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HEAVY DOPING EFFECTS IN HIGH EFFICIENCY SILICON SOLAR CELLS

Quarterly Report

For Period Covering
July 1, 1984 - September 30, 1984

By:

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1. INTRODUCTION

This report describes technical findings of work supported by contract no. 756525 for the period, July 1, 1984 to Sept. 31, 1984. Details of the findings appear in the Appendix. In this section, we briefly summarize these findings and indicate their practical implications for solar-cell design.

A controversy exists about several of the key parameters describing the heavily doped regions of Si solar cells. This controversy relates particularly to experimentally determined energy-gap narrowing and to the minority-carrier diffusivity and mobility. To explain the origin of this discrepancy, let us denote the energy-gap (or bandgap) narrowing by $\Delta E$ and the minority-carrier diffusivity and diffusivity by $D$ and $\mu$. We omit subscripts for brevity.

1.1 Some Equations for Heavily Doped Silicon

All experimental determinations of $\Delta E$, except those employing photoluminescence or optical absorption, depend on measurement of minority-carrier current $J$ in the heavily doped region. If we assume n-type heavily doped Si for illustration, this current is given by

$$J = \mu n V_{EV} - eD n P$$  \hspace{1cm} (1)

where

$$V_{EV} = V_E - V_g$$  \hspace{1cm} (2)
is the quasi-field acting on the minority holes. Note that the field acting on the holes differs from that acting on the electrons and differs also from the electric field (the gradient of the electrostatic potential). Eq. (2) follows from the definition of the energy gap and from the condition, from the quantum theory of solids, that a particle at a band edge has only potential energy (no kinetic energy).

For low-injection conditions, which hold always in a heavily doped region of a Si solar cell,

$$P(r) = \left[ \frac{n_i^2}{N(r)} \right] \exp[F_n - F_p]$$

where the argument of the exponential in Eq. (3) is the difference between the electron and hole electrochemical potentials (or quasi-Fermi levels) normalized by $kT/e$ (or $kT$).

The effective intrinsic density is given by

$$n_{ie}^2 = \frac{N_i P_o}{n_i^2} = n_{ie}^2 \exp[\Delta E'] F_{1/2}[(E'_f - E'_e)] + \exp[\Delta E']$$

where the primes mean normalization by $kT$ and where $F_{1/2}$ denotes the Fermi-Dirac integral of order 1/2.

A simple, nearly tutorial, development of the facts stated above appears in Ref. 1 for this Section.

1.2 Measured Recombination Current

Now we are in a position to examine the measured
recombination current $J$ of a heavily doped region; we continue assuming n-type Si for illustration. By integrating the hole continuity equation across the quasineutral portion of the heavily doped region, we obtain

$$\frac{J}{e} = \int \frac{\Delta P}{\tau} dx + J_{\text{surface}} \tag{5}$$

in which $\Delta P$ is the hole density in excess of the equilibrium density, $\tau$ is the position-dependent hole lifetime, and $J_{\text{surface}}$ is the hole recombination current at the surface. Eq. (5) displays the hole recombination current of the n+ region as a sum of volume and surface recombination.

One can measure $J$ by EBIC, by dark current in presence of applied forward voltage, or by selectively illuminating the quasineutral n+ region and measuring the short-circuit current. However the measurement is made, the problem in using $J$ to determine $\Delta E$ lies in separating the volume and surface recombination components of (5) and connecting then to $\Delta E$ via Eqs. (1) to (5).

1.3 A Key Assumption and a Questionable Tradition

From Eqs. (1), (3) and (4), we see that $D$, $\mu$, and $\Delta E$ interplay to determine $J$. Thus, in principle, one must determine $D$ and $\mu$ (linked by $D/\mu = kT/e$) separately from $\Delta E$.

It has been the tradition in all but recent work by Arnost Nuegroschel and me on heavily doped Si to avoid determination of
D and $\mu$. Rather, it has been assumed that the majority carrier and minority carrier $D$ and $\mu$ are equal. This assumption underlies all models for $\Delta E$ that are widely used, beginning with the first experimental determination by Slotboom and de Graaf. In particular, this includes the models now in computer programs at JPL.

To my knowledge, there is no reason, experimental or theoretical, for making this assumption. It is a convenient assumption because the majority carrier mobility is easily determined experimentally. Minority-carrier mobility, prior to our recent work, was only measured for dopant concentrations up to $10^{19}/\text{cm}^3$. From a theoretical viewpoint, Bennett (1983) of the National Bureau of Standards has proposed that the majority carrier mobility is less than the minority carrier mobility by reason of the sum rule of quantum theory. Kane (1984) of Bell Laboratories, in a preprint sent to Prof. Neugroschel, has indicated his belief that the majority carrier mobility exceeds the minority carrier mobility. His reasoning relies on the simple observation that the kinetic energy of the majority carriers able to conduct greatly exceeds the kinetic energy of the minority carriers. Hence, in a quasi-classical picture, the majority carriers spend less time in the vicinity of the force field of a scattering center such as an impurity ion. Consequently they are scattered less than are minority carriers and their mobility ($\mu = $
e^{\text{scattering}/m^*}) may be expected to be larger.

1.4 Suggestions from our Recent Experiments

In our work on the experimental determination of $\Delta E$ and $\mu$ and $D$ (of the minority carriers), we avoided the assumption of equal majority and minority carriers by exploring the temperature dependence of $J$ in a small range of temperature. This led to Ref. 2 (below) on $\Delta E$ and to Ref. 3 (below) on $\mu$ and $D$. In these methods $d\log J/dT$ is explored. The activation energy thus revealed yields $\Delta E$ (1982); use of this $\Delta E$ together with the value of $J$ then yields the minority-carrier $D$ and $\mu$ (1983). This work in 1983 suggested evidence for minority-carrier mobility that was about one order of magnitude below the majority carrier mobility. We suggested a model consistent with this evidence, in which minority carriers made transitions to trap levels energetically near the edge of the minority carrier band edge (mobility edge) and subsequently were released. This removal from the conducting state, for a time characterized in the Appendix by $T_{\text{trapping}}$, decreases the minority carrier mobility. The model of Kane also leads to this same result. Either model may explain the experimental evidence.

1.5 Contents of the Appendix

This model is explored further in the Appendix. There we excite by short wavelength illumination and demonstrate activation behavior of the minority-carrier mobility and
diffusivity. Short-circuit current is the measured variable. In our interpretation, the activation energy is determined from the measurement to be of the order of kT, which is expected for bandtail states but does not rule out an acceptor level as the dominant trap.

We argue further that the short-circuit current times temperature to the mth power, that is

$$I_{SC}T^m \times 1/T,$$

shows activation behavior. Thus, based on our experiments, the assumption that $\mu_{(majority)} = \mu_{(minority)}$ is always wrong. This is implied in Eq. (8) of the Appendix.

1.6 Conclusion

From a technical standpoint, there is no conclusion or anything approaching a conclusion at present. We have suggested evidence for our findings for $\Delta E$ which are inextricably linked to our findings for the minority-carrier mobility and diffusivity. The Appendix of this report extends that evidence. But we recognize that concentration on activation energies, for the problem under study, relies on values of slopes derived from current measured as a function of $1/T$. A small error in the slope can produce a large error in the measured $\Delta E$ and $D$ and $\mu$. We continue work toward decreasing this error.

Other workers have dogmatically insisted that values of $\Delta E$
of Slotboom and deGraaf and subsequent workers, which are markedly lower than our suggested values, are in fact correct. This is done even though there is no reason to believe the equality of majority and minority-carrier mobilities for concentrations well above $10^{19}/\text{cm}^2$. This equality is equivalent to believing in the lower values of energy-gap narrowing.

1.7 Practical Consequences

The performance parameter of silicon solar cells that probably links most closely with $\Delta E$ is the open-circuit voltage. For existing solar cells, use of our values of $\Delta E$ (vs impurity concentration) in any of the common computer codes will probably yield the measured open-circuit voltage, to a good approximation, provided one uses our values of $\mu$ and D. On the other hand, use of the more widely accepted values of $\Delta E$ together with the assumption that $\mu(\text{majority}) = \mu(\text{minority})$ will probably also yield the measured open-circuit voltage. The reason for this one can see by inspection of the equations given above. Open-circuit voltage is determined by J, primarily; and J derives from P, which is determined by $\Delta E$, and from D and $\mu$, together with the quasi-field of Eq. (1) which depends on $\Delta E$ (Eq. 2).

Thus this simple test will not discriminate between the adequacy of the models. Better tests may include:

(a) sensitivity of the open-circuit voltage to the surface recombination velocity $S$. 

(b) temperature dependence of the open-circuit voltage. It is not clear whether the spectral response will provide an adequate test for the models because of the connections among $\Delta E$, $\mu$ and $D$ that underlie the spectral response. The temperature dependence of the spectral response may be more revealing. Indeed, the Appendix explores the temperature dependence of the short-wavelength current; the tentative result there favors the data of Ref. 3 rather than the assumption of the equality of the majority- and minority-carrier mobilities.

Because many solar cell designs of the present depend for their quality on the surface recombination velocity, much more work is needed aiming to answer the questions about $\Delta E$, $\mu$ and $D$ raised here. It is probable that the values for $\Delta E$, $\mu$ and $D$ determined in Refs. 2 and 3 are inaccurate, for reasons discussed. So also are the values of these parameters widely in use (including in JPL computer codes). Until more accurate values become available, computer-assisted evaluation of new designs will be misleading, as will the determination of values of other parameters such as the surface recombination velocity bordering a highly doped emitter region.

REFERENCES FOR THIS SECTION


APPENDIX

TRAP CONTROLLED MINORITY-CARRIER MOBILITY IN HEAVILY DOPED SILICON

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Recently [1], we presented experimental evidence for low diffusivity and mobility of minority holes in highly arsenic doped (concentrations \( \sim 10^{20} \text{ cm}^{-3} \)) n-type Si. This evidence suggests that the minority-carrier diffusivity (and mobility) may be about an order of magnitude smaller than the majority-carrier hole diffusivity in comparably doped p-type Si. As an explanation, we suggested a simple transport model that emphasized trapping by localized tail states in the minority band. The commonly used assumption of equal minority and majority-carrier mobilities and the neglect of the tail-states effects on the minority-carrier mobility was also questioned in a review article by Abrams et al. [2]. Here we report qualitative evidence that minority-carrier diffusion in n\(^+\) Si may be trap limited.

Figure 1 illustrates the band structure, including the tail states, for n\(^+\) Si. As was already discussed in [1], for low-level injection, the minority holes occupy energy levels near the mobility edge \( E_V \). In the model proposed, the holes from the extended states in the valence band can be captured by the localized tail-states for some mean time \( t_{\text{trapping}} \), and then released back into the valence band. This process, shown by arrows in the Fig. 1, will
decrease the hole mobility. If the scattering rate of holes inside the band is comparable with the hole trapping rate, it is useful to generalize the Boltzmann equation to include band-bound transitions. This generalization, discussed, for example, by Smith, Janak, and Adler [3], and worked out in detail by Sah and Lindholm [4], involves approximating the collision integral, for small departures from equilibrium, by the sum of two terms of the form, \((f - f_0)/\tau\). Here the first term is the customary relaxation time approximation for the nonequilibrium distribution function in which \(\tau_{\text{scatt}}\) is the scattering time that characterizes intraband transitions. In the second term, \(\tau_{\text{trapping}}\) is mean trapping time for localized states near the valence-band edge. Thus

\[ \mu_p = e^{\tau_{\text{coll}}/m^*}, \quad 1/\tau_{\text{coll}} = 1/\tau_{\text{scatt}} + 1/\tau_{\text{trapping}}. \]  

We investigate the temperature dependence of \(\mu_p\) by estimating \(\tau_{\text{trapping}}\) [4]:

\[ 1/\tau_{\text{trapping}} = e \propto A T^m \exp \left[-(E_T - E_V)/kT\right] \]  

where \(A\) is a temperature independent constant. In (2) we have assumed, for simplicity, trapping at one shallow level (close to \(E_V\)) in the tail band or at an acceptor level in the \(n^+\) region. Such an acceptor level can come from the dopant acceptor (boron in our case) in the p-type substrate of a diffused or ion implanted \(n^+/p\) diode. For a parabolic valence band and no degeneracy, \(m = 2 [4]\). However, for a band-tail distorted band, the value of \(m\) is not known and must be determined experimentally, as is attempted below. At low and high temperatures, respectively, (1) reduces to
\[
1/\tau_{\text{coll}} \bigg|_{\text{low } T} \approx 1/\tau_{\text{scatt}}, \quad 1/\tau_{\text{coll}} \bigg|_{\text{high } T} \approx 1/\tau_{\text{trapping}}. \tag{3}
\]

If \(1/\tau_{\text{trapping}}\) is dominant, (1)-(3) suggest

\[
\mu_p(\text{trapping}) = \left[\frac{(e/m^*_p)}{(AT^M)}\right] \exp\left(E_A/kT\right) \tag{4}
\]

where \(E_A = E_T - E_V > 0\) is the activation energy of the bound-state level \(E_T\).

The physical interpretation of (1) - (4) is as follows. In heavily doped n-type Si, holes reside mainly in the delocalized states of the valence band. Only a small fraction of the holes is trapped in the localized states of the narrow band tail. At low temperatures, the holes in the tail states are frozen there. Thus \(\mu_p\) is determined entirely by the intraband scattering: \(1/\tau_{\text{coll}} \approx 1/\tau_{\text{scatt}}\). As temperature increases, trapping transitions become important (see Eq. 2) and \(\mu_p\) decreases (see Eq. 1), which allows \(E_A\) to be determined using (4).

Experiments were done to provide qualitative support for the hole-trapping model. The experiments involved a measurement of the temperature dependence of the photocurrent response of both \(n^+ / p\) and \(p^+ / n\) photodiodes. The wavelengths of the incident light used create electron-hole pairs almost entirely in the heavily doped \(n^+\) or \(p^+\) region. Transport of photogenerated minority carriers to the collecting p/n junction and the consequent short-circuit current \(I_{SC}\) depends on the minority-carrier mobility \(\mu\) and diffusivity \(D\) [5]. Hence \(I_{SC}\) and its temperature dependence supplied a vehicle for studying \(\mu\) and \(D\).

The devices for which we report findings here were fabricated by arsenic implantation into 5 Ω-cm p-type Si substrates followed by 1200°C anneal for 30 minutes. The resulting \(n^+\) layer was 1.2 μm deep and the sheet resistance
was 10 Ω/square. The As concentration was \( \sim 10^{20} \text{cm}^{-3} \) and nearly independent of position \( x \) over about 0.6 µm below the surface \( (x = 0) \); for \( x > 0.6 \) µm it slowly decreases becoming about \( 3 \times 10^{18} \) cm\(^{-3} \) at 1 µm. The surface was unpassivated, covered only by a thin (~10 Å) native oxide layer. Other devices with both unpassivated and SiO\(_2\) passivated surfaces were also studied. The results are similar to those to be presented here. The metal contacts covered less than 10% of the area of the front surface.

The \( I_{SC}(T) \) dependence was measured in the wavelength range \( \lambda = 0.38 \) µm to 0.4 µm for which the electron-hole generation rate follows \( G(x) = G(0)\exp(-\alpha x) \) [5], where \( \alpha > 10^5 \) cm\(^{-1}\) [6]. Hence contributions of \( G(x) \) to \( I_{SC} \) originating in the p/n junction space-charge region and in the p-type substrate are negligible. Thus [5] for \( (\alpha L_p)^2 >> 1 \)

\[
I_{SC} = \frac{A q F (1 - R)}{a D_p + S_p} \frac{a D_p + S_p}{p^2} \frac{D_p}{p} \sinh \left( \frac{W}{L_p} \right) + \cosh \left( \frac{W}{L_p} \right)
\]  

(5)

Here \( A \) is the device area, \( F \) is the illumination flux density, \( R \) is the reflection coefficient, \( S_p \) is the effective hole surface recombination velocity, \( W = 1.3 \) µm is the thickness of the quasineutral \( n^+ \) layer, \( L_p = (D_p \tau_p)^{1/2} \) is the hole diffusion length, \( \tau_p \) is the hole lifetime, and \( D_p \) is the hole diffusivity.

The analysis of (5) is complicated if one wishes to obtain the magnitude of the diffusivity \( D_p \) or mobility \( \mu_p = D_p (kT/q) \) from the measured \( I_{SC} \). In this note we are interested, however, only in qualitative trends and try to present a simple picture consistent with the data. For this purpose we consider now the temperature dependence of \( I_{SC} \). The temperature dependences
of $\alpha$ and $R$ [7] and $\tau_p = \tau_A$ (Auger lifetime) [8] are very small. This leaves $S_p$ and $D_p$ as the only temperature dependent parameters in (5). We neglect the temperature dependence of $S_p$, for a moment, later justifying this assumption based on experimental results and on theoretical predictions.

Recent measurements indicate that $L_p \leq 1 \mu m$ in the $n^+$ silicon doped at about $10^{20} \text{ cm}^{-3}$ [9]. Since $W/L_p = 1$ (where $W = 0.5 \mu m$ is the width of the highly doped portion of the emitter at the surface) we can approximate (5) as:

$$I_{SC} = \frac{aD_p + S_p}{a[S_p + (D_p/L_p)]}$$

where $B = AqF(1-R)/L_p\sinh(W/L_p)$ is almost temperature independent. Consider (6) for three special cases. First, if $S_p \gg aD_p$ and $S_p \gg D_p/L_p$, $I_{SC} = B/\alpha$. In this case $I_{SC} \neq f(T)$. This contradicts our experimental result that $I_{SC}$ increases with $T$ (Fig. 2). Second, if $S_p << D_p/L_p$ and $S_p \ll aD_p$, $I_{SC} = BL_p = B(\tau_pD_p)^{1/2}$, i.e. $I_{SC} = D_p^{1/2}$. Third, if $(D_p/L_p) < S_p < aD_p$ (for our device $2 \times 10^3 \text{ cm/sec} < S_p < 10^5 \text{ cm/sec}$, with $D_p \sim 0.2 \text{ cm}^2/\text{sec}$ [1], $\alpha > 10^5 \text{ cm}^{-1}$, $L_p = 10^{-4} \text{ cm}$), then $I_{SC} = B(D_p/S_p)$. We assume now that the third case prevails in our devices, although the analysis below will also accommodate the second case and thus the range $0 \leq S_p \leq 10^5 \text{ cm/s}$. Lastly, the assumption $(aL_p)^2 \gg 1$ used to derive (5) is also valid, since $(aL) \sim 10$. Hence, the analysis is self-consistent.

To obtain a simple picture, we try the assumption, $m=0$, and find from (4) and (6) that

$$I_{SC}/T = C \exp(E_A/kT)$$
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moves $E_{FP}$ closer to $E_V$ (Fig. 1) which increases the occupation of the tail states closer to $E_V$ and $E_A = (E_T - E_V)/kT$ is expected to decrease, as observed. In the temperature range from about 70 K to about 160 K, where the mobility activation behavior is observed, the variation of the energy gap with $T$ is very small [11], which justifies our assumption of nearly temperature independent $\alpha$ and $R$ [7].

The effect of the temperature variation of the effective surface recombination velocity $S_p(T)$ on $I_{SC}(T)$, which was neglected, is now made credible by the following considerations. First, if $S_p(T)$ is important, $E_A$ is expected to be about $E_G/2 = 0.55$ eV in a Shockley-Read-Hall model even though the surface has distributed states in the energy gap [12]. Second, $S_p$ at the heavily-doped $n^+$ surface is likely dominated by temperature insensitive Auger effects [12]. Third, results similar to those shown in Fig. 2 were also obtained from the devices for which passivation by SiO$_2$ sharply decreased $S_p$.

The fact that $I_{SC}$ is not negligible below ~100 K indicates that most of the minority holes are in the extended band states at $T \lesssim 100$ K with only a small fraction trapped at the tail states and immobilized. For the excitations used to measure $I_{SC}(T)$ and also for low-level hole injection in the dark used in [1], the hole concentration in the $n^+$ region is very small. We can then conjecture that the penetration of the localized tail states into the energy gap is only a very small fraction of the energy gap. This supposition, based on our data, agrees with recent theoretical calculations of the band structure of heavily doped Si [13].

It follows directly from our trapping model that $\mu(\text{minority}) < \mu(\text{majority})$ could apply also in the absence of the tail states because shallow impurity levels can act as traps near the minority-band edge (Fig. 1). This suggests that $\mu(\text{minority})$ may strongly depend on compensation. A lack of
compensation in their epitaxial p/n diodes may be responsible for the experimental observation by Dziewior and Silber [14] that $\mu_{\text{minority}} = \mu_{\text{majority}}$ for concentration in Si < $10^{19}$ cm$^{-3}$.

Although the assumptions needed to derive (7) from (5) introduce some inaccuracy in the model for the activation energy of minority-carrier mobility (diffusivity), the general conclusions derived by comparing (7) with the experimental trends exhibited in Fig. 2 are anticipated to remain valid. The exact value of the activation energy in a single-trap model remains in question. When more detailed knowledge concerning the values and the temperature dependencies of parameters in (5) become available, one can then use data presented here to explore aspects of the minority-carrier band tail.

The purpose here is less ambitious. We have demonstrated activation behavior of the minority-carrier mobility and diffusivity, exhibiting thereby an activation energy of the order of $kT$ (for 300 K) as one expects for the prominently active tail states. Moreover, our data in Fig. 2, as interpreted here, supports the inadequacy of the commonly used assumption of equal majority- and minority-carrier mobilities; in turn, this supports interpretations, such as that in [1], of larger values of energy-gap narrowing than is common in the literature.

Lastly, we point out that the assumed value, $m = 0$, and values $m < 0$ in (4) are self-consistent with the experimental results of Fig. 2, but values $m > 0$ are not. However, regardless of the value of $m$, the $I_{\text{SC}}m$ vs. $1/T$ plot shows an activation behavior, thus the assumption of $\mu_{\text{majority}} = \mu_{\text{minority}}$ is always wrong (see Eq. 8).

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FIGURE CAPTIONS

Fig. 1. Qualitative illustration of the band edges of heavily doped $n^+$-silicon. The broken lines show the unperturbed parabolic bands. The positions of both the electron and hole quasi-Fermi levels is also indicated. The arrows near $E_V$ indicate hole capture and emission by the tail states and by the acceptor level from the p-type substrate. The penetration of the tail states into the forbidden gap is assumed to be very small in comparison with the bandgap $E_G = E_C - E_V$.

Fig. 2. Normalized short-circuit photocurrent versus $1/T$ for $\lambda = 0.4 \mu m$. The illumination density for curve 1 is five times larger compared to that of curve 2.
Fig. 1
Fig. 2
May 3, 1985

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Very truly yours,

Arlene Ann Rush  
Document Review Group  
Documentation Section

AAR:dk

Enclosures
cc:  P. French  
Acquisitions Branch

*One copy only being sent.*