradients are strongest in the most heavily doped region, both factors must be treated simultaneously. This was done recently in developing a revised model with which to analyze such strongly asymmetric junctions [6]. It was found there that for such junctions the space charge, field, and potential all vary over a much wider region on the heavily doped side than is predicted by the conventional junction model. These differences are direct consequences of the doping gradients in these junctions, gradients that extend far beyond the conventional-model space-charge region on the HD side. Doping gradients produce electrostatic fields whose derivatives are the space-charge densities and whose integrals are potentials.

For the typical solar cell used as an example here, the correct solution of Poisson's equation has been calculated numerically, using a self-consistent procedure in which the local carrier concentration is adjusted everywhere to be compatible with the local potential that is the solution of the calculation [6]. The results of that calculation for the electric field E are shown in Fig. 2. Because the doping gradient extends all the way to the surface, so does the field, even though the conventional model would have zero field over 4/5 of this region. In this case, moreover, the field strength exceeds 10^4 V/cm throughout the diffused layer. The nearly constant field near the surface is a coincidence resulting from the particular profile used; generally the field is nonuniform. Therefore, there is usually no quasi-neutral region on the HD side and the conventional models based on such a region are not applicable.

In addition, the high field strengths cause minority-carrier current flow to be often field-controlled, rather than diffusion-controlled, thus making the use of Eq. (2) inappropriate apart from other considerations. This conclusion follows from comparing x_j to the drift distance

$$d = E\mu_p \tau_p$$

Fig. 2. Electric field distributions in the conventional and revised junction models for the solar cell used as an example here.

where we can take the hole mobility to be $\mu_p = 40 \text{ cm}^2/\text{V/s}$, independent of N_D in the heavily doped region. Using the value of E from Fig. 2 and the Auger lifetime, $\tau_p = \tau_{pA}$, it turns out that for most shallow junction devices $d > x_j$. Therefore, the field can sweep nearly all holes to the junction before recombination, thus leading to the conclusion that transport is field-controlled in the diffused region.

This interpretation of field-controlled minority-carrier transport ignores one other consideration, however. That is the effect of possible BGN which tends to reduce the effective field for minority carriers from the value of the electrostatic field. That effect is neglected here because we have demonstrated both here and in Ref. 4, that the previous analyses of BGN [5] cannot be quantitatively correct. For the present, the question of how strong the effective field is remains unanswered, but there is no disagreement that in solar cells with good blue-response (i.e., for strongly absorbed light) most of the minority carriers in the diffused layer do reach the junction.

C. ALTERNATIVE METHOD OF CALCULATING J_o

We next make use of the nearly complete sweepout of minority carriers in the HD region as a basis for a different method of calculating J_o . In its present form, therefore, this method applies only to such cases, those that are sometimes called the "transparent-emitter approximation" in transistor analysis. Nevertheless, the analysis given in the preceding subsection shows that the approximation is applicable to solar cells of interest, viz., those having good blue-response.

For such cases, the contribution from holes in the diffused layer, J_{op} , can be well approximated by just integrating the dark generation rate $g(x)$ over the entire thickness of the diffused region. So,

$$J_{op} \simeq q \int_0^{x_j} g(x) dx. \quad (5)$$

The function $g(x)$ can be determined in equilibrium using the universal relation $p_{no} = g\tau$. In the heavily doped region where Auger processes dominate τ , we can use Eq. (3) to evaluate τ so that

$$J_{op} \simeq q \int_0^{x_j} p_{no}(x) C_n [N_D(x)]^2 dx. \quad (6)$$

This shows qualitatively that the decrease in p_{no} caused by increased doping can be offset by the rate factor $C_n N_D^2$. This result agrees with observations [1,2], but the conventional Eq. (2) does not.

D. CALCULATIONS OF J_o AND BANDGAP NARROWING WITH ALTERNATIVE METHOD

The method of Eq. (6) has been used in two calculations, at different levels of approximation, to evaluate J_o and any associated BGN that might be inferred from it. In the first calculation, the basic approach used in Ref. 5 is followed in the sense of simply averaging the effects in the diffused layer and inferring an average value of BGN. The purpose of this calculation is to find out how much difference is caused by the inclusion of Auger processes which were ignored in Ref. 5. The second calculation improves on this averaging approach by use of position-dependent values for both E_G and τ_p , as well as the use of a variety of proposed dependences of E_G on N_D .

1. Effects Averaged Over Diffused Layer

Since this calculation was intended for comparison with the results of Ref. 5, we have used the concept of an average value for $p_{no}(x)$, labeled $\langle p_{no} \rangle$, caused by some average value of BGN over the diffused region, with the extra carriers accounting for observed values of J_o . In this case, Eq. (6) simplifies to

$$J_{op} \cong qC_n \langle p_{no} \rangle \int_0^{x_f} [N_D(x)]^2 dx \quad (7)$$

where the upper bound on the integral, x_f , is the largest value of x for which the Auger lifetime is dominant. In our example having $N_D = 2 \times 10^{20} \text{ erfc}(x/0.084 \text{ } \mu\text{m}) \text{ cm}^{-3}$ and $x_j = 0.25 \text{ } \mu\text{m}$, we find $x_f = 0.14 \text{ } \mu\text{m}$. So Eq. (7) may slightly underestimate the integral and therefore overestimate the needed $\langle p_{no} \rangle$ and the associated BGN. With these conditions and the experimental value $J_{op} = 10^{-12} \text{ A/cm}^2$, Eq. (7) leads to $\langle p_{no} \rangle = 200 \text{ cm}^{-3}$.

To compare with that value needed to account for the observed $J_o \simeq 10^{-12} \text{ A/cm}^2$, we calculate next the values of $\langle p_{no} \rangle$ associated with various values of BGN. Since bandtail effects are neglected in such calculations, we have

$$p_{no}(x) = N_v \exp \left[- \left(\frac{E_F - E_v(x)}{kT} \right) \right] \quad (8)$$

where N_v is the usual effective density of states of the valence band and E_v is the valence band maximum. Now $E_F - E_v = E_F - E_c + E_g$ where E_g is the gap energy. The averaging procedure of this type of calculation assumes that there is an average value of E_g which will permit the evaluation of $\langle p_{no} \rangle$ by

$$\langle p_{no} \rangle = \frac{N_v}{x_f} \exp \left(- \frac{E_g}{kT} \right) \int_0^{x_f} \exp \left[- \left(\frac{E_F - E_c(x)}{kT} \right) \right] dx \quad (9)$$

To evaluate this integral, knowing $N_D(x)$, all that is needed is a relation that gives $(E_F - E_c)$ and is valid for $N_D \lesssim 2 \times 10^{20} \text{ cm}^{-3}$. For this we use an approximation

formula that has been shown [8] to be within 1% of the exact value of $(E_F - E_c)/kT$ for N_D up to $1.9 \times 10^{21} \text{ cm}^{-3}$. This formula is

$$\exp \left[- \left(\frac{E_F - E_c}{kT} \right) \right] = \frac{1}{u} \exp(-B) \quad (10)$$

where

$$B = \frac{u}{[64 + 0.005524 u (64 + u^{1/2})]^{1/4}}$$

and $u = N_D/N_c$ with N_c the usual effective density of states of the conduction band [8]. Then Eq. (9) becomes

$$\langle p_{no} \rangle \cong \frac{n_i^2}{x_f N_o} \int_0^{x_f} \frac{\exp(-B)}{\text{erfc}(x/x_o)} dx \quad (11)$$

since $n_i^2 = N_c N_v \exp(-E_g/kT)$.

This integral can be evaluated numerically and the necessary value for E_g can be determined that will cause $\langle p_{no} \rangle = 200 \text{ cm}^{-3}$. That value of E_g corresponds to a gap shrinkage of 0.073 eV, which is to be compared to the result of 0.230 eV obtained by Lindholm [5]. [The result 0.170 eV published in Ref. 5 neglected the effects of degenerate statistics. It has since been corrected to 0.230 eV by Lindholm for this reason.] It may be noted that neither calculation considered possible contributions to J_o from surface effects at the front. But, if such effects are significant, they would decrease the effective lifetime and further reduce the inferred BGN which affects only p_{no} .

It must be emphasized that the present calculation and its value of BGN are not presented as a correct solution to this problem. They are offered to demonstrate the major impact that Auger processes can have on such analyses. It is highly unlikely that any good solution to this type of problem can be found until HD effects on the density of states can be incorporated into $p_{no}(x)$. The theory for bandtails, however, is not yet sufficiently quantitative to serve this need. What can be said qualitatively is that the bandtail that must occur above the valence band of HD, n-type material will provide some extra holes, thus reducing further any rigid-bandgap shrinkage needed to account for high values of J_o .

8. N. G. Nilsson, Appl. Phys. Lett. 33, 653 (1978).

2. Position-Dependent BGN

This calculation incorporated two improvements over the one just described. First, the calculation is no longer restricted to regions so heavily doped that τ_p^{-1} can be taken to be equal to the Auger value $\tau_{pA}^{-1} = C_n n^2$. For this purpose we take

$$\tau_p^{-1}(x) = \tau_o^{-1} + \tau_{pA}^{-1} \cong \tau_o^{-1} + C_n [N_D(x)]^2 \quad (12)$$

where τ_o is a parameter representing the defect-limited lifetime that must dominate in regions of lower doping. Although this permits the integral in Eq. (6) to be carried to x_j , a potential new problem is introduced: that is, as x approaches x_j , the values of n and N_D differ increasingly so that the use of N_D for n in Eq. (12) becomes incorrect close to the junction. Since both of these quantities are small in this region, however, τ_o dominates the lifetime, and this discrepancy is unimportant.

The second improvement in the calculation of J_o by means of Eq. (6) is based on the use of actual functions for $p_{no}(x)$ instead of averages over the diffused layer. This, too, becomes unreliable close to the junction since $p_{no}(x)$ is determined by the Fermi energy, which in turn must be consistent with $n(x)$. Since $n(x) \neq N_D(x)$ close to the junction, we do not know the correct Fermi energy there. This problem will be considered in the resulting calculations by testing the sensitivity of the calculated value of the integral to variations in the upper limit that can cut off regions near the junction.

For the present calculation we still use the notion of rigid-band narrowing of the energy gap due to heavy doping, even though the quantitative analyses based on Eq. (2) are known to be wrong. The reasons for continuing this representation of heavy-doping effects are that: (1) quantitative theories of energy bandtails are inadequate; and (2) we can establish certain trends without reliance on the quantitative values. Thus, we still take

$$p_{no}(x) = N_v \exp \left[-\frac{E_G(x)}{kT} \right] \exp \left[-\left(\frac{E_F - E_C(x)}{kT} \right) \right] \quad (13)$$

where we will let $E_G(x)$ have any functional relationship desired. Of course, this function actually is found as $E_G(N_D)$, and we take $N_D(x) = N_o \operatorname{erfc}(x/\ell)$. The quantity $[E_F - E_C(x)]$ is again evaluated by the approximation of Eq. (10).

Calculations of J_0 by use of this method have been performed with four alternatives for $E_G(N)$: the normal fixed-energy gap and three different published relations for $E_G(N)$ [9-11]. The values of E_G from Ref. 11 were fitted to a simple formula which is used here, even though those values were obtained by an averaging procedure.

The integral in Eq. (6) was evaluated by a computer program called VARGAP, which incorporates position-dependent doping, energy gap, and lifetime. The junction depth was taken to be $x_j = 0.25 \mu\text{m}$, and three values of N_0 were used, covering the range of interest for solar cells. For reasons given above concerning errors near the junction, the upper limit of integration was varied from $0.5 x_j$ to x_j . The principal results of these calculations are given in Table 1, in which lower rows contain larger amounts of BGN, according to the various authors cited.

These results contain two qualitative trends which can be interpreted by recalling that near the surface ($x = 0$) the high values of N_D cause the Auger rate factor in $g(x)$ to be very large and the hole-density factor to be very small. One reason for these calculations is to learn what the net effect is on J_0 . Looking across an upper row (no BGN), we see the dependence of J_0 on N is almost nil, illustrating the near-cancellation of the doping dependence of the two factors, p_{no} and τ_p^{-1} that was alluded to in Sec. II.A. When BGN is present (lower rows), it causes p_{no} to be larger than for no BGN near the surface where N_D is high, and we find that J_0 increases as N_D increases. This trend, which agrees with observations on heavily doped solar cells, should be the same if band-tails, instead of BGN, caused the increase in p_{no} .

The effect of changing the upper limit of integration in Eq. (6) is seen by comparing any set of results in one column for any choice of BGN models. It is clear that changing this upper limit has the largest effect for "no BGN" and has virtually no effect in the cases of increased BGN (i.e., the lowest rows of data). This implies that the region near the junction (where the greatest uncertainties are) contributes little to J_0 when p_{no} is increased significantly in the near-surface region over its unperturbed values. We can thus conclude

9. A. A. Vol'fson and V. K. Subashiev, Sov. Phys. Semicond. 1, 327 (1967).
10. J. W. Slotboom and H. C. DeGraaff, Solid-State Electron. 19, 857 (1976).
11. F. A. Lindholm, presented at Polycrystalline Silicon Solar Cells DOE/SERI Contractors Rev. Mtg., Arlington, VA, June 14-15, 1979.

TABLE 1. SATURATION CURRENT DENSITY ($A\ cm^{-2}$)
Computed by VARGAP

$$N_D = N_O \operatorname{erfc}(x/\ell); x_j = 0.25\ \mu m$$

$E_G(N)$	Fraction of x_j	SATURATION CURRENT DENSITY ($A\ cm^{-2}$)		
		$N_O = 1 \times 10^{20}\ cm^{-3}$	$N_O = 2 \times 10^{20}\ cm^{-3}$	$N_O = 5 \times 10^{20}\ cm^{-3}$
No BCN	1.0	1.6×10^{-14}	1.5×10^{-14}	1.4×10^{-14}
	0.75	3.2×10^{-15}	3.6×10^{-15}	3.0×10^{-15}
	0.5	2.9×10^{-15}	3.3×10^{-15}	2.7×10^{-15}
Vol'fson & Subashiev	1.0	3.1×10^{-14}	7.5×10^{-14}	2.3×10^{-13}
	0.75	1.7×10^{-14}	6.4×10^{-14}	2.2×10^{-13}
	0.5	1.7×10^{-14}	6.4×10^{-14}	2.2×10^{-13}
Slotboom & DeGraaff	1.0	2.6×10^{-13}	4.1×10^{-13}	4.4×10^{-13}
	0.75	2.5×10^{-13}	4.0×10^{-13}	4.2×10^{-13}
	0.5	2.4×10^{-13}	3.9×10^{-13}	4.2×10^{-13}
Lindholm	1.0	4.2×10^{-12}	7.3×10^{-12}	8.4×10^{-12}
	0.75	4.1×10^{-12}	7.3×10^{-12}	8.4×10^{-12}
	0.5	4.1×10^{-12}	7.3×10^{-12}	8.3×10^{-12}

that the near-surface region dominates the integral when a significant increase in p_{no} occurs there. As in the last paragraph, we comment that the same interpretation should apply, no matter what physical mechanism is responsible for an increase in p_{no} in the most heavily doped region near the surface.

SECTION III

EXPERIMENTS ON DOPING-GRADIENT EFFECTS

A series of experiments has been started to provide information on effects due to the fields caused by doping gradients that were predicted in Ref. 6. To have the desired control over the details of doping profiles, a substantial expertise in Si device processing is required and is being provided by in-house capabilities. Similarly, the detailed characterization of these profiles requires a number of analytical techniques; local capabilities are also being exploited in this area.

The motivation for the present experiments is the question of how strong is the effective field near the front of a diffused layer that was mentioned in Sec. II.B. For the representative example used in Fig. 1, it has been shown (see Fig. 2) that the electrostatic field is $>10^4$ V/cm everywhere in that layer, with consequent important effects on minority-carrier transport processes. The effective field, however, is lower if BGN occurs and the controversy about the magnitude of BGN thus extends to the field values and their consequences. Good blue-response in cells was interpreted in Section II to be a consequence of high fields, but it might result from just diffusive processes if the effective field is low and the diffusion length is large enough. In this HD region where Auger processes dominate the minority carrier lifetime, the diffusion length, L_p , depends on the doping concentration, whereas the drift distance depends on the doping gradient.

Therefore, if diffused layers can be prepared with equal values of N_0 , but with different gradients near the surface, it might be possible to distinguish between the mechanisms. One way of making such a distinction is to look for effects of surface recombination on cell performance since the gradient field always drives minority carriers away from the surface. If the effective field is low, carriers may diffuse to the surface as readily as to the junction. So surface recombination would have a greater impact where the field is low, than where fields are high. This conclusion is strengthened for cases in which the field (i.e., doping gradient) extends all the way to the surface. (Strictly speaking, the field should extend only to within a screening length of the surface, but that distance is $\sim 10^8$ Å for doping levels used in solar cells.) In such cases there must be a surface ~~charge~~ layer on which the field lines can

terminate, and such charge layers further repel minority carriers from the surface, thereby reducing further the possible effects of surface recombination.

To study the effects of different doping gradients and surface recombination velocities on solar-cell response, a collection of samples has been prepared in which those parameters differ. The doping gradient is controlled by the choice of diffusion temperature and the details of the thermal schedule that is used. The substantial variation in profile that can be obtained is illustrated by the secondary ion mass spectrometry (SIMS) profiles shown in Fig. 3. These preliminary test diffusions and the analytical measurements have confirmed the well-known presence of unexplained anomalies in phosphorus diffusion into Si. Therefore, the properties of every sample are monitored with spreading resistance, chemical staining, SIMS, and four-point sheet-resistance measurements at every step of the processing. Nevertheless, Fig. 3 makes it clear that we can achieve marked differences in gradient without much change in the doping concentration.

For the surface recombination variation, these samples have been prepared with a thermally grown oxide. The oxide is known to passivate the surface by reducing the density of surface states responsible for surface recombination. This passivation effect can be increased by certain annealing processes which have been taken from commercial device-processing schedules. Half of the samples with each type of doping profile have had the oxide etched off to remove the passivation while preserving all other properties of the material. Thus, a matrix of sample properties is available for comparisons.

The principal measurement to characterize the electrical properties of these devices is the blue (and violet) response of solar cells. For this purpose 1x2 cm cells are fabricated on each sample, along with diagnostic "dots," by standard photolithographic processes. The comparison of photovoltaic response is made on the basis of quantum-efficiency measurements at 4000 Å and 4500 Å. It is also necessary, however, to have independent measurements of the effects of oxide layers on the reflectance. These measurements have been completed on the entire set of samples designated as series SC-1. Within this set, the junction depths were in two groups, one $\sim 0.4 \mu\text{m}$ and the other $\sim 0.7 \mu\text{m}$ with the deeper junctions intended to have doping profiles with smaller gradients near the surface.

One facet of this experiment did not succeed because of an unexpected effect of the growth of thermal oxide for passivation. It turns out that such oxide

Fig. 3. Phosphorus profiles measured by SIMS after diffusion into Si from POCl_3 . Left: diffusion temperature 1000°C, $x_j \approx 1 \mu\text{m}$. Right: diffusion temperature 850°C, $x_j \approx 0.6 \mu\text{m}$.

growth is much faster on heavily doped Si than in lightly doped Si, and too much of the near-surface region was consumed by the oxidation process. This resulted in the loss of some of the low-gradient material from the surface regions of the samples with deeper junctions. Therefore we have been unable to compare the results of very different gradients near the surface. Nevertheless, other useful results have been obtained from series SC-1.

The first measurement stresses the internal quantum efficiency (QE) of these cells when exposed to very strongly absorbed light ($\lambda = 0.4 \mu\text{m}$). This light generates carriers closest to the front surface so that effects of both surface recombination and strong doping gradients can be seen most clearly. To obtain the internal QE, however, from the normal QE measurement, it was necessary to measure the reflectance spectrum $R(\lambda)$ of every sample and use it to correct the external QE at each wavelength. The results for the shorter wavelengths of light are shown in Table 2 (blanks indicate broken samples). From these data we see two significant results. First, there is a marked difference between the responses at a wavelength of $0.4 \mu\text{m}$ for the set of samples with oxide compared to those without. Thus, there are significant effects of surface recombination velocity on solar-cell performances, at least for these rather extreme cases of bare Si and well-passivated Si. This result disagrees with the published report of Lindmayer and Allison [12], but confirms the results of Fossum and Burgess [13].

The second result of significance from Table 2 is the very high values of internal QE of oxide-passivated cells at $0.4\text{-}\mu\text{m}$ wavelength. This implies that most losses observed in the violet response of real solar cells are due either to reflection or to surface recombination. Thus the internal performance is better than is often thought, even in cells with rather deep junctions. There is a good prospect, therefore, of improving the external QE by relatively straightforward means.

In addition to the measurements of spectral dependence of QE shown in Table 2, the solar-cell characteristics (I_{sc} and V_{oc}) of series SC-1 have been measured by means of a solar simulator with $\sim 97\text{-mW/cm}^2$ irradiance. These measurements were to supplement the QE data so that correlations with actual cell performance can be made. The results are presented in Table 3 where, again,

12. J. L. Lindmayer and J. F. Allison, COMSAT Tech. Rev. 3, 1 (1973).
13. J. G. Fossum and E. L. Burgess, Appl. Phys. Lett. 33, 238 (1978).

TABLE 2. INTERNAL QUANTUM EFFICIENCIES (PERCENT)
FOR SERIES SC-1

Wafer		AA	B	E	F		C	D	G	H
Junction Depth (μm)		0.43	0.38	0.38	0.42		0.72	0.64	0.70	0.68
Light Wavelength (μm)										
With Oxide	0.40	92	94	98	91		85	84	-	84
	.45	94	92	97	84		84	73	-	86
	.50	91	91	93	90		90	74	-	90
	.60	92	92	92	92		84	76	-	90
Oxide Removed										
	0.40	58	54	56	59		-	47	47	50
	.45	73	70	75	74		-	68	63	67
	.50	86	85	86	85		-	85	79	79
	.60	92	93	91	93		-	95	90	91

Shallow Junctions
Deeper Junctions

TABLE 3. SOLAR-CELL PERFORMANCE OF SERIES SC-1

Wafer		AA	B	E	F		C	D	G	H
Junction Depth(μm)		0.43	.38	.38	.42		0.72	.64	.70	.68
With Oxide	J_{sc} (mA/cm^2)	30.4	30.9	26.2	30.3		30.6	26.4	31.4	30.4
	V_{oc} (V)	.588	.589	.598	.589		.583	.587	.591	.593
Oxide Removed	J_{sc} (mA/cm^2)	22.1	22.3	22.4	22.5		-	22.1	22.3	22.2
	V_{oc} (V)	.570	.570	.568	.572		-	.578	.578	.581

the data have been grouped by surface condition. It is obvious that all the values of J_{sc} for the passivated cells are much higher than those of the bare-Si cells. But these differences cannot be interpreted directly in terms of the differences in the internal properties of the cells because the oxide provides an antireflection (AR) coating for the light in addition to the passivating effect on the electronic surface states. The difference in ability to interpret the QE measurements and solar-cell measurements is that the $R(\lambda)$ spectrum provided the necessary factor to give internal QE results. To perform an analogous correction for J_{sc} , it would be necessary to include the spectral characters of R , QE , and the light flux density. Although that can be done, it is laborious; a new method has been developed for accomplishing this simply and accurately, and is described in the next Section.

Further experiments on doping gradients are under way.

SECTION IV

NEW METHOD FOR EVALUATING ANTIREFLECTION COATINGS AND INTERNAL DEVICE PROPERTIES

A. INTRODUCTION

For the sake of explicitness, this discussion will be presented in terms of its application to a solar cell, although it will be clear that very similar considerations apply to other light detectors. We start, therefore, with the general expression for the short-circuit current density of a solar cell

$$J_{sc} = q \int_{\lambda} F(\lambda) [1 - R(\lambda)] Q_i(\lambda) d\lambda \quad (14)$$

where $F(\lambda)$ is the light flux density (in photons/s/unit area), $R(\lambda)$ is the reflectance of the device with whatever coating it may have, and $Q_i(\lambda)$ is the internal quantum efficiency of the device. The range of integration should include all wavelengths for which any significant photocurrent is generated.

It is clear from Eq. (14) that the choice and the effectiveness of an AR coating must depend not only on $R(\lambda)$ but also on the functions $F(\lambda)$ and $Q_i(\lambda)$. In qualitative terms, the AR coating should have its best performance in the spectral range in which both F and Q_i are high. The difficulty arises in quantifying this notion. Representative curves for the three functions in the integrand of Eq. (14) are displayed in Fig. 4. The airmass-one solar irradiance is a smoothed version of Hulstrom's calculations [14]. The reflectance curve was measured on a polished silicon wafer coated by evaporation of a layer of ZrO_2 ($n \cong 2$) to a thickness of 800 Å. The curve for Q_i was obtained from a measured spectrum of the external quantum efficiency Q_e of a Si solar cell having the same AR coating by use of the relation $Q_i = Q_e / (1 - R)$. The complexity of curves such as these illustrate the difficulty in evaluating an AR coating.

B. PRINCIPLES OF THE METHOD

For any expression like Eq. (14) it is well known that there must exist a number $\langle R \rangle$ (within the range of values of $R(\lambda)$) such that

$$J_{sc} = q(1 - \langle R \rangle) \int F(\lambda) Q_i(\lambda) d\lambda \quad (15)$$

14. R. Hulstrom, SERI, private communication.

Fig. 4. Representative curves for the three functions relevant to the performance of the AR coating of a silicon solar cell. F is the airmass-1 solar spectrum, R the cell reflectance, and Q_i the internal quantum efficiency of the cell measured in this work.

where

$$\langle R \rangle = \frac{\int R(\lambda) F(\lambda) Q_i(\lambda) d\lambda}{\int F(\lambda) Q_i(\lambda) d\lambda} \quad (16)$$

This $\langle R \rangle$ is an average of $R(\lambda)$ over the spectral range of interest, weighted by the product of the two other functions that are relevant to the device performance. It is apparent from Eq. (15) that this $\langle R \rangle$ is the optimization parameter for AR coatings since minimum $\langle R \rangle$ produces the maximum J_{sc} . The significance of this optimization is that for any given light spectrum and cell properties, variations in the coating should be made to minimize $\langle R \rangle$. Any change in either $F(\lambda)$ or $Q_i(\lambda)$ will, in general, require some change in the optimum coating.

It follows immediately that a quantitative comparison of any two surface conditions of a given device can be made by the ratio of their values of $(1 - \langle R \rangle)$ since that must be the ratio of the values of J_{sc} .

Moreover, if $\langle R \rangle$ is known, a measurement of J_{sc} and use of Eq. (15) provide a means of evaluating the integral over $(F Q_i)$, which is the ultimate possible performance that the cell is capable of in the light F . This latter quantity is of interest for assessing the internal properties of such devices independent of the effects of reflections at the surface.

For these reasons, a simple experimental procedure for quantitative determination of the value of $\langle R \rangle$ would be useful. Such a procedure is now described, based on the use of the surface properties of a device in two ways, once as the normal face of a test cell, and once as a simple reflecting surface as illustrated by A' in Fig. 5. The procedure thus requires having a second piece of the same cell material with the same AR coating and no metal on the front.

Fig. 5. Experimental procedure for determining $\langle R \rangle$. The test cell is designated as A and the reflector A' has the same reflectance spectrum as A . The measurements required are the short-circuit currents of cell A in the two cases.

Two measurements of J_{sc} of the test cell A are made as shown. In the first, the direct light is used. For the second measurement, the same light is reflected from the matching surface A' before reaching the test cell, so the incident light on the cell in the second case is $F(\lambda)R(\lambda)$. Thus, the requirements of this procedure are that $R_A(\lambda) = R_{A'}(\lambda)$ and that the surface A has specular reflection. The matching of R_A and $R_{A'}$ can best be done by preparing them simultaneously with a reliable coating process. This is not difficult and has been done for the measurements to be described below.

The use of these two measurements is seen from the relations

$$\frac{J_1}{q} = \int (1 - R) F Q_i d\lambda = \int F Q_i d\lambda - \langle R \rangle \int F Q_i d\lambda \quad (17)$$

$$\frac{J_2}{q} = \int R(1 - R) F Q_i d\lambda = \langle R \rangle \int F Q_i d\lambda - \langle R^2 \rangle \int F Q_i d\lambda \quad (18)$$

where the last term contains the weighted average of $R^2(\lambda)$,

$$\langle R^2 \rangle = \frac{\int R^2(\lambda) F(\lambda) Q_i(\lambda) d\lambda}{\int F(\lambda) Q_i(\lambda) d\lambda} \quad (19)$$

From Eqs. (17,18) we find

$$\frac{J_2}{J_1} = \frac{\langle R \rangle - \langle R^2 \rangle}{1 - \langle R \rangle} \quad (20)$$

It will be shown by numerical computations that in cases of interest the approximation $\langle R^2 \rangle \cong (\langle R \rangle)^2$ turns out to be quite good. To the extent that this approximation holds, Eq. (20) can then be approximated by

$$\frac{J_2}{J_1} \cong \langle R \rangle \quad (21)$$

This provides the simple procedure for determining $\langle R \rangle$.

C. CALCULATIONS AND MEASUREMENTS

Since the use of the simplified expression, Eq. (21), depends on the near equality of $\langle R^2 \rangle$ and $(\langle R \rangle)^2$, these latter two quantities have been computed using Eqs. (16,19) for two widely different surface conditions, for Si solar cells with three different Q_1 curves, and for three light spectra corresponding to solar spectra at airmass 0,1,2. For these computations $Q_1(\lambda)$ values were calculated by use of a fairly standard, one-dimensional computer model of the quantum efficiency of a crystalline Si solar cell. The program by which Q_1 is calculated has seven parameters: the thickness, minority carrier diffusion length, and surface recombination velocity of the base region; the three analogous parameters of the front region; and the thickness of a possible "dead layer" at the front of the Si.

For the $R(\lambda)$ data, measured spectra were used for wafers of polished, bare Si and for a coating of mixed SiO_2 and TiO_2 about 825 Å thick. (This latter choice was based on the presence of that reflectance spectrum in the pre-existing computer program.) The curve for $R(\lambda)$ of ZrO_2 in Fig. 4 is quite close to the corresponding curve used in these computations.

The results of these calculations are presented in Table 4. The cell types correspond to various combinations of minority carrier diffusion lengths in the front (for blue-response) and base (for red-response) regions. In every case, the values of $\langle R \rangle$ and $\langle R^2 \rangle$ were computed and the exact value of J_2/J_1 was calculated using Eq. (20). The exact value was compared with $\langle R \rangle$ and the fractional error, $(\langle R \rangle - J_2/J_1)/\langle R \rangle$, was determined, with the results shown as percent errors in Table 4.

The central result is apparent: all the errors are small, viz., 5 to 8%. The errors for bare Si are $<1/2\%$ because the range over which $R(\lambda)$ varies (31% - 45%) for bare Si is much smaller than the range covered by the AR-coated Si (see Fig. 4). [Of course, in the limit of $R(\lambda) = \text{constant}$, $\langle R^2 \rangle \equiv (\langle R \rangle)^2$.] In the case of coated cells, moreover, the several percent errors have a still smaller impact on the quantity $(1 - \langle R \rangle)$ which is of principal concern for evaluating the actual J_{sc} and for determining the internal performance properties of such devices. [The fractional error in $(1 - \langle R \rangle)$ is a factor $\langle R \rangle/(1 - \langle R \rangle)$ times the fractional error in $\langle R \rangle$.] As a secondary result, the variation in the light spectrum is of little importance in the magnitudes of $\langle R \rangle$ and the errors.

TABLE 4. COMPUTED VALUES OF $\langle R \rangle$ FROM Eq. (16) AND THE ERRORS PRODUCED BY THE USE OF Eq. (21).

SAMPLE	LIGHT	BARE SILICON		SILICON WITH TiO ₂ - SiO ₂ COATING	
		$\langle R \rangle$	ERROR ^a (%)	$\langle R \rangle$	ERROR ^a (%)
"AVERAGE" CELL	AM0	0.330	0.3	0.073	6.1
	AM1	.330	.3	.067	6.0
	AM2	.329	.3	.064	5.5
GOOD-BLUE CELL	AM0	0.335	0.4	0.084	8.4
	AM1	.334	.4	.077	8.2
	AM2	.332	.3	.072	7.5
GOOD-RED CELL	AM0	0.329	0.3	0.074	5.6
	AM1	.329	.3	.068	5.5
	AM2	.327	.2	.066	5.0

a. Error = $(\langle R \rangle - J_2/J_1) / \langle R \rangle$.

A series of measurements was performed to demonstrate this method on solar cells of both bare and coated Si by use of a Xe lamp solar simulator. Each cell had a matching wafer with the same surface treatment for use as reflector A' in Fig. 5. Since it is known that the collimation of light from the solar simulator is imperfect, and the test cell is placed at different distances for the two measurements shown in Fig. 5, a modification of the procedure was found to be desirable. In the modified version, both measurements are made with the test cell in the same location, viz., that shown for measurement 2 in Fig. 5. The difference between the two measurements is obtained by using a plane aluminum, front-surface mirror in place of reflector A' for measurement 1.

With this modified procedure, account must be taken of the actual reflectance R_m of the mirror since the incident flux for measurement 1 is now $R_m F$. The reflectance spectrum of the mirror used here was measured and found to be within 1% of that of a standard Al mirror whose $R_m = 0.87 \pm 0.01$ over the spectral range $0.4 \mu\text{m} \leq \lambda \leq 1.1 \mu\text{m}$. With these results, the approximate expression for $\langle R \rangle$ changes from Eq. (21) to

$$\langle R \rangle = 0.8 / \frac{J_2}{J_1} \quad (22)$$

This slight modification of the procedure has two other benefits: (1) simplicity in measurements, since the test cell remains fixed; and (2) freedom from uncertainties due to possible nonuniformities in the illumination, since they are identical for the two measurements. A fixed-position mount for the mirror and reflector A' ensures reproducible geometry of the light.

The measurements on the bare Si solar cell gave $\langle R \rangle = 0.32$ by Eq. (22) and for the coated cell whose properties are shown in Fig. 4, $\langle R \rangle = 7.5\%$. These agree very well with the calculated values in Table 4, but exact comparisons are not possible because the three functions (R , F and Q_1) involved in these calculations were not identical to those of the experiment. There appears to be no method that is more accurate than the present one so that better accuracy determination cannot be made now.

From these measured values we can deduce the improvement factor caused by the AR coating from the ratios of $(1 - \langle R \rangle)$ to be 1.36. This compares with the maximum possible improvement of 1.47 for a perfect AR coating for which $\langle R \rangle = 0$.

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WPC#822763