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EXTRACTION OF THE SURFACE RECOMBINATION VELOCITY OF PASSIVATED PHOSPHORUS-DOPED SILICON EMITTERS

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ABSTRACT

An analytical procedure to extract the surface recombination velocity of the SiO_2/n type silicon interface, S_p , from PCD measurements of emitter recombination currents is described. The analysis shows that the extracted values of S_p are significantly affected by the assumed material parameters for highly doped silicon: τ_p , μ_p and ΔE_g^{app} . Updated values for these parameters are used to obtain the dependence of S_p on the phosphorus concentration, N_D , using both previous and new experimental data. The new evidence supports the finding that S_p increases strongly with N_D .

INTRODUCTION

The knowledge of the surface recombination velocity, S_p , as a function of the surface dopant density is essential to model and design the emitter regions commonly used in high efficiency silicon solar cells. The purpose of the present investigation is to reexamine previous experimental data [1], report new measurements and describe a new theoretical model to discriminate surface and bulk recombination in nonuniformly doped emitters. As in [1], our approach is to analyze several phosphorus diffusions having different surface dopant concentrations but similar surface passivation conditions. The dopant profiles are measured by SIMS and the total recombination in the emitters, that is, the saturation currents, J_{0e} , are measured by the PCD (photoconductance decay) technique [2]. This approach closely replicates the actual conditions found in silicon solar cell processing.

The extraction of S_p from the measured J_{0e} and $N_D(x)$ is not straightforward, since it can be significantly affected by the remaining material parameters that characterize highly doped silicon: τ_p , μ_p , n_i and ΔE_g^{app} ; the minority-carrier lifetime and mobility, the intrinsic carrier density, and the appar-

ent energy bandgap narrowing, respectively. Accordingly, we have critically reviewed the published data for these parameters, and collected them in Appendix 1. The new $n_i = 1.0 \times 10^{10} \text{ cm}^{-3}$ measured recently at 300 K [3] and the updated values for ΔE_g^{app} and $\mu_p(N_D)$ in [4] have been adopted in this work, together with the Auger recombination coefficient in [5].

THEORETICAL MODEL

The analysis of an emitter region requires sophisticated modeling to account for the position dependence of the material parameters. Extracting S_p with a general purpose computer program would require a trial and error procedure. Approximate analytical models with the necessary degree of sophistication, combined with a reasonable degree of mathematical simplicity [6] allow for S_p to be explicitly written as a function of J_{0e} , which makes an iterative procedure unnecessary and shows the functional dependences of S_p . The following expressions describe a third order approximation for S_p that guarantees sufficient accuracy for all the diffusions to be analyzed here. The surface is situated at $x=W$ and the pn junction at $x=0$.

$$S_p^{\text{av}} = \frac{1}{\mu_p(W)} \frac{\frac{J_{0e}}{q} (1 + B_2) (\bar{A}_1 + \bar{A}_2)}{1 + B_2 - \frac{J_{0e}}{q} (A_1 + A_2)} \quad (1)$$

$$A_1(W) = \int_0^W \frac{dx}{D_p(x) \rho_0(x)} \quad (2)$$

$$\bar{A}_1(W) = \int_0^W \frac{\rho_0(x)}{\tau_p(x)} dx \quad (3)$$

$$B_2(W) = \int_0^W \frac{\bar{A}_1(x)}{D_p(x) \rho_0(x)} dx \quad (4)$$

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$$\bar{B}_2(W) = \int_0^W A_1(x) \frac{p_0(x)}{r_p(x)} dx \quad (5)$$

$$A_2(W) = \int_0^W \frac{\bar{B}_2(x)}{D_d(x) p_0(x)} dx \quad (6)$$

$$\bar{A}_3(W) = \int_0^W B_2(x) \frac{p_0(x)}{r_p(x)} dx \quad (7)$$

As equation (1) shows, the magnitude that can be extracted from measurements of J_{sc} is $p_0(W)S_p$, where p_0 is the equilibrium minority carrier density, which includes the energy bandgap narrowing:

$$p_0(x) = \frac{n_i^2}{N_D(x)} \exp\left(\frac{\Delta E_g^{app}(x)}{kT}\right) \quad (8)$$

To obtain S_p it is, therefore, necessary to know p_0 —or, equivalently, ΔE_g^{app} , n_i , and N_D —accurately. In the PCD technique, the measured magnitude is J_{sc}/n_i^2 [1], that allows for the determination of $S_p \exp(\Delta E_g^{app}/kT)$ only, provided N_D , the concentration of donors at the surface, is known. The recent changes in the accepted values for n_i and ΔE_g^{app} make a re-extraction of S_p necessary.

SURFACE RECOMBINATION VELOCITY

We have extracted S_p again from the measurements of J_{sc}/n_i^2 made at Stanford [7] using the updated parameters mentioned in the Introduction. The results have been plotted in Fig. 1. In addition, the effect of the uncertainties in the energy bandgap narrowing and the hole lifetime on the extraction is examined in the next section.

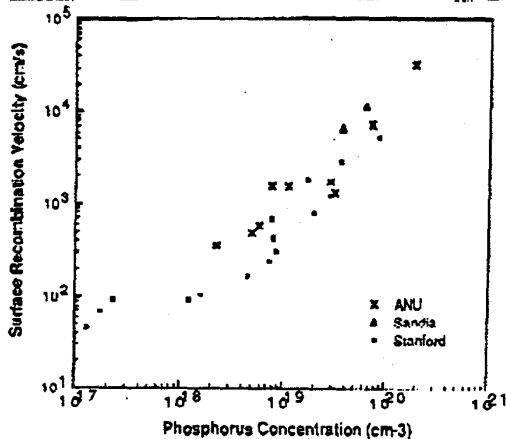


Figure 1. Surface recombination velocity of oxidized n-type silicon as a function of phosphorus concentration.

Additional samples have been prepared at Sandia Labs and ANU, following slightly different process sequences. POCl_3 was used at Sandia as the dopant source, and a sili-

con dioxide layer was grown in the same thermal step, at 875°C and 900°C, respectively, for the two emitters considered here. At ANU the phosphorus diffusion was performed at 830°C using a solid source, followed by a dry oxidation at 1000°C and a forming gas anneal at 400°C. The oxidation and diffusion furnaces were routinely gettered with TCA prior to their use, whereas the actual oxidation was performed in the absence of TCA. The oxidation step was terminated with a ramp down of the temperature in a nitrogen ambient. These oxidation conditions are essentially identical to those used at Stanford [1]. Photoconductance decay measurements of all the samples were performed at Sandia using a microwave-detection apparatus [2]. The phosphorus concentration as a function of position was measured by SIMS, for the ANU samples, at the Lab. Phys. Mat., CNRS, Lyon. For the modeling, the measured dopant profiles were fitted using a polynomial expression.

At Stanford, and also at Sandia, high resistivity n-type wafers were used to determine the recombination currents of the n⁺ emitters. A possibly significant difference with previous experiments has been the use at ANU of 50 Ωcm p-type wafers. The two depletion regions thus formed between the diffused layers and the substrate might introduce additional recombination and distort the interpretation of the PCD data. We have verified that the effect of the depletion regions is negligible, except at low carrier concentrations. As an additional confirmation, we have also used some 12 Ωcm n-type wafers, and found that the corresponding J_{sc} are within one standard deviation of the p-type wafer results. Some of the samples have remarkably low emitter recombination currents and high bulk lifetimes, which indicates that the processing conditions have been satisfactory in terms of quality control.

As can be observed in Fig. 1, the new data points agree reasonably well with those from [1]. The old values of S_p , originally extracted in [1] using del Alamo's data [8] for the energy bandgap narrowing and hole lifetime, are not very different from those in Fig. 1 because we have used a higher ΔE_g^{app} and lower τ_p . The experimental results indicate that S_p is linearly proportional to N_D for dopant densities higher than $7 \times 10^{17} \text{ cm}^{-3}$, approximately. This supports the conclusions in [1]. The data points in Fig. 1 can be fitted with the following expressions:

$$S = S_0, \text{ for } N_D < N_{ref}$$

$$S = S_0 \left(\frac{N_D}{N_{ref}} \right), \text{ for } N_D > N_{ref} \quad (9)$$

with $S_0 = 70 \text{ cm/s}$ and $N_{ref} = 7 \times 10^{17} \text{ cm}^{-3}$. Although Fig. 1 and equation (9) indicate that S_p is nearly constant for low phosphorus concentrations, it should be noted that surface recombination velocities smaller than 70 cm/s have been measured for dopant densities below $1 \times 10^{17} \text{ cm}^{-3}$ [1, 7]. At such low dopant densities the surface recombination velocity has been found to be dependent on the injection level in the substrate [7].

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UNCERTAINTY ANALYSIS

The photoconductance decay measurements were performed five times on each of the two sides of every sample. Some of the measurements were rejected due to poor signal-to-noise ratio and the rest averaged. The standard deviation of the extracted J_0 is typically less than 20%; this is similar to the measured uncertainty in [1]. The possible error in the SIMS measurements of the phosphorus concentration is less than $\pm 15\%$. Differences in sheet resistance between the two sides of the wafer are also less than $\pm 15\%$. In general, the sheet resistances calculated from the SIMS profiles agree well with the measured values. The actual dopant concentration at the surface affects the results critically, for some samples. This is compounded with the fact that the first data points obtained by SIMS have to be discarded, and the surface concentration can only be evaluated by extrapolation. We have considered three possible different models for the energy bandgap narrowing, as described in the Appendix. The dependence of ΔE_g with N_D proposed by Klaassen [4] has been adopted here because it represents a moderate, intermediate assumption. Del Alamo's model [8] gives lower ΔE_g at moderate dopant densities ($\sim 27\%$) and nearly the same values at high doping levels ($\sim 2\%$). The additional correction introduced by the new $n_i = 1 \times 10^{10} \text{ cm}^{-3}$ implies a 17% to 10% higher ΔE_g than Klaassen's model. Additionally, the three models are affected by an experimental uncertainty of about $\pm 9 \text{ meV}$ [8]. Three different Auger recombination coefficients have been considered, as described in the Appendix; they represent an uncertainty in the hole lifetime between -18% and $+27\%$.

Sample A1	Parameter uncertainty		
	J_0 ($\pm 25\%$)	τ_A (high, low)	ΔE_g (high, low)
Uncertainty in S_p	+270%, -970%	+100%, -146%	-207%, +243%

Table 1. Uncertainty in the surface recombination velocity extracted for sample A1. $N_{D0} = 7 \times 10^{19} \text{ cm}^{-3}$, $x_j = 1.6 \mu\text{m}$.

We have found that the extracted values of S_p are significantly affected by the assumed bulk material parameters, especially by the energy bandgap narrowing and the minority carrier lifetime. This is particularly noticeable for highly doped, relatively deep diffusions. Table 1 shows the uncertainty in S_p extracted for a relatively heavily doped sample as a consequence of the uncertainties in the measured J_0 and in the lifetime and energy bandgap shrinkage. Negative values of the surface recombination velocity are obtained for some combinations of the Auger recombination coefficient and bandgap narrowing. This points out that, for some of the most heavily doped samples, the uncertainties in ΔE_g , τ_A , lifetime and J_0 make it difficult to extract S_p with a reasonable degree of confidence.

As Table 2 shows, the uncertainties are significantly lower for moderately doped samples, the main source of uncer-

tainly now being ΔE_g . Considering these uncertainties, which also affect the previous determination of S_p [1], the agreement between the different sets of data can be considered acceptable.

Sample A5	Parameter uncertainty		
	J_0 ($\pm 15\%$)	τ_A (high, low)	ΔE_g (high, low)
Uncertainty in S_p	+21%, -21%	+5.5%, -8.5%	-40%, +103%

Table 2. Uncertainty in the surface recombination velocity extracted for sample A5. $N_{D0} = 5 \times 10^{18} \text{ cm}^{-3}$, $x_j = 0.96 \mu\text{m}$.

It is convenient, especially for the most highly doped samples, to calculate an upper bound on S_p assuming an infinite lifetime (transparent approximation):

$$S_{p,transp} = \frac{J_0}{q A_1(W)} \frac{1}{1 - \frac{J_0}{q A_1(W)}} \quad (10)$$

The values of the upper bound on S_p have been plotted in Fig. 2. The spread of points is much less than in Fig. 1, as a result of a reduced uncertainty, and the agreement between the different sets of data is better.

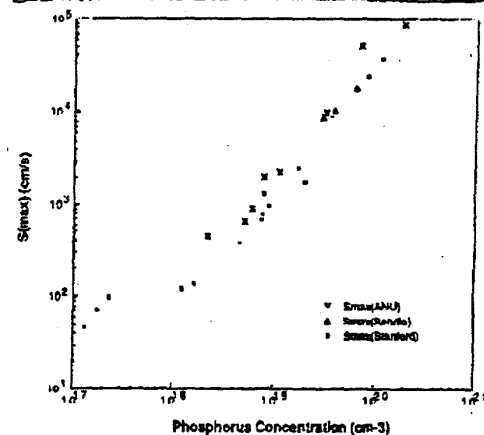


Figure 2. Upper limit of the surface recombination velocity for the samples in Fig. 1.

CONCLUSIONS

The extraction of S_p from diffused emitters is subject to several sources of uncertainty. This includes not only the error in the measurements of J_0 and the dopant profile but also the assumed energy bandgap narrowing and minority carrier lifetime, especially for deeply diffused samples. Under the assumption of intermediate values for these parameters, from [4] and [5], respectively, we conclude that the surface recombination velocity of the Si/SiO₂ interface increases linearly with the phosphorus concentration at the surface, for

$N_D \geq 7 \times 10^{17} \text{ cm}^{-3}$. S_p is a process dependent parameter: the previous conclusion applies to dry oxidations performed in the absence of TCA in the range $875^\circ\text{C} \leq T \leq 1000^\circ\text{C}$, followed by a 400°C anneal in forming gas.

APPENDIX: Parameters of highly doped silicon

The apparent energy bandgap shrinkage, ΔE_g^{app} , has been extracted by several authors from steady-state measurements of ρ , D_p , and L_p combined with an additional transient measurement of the lifetime, together with the assumption of a certain n_i . If values for n_i or μ_p different from those assumed in the original work are to be used, ΔE_g^{app} must be corrected so that ρ , D_p remains unaltered. The experimental data can be fitted with the following expression:

$$\Delta E_g^{\text{app}}(N_D) = A \ln\left(\frac{N_D}{N_{\text{ref}}}\right) \quad (11)$$

for $N_D > N_{\text{ref}}$, and $\Delta E_g^{\text{app}} = 0$ for $N_D \leq N_{\text{ref}}$. Table 3 gives the values of the coefficients A and N_{ref} for n -type silicon corresponding to three different levels of correction. These three dependences are based on the same set of experimental data reported in [8], which were affected by an uncertainty of about $\pm 9 \text{ meV}$ at a dopant density of $5 \times 10^{19} \text{ cm}^{-3}$. Del Alamo's model, in the first row of Table 3, assumes $n_i = 1.456 \times 10^{10} \text{ cm}^{-3}$ at 300 K [8]. Klaassen et al. [4] have corrected it to account for a different minority hole mobility, as well as $n_i = 1.19 \times 10^{10} \text{ cm}^{-3}$. The additional correction shown in the third row of Table 3 is consistent with the new $n_i = 1.0 \times 10^{10} \text{ cm}^{-3}$ at 300 K (based on $1.0/6 \times 10^{10} \text{ cm}^{-3}$ proposed in [9], $1.01 \times 10^{10} \text{ cm}^{-3}$ reported in [3] and $9.7 \times 10^9 \text{ cm}^{-3}$ measured in [10]). The use of this fully updated ΔE_g^{app} in the extraction of S_p gives negative values of S_p for several samples. Because of this, and considering the $\pm 9 \text{ meV}$ uncertainty in the original data for ΔE_g^{app} , we have decided to adopt the model in [4], described by the coefficients in the middle row of Table 3.

ΔE_g^{app}	$A \text{ (meV)}$	$N_{\text{ref}} \text{ (cm}^{-3}\text{)}$	Reference
low	18.7	$7 \cdot 10^{17}$	del Alamo, 1985 [8]
mid.	13.9	$1.3 \cdot 10^{17}$	Klaassen, 1992 [4]
high	13.9	$7 \cdot 10^{16}$	updated n_i and μ_p

Table 3. Energy bandgap narrowing in n -type silicon.

The hole lifetime is frequently given by an expression of the form:

$$\tau_p^{-1} = B N_D + C_{\text{RA}} N_D^2 \quad (12)$$

In this work we have used $C_{\text{RA}} = 2.2 \times 10^{-31} \text{ cm}^{-6} \text{ s}^{-1}$ [5] and $B = 2 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$, to fit available experimental data. Transient decay measurements of the lifetime are not dependent on n_i , so a correction for the lifetime is not necessary. The literature exhibits a range of values for C_{RA} , the Auger recombination coefficient, from $C_{\text{RA}} = 1.8 \times 10^{-31} \text{ cm}^{-6} \text{ s}^{-1}$ [8] to $C_{\text{RA}} = 2.8 \times 10^{-31} \text{ cm}^{-6} \text{ s}^{-1}$ [10].

For $N_D \geq 1 \times 10^{19} \text{ cm}^{-3}$ there is good agreement between del Alamo's [8] and Wang's [5] measurements of the minority carrier mobility and Klaassen's recent theoretical study [4], all of them indicating that $\mu_{\text{minor}} > \mu_{\text{major}}$. The latter predicts slightly higher μ_p than del Alamo's fit at the heaviest dopings. With respect to the lower doping range, $N_D = 1 \times 10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$, Klaassen et al. [4] contend that the data of Dziewior and Silber [12], which were used by del Alamo, are too high and too scattered. Klaassen's model predicts that the minority carrier mobility should equal the majority carrier mobility for $N_D < 1 \times 10^{17} \text{ cm}^{-3}$. Recent measurements of the minority-carrier diffusivity by Sproul [13] have confirmed that $\mu_{\text{minor}} = \mu_{\text{major}}$ for $N_D < 3 \times 10^{16} \text{ cm}^{-3}$. The following expression for $\mu_{p(\text{min})}$ has been used in this work. It describes approximately both Klaassen's model, the experimental data in the moderate doping range [14] and in the heavy doping range [5,6], and the majority-carrier mobility [15] for $N_D < 1 \times 10^{17} \text{ cm}^{-3}$.

$$\mu_{p(\text{min})} \approx 155 + \frac{315}{1 + \left(\frac{N_D}{10^{17}}\right)^{0.8}} \quad (13)$$

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