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High-Efficiency Concentrator Silicon Solar Cells: Final Report

R. A. Sinton, A. Cuevas, R. R. King, R. M. Swanson
Solid State Electronics Laboratory
Stanford University
Stanford, CA 94305

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R.A. Sinton, A. Cuevas, R.R. King, R.M. Swanson
Solid State Electronics Laboratory
Stanford University
Stanford, CA 94305

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ABSTRACT

This report presents results from extensive process development in high-efficiency Si solar cells. An advanced design for a 1.56-cm² cell with front grids achieved 26% efficiency at 90 suns. This is especially significant since this cell does not require a prismatic cover glass. New designs for simplified backside-contact solar cells were advanced from a status of near-nonfunctionality to demonstrated 21-22% for one-sun cells in sizes up to 37.5 cm². An efficiency of 26% was achieved for similar 0.64-cm² concentrator cells at 150 suns. More fundamental work on dopant-diffused regions is also presented here. The recombination vs. various process and physical parameters was studied in detail for boron and phosphorous diffusions. Emitter-design studies based solidly upon these new data indicate the performance vs. design parameters for a variety of the cases of most interest to solar cell designers. Extractions of p-type bandgap narrowing and the surface recombination for p- and n-type regions from these studies have a generality that extends beyond solar cells into basic device modeling.
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Chapter 1

Introduction

The work performed during for this contract, 75-6318, was primarily in three areas. The first of these was a detailed study of the diffused regions in the solar cell. The recombination in the diffused regions on high-efficiency solar cells tends to depend heavily upon the surface recombination velocity at the Si-SiO₂ interface. This has been repeatably demonstrated in the past few years with experiments comparing passivated and unpassivated front surfaces in solar cells. Despite this critical dependence upon the passivation quality, modeling for these regions has been limited by a lack of knowledge concerning the surface recombination velocity as a function of the doping level at the surface. Typically, an assumption was made about the value to be used in simulations for this parameter. For example, many studies assume $S=1000$ cm/sec, independent of doping level. Experimentally, undoped surfaces have been demonstrated with $S=2$ cm/sec. So, modeling studies for emitter saturation current density and emitter quantum efficiency used different, sometimes rather arbitrary assumptions about the surface recombination velocity as a function of the doping. We intended to measure this dependence for phosphorus for several different surface process conditions and topographies. These data, along with a set of modelled results for several of the key figures-of-merit for solar cell emitters, are presented in Chapter 2.

The same study was done for boron. The data analysis for this case was not as straightforward. In order to obtain a complete and consistent description of the data, a
revision of the band-gap narrowing as a function of the doping level was derived. With this new result, the surface recombination velocity was found, although in the case of boron it is injection-level dependent. The modeled curves of the emitter figures-of-merit for solar cell design are presented based upon this data.

Some comments on the use of alternative dopant sources; POCl₃, BBr₃, and Al; are appended onto this chapter.

Next, in Chapter 3, we show the progress that has been made in new simplified backside contact solar cells. In the previous final report, for contract 02-7063A, we presented a set of ideas for some simplified cell designs. Although we had almost convinced ourselves that they would work well, the results at that point indicated nearly nonfunctional cells. The best result was a 15.4% cell at 40 suns. In this current research, we follow up these ideas and demonstrate several one-sun cells. 10.2 cm² cells achieved 22% efficiencies and 37.5 cm² cells reached efficiencies of 21%. These results were from processes that used one mask alignment. In more detailed studies presented here, we clearly prove that even this single alignment is unnecessary. This makes these the simplest cells to fabricate that have reached the 21-22% efficiency level. Concentrator cells made with the same basic design reached about 26%. 32 of these were delivered to Sandia for use in modules.

Chapter 4 reports experimental results for cells with frontside grids. The focus of this research was to attempt to demonstrate 25% efficiencies using designs that did not require the prismatic cover-glasses to reduce the grid reflection. Numerous schemes were hatched during the course of this effort. One worked quite well. 26% efficiencies were obtained at 90 suns. This cell was rather difficult to make. Another design that proved considerably easier to fabricate achieved 25% at low concentrations, 25 suns, and 24.5 at 150 suns. Also, another design far less fabricable reached this same 24.5% performance. This study finished off with some exotic structures intended to provide the lowest possible frontside stable passivation on a p-i-n solar cell. These initial attempts did not work too well. However, use of the emitter data from Chapter 2 allowed a complete study of the potential for these designs using a computer and an array of appropriate modeling programs. This study models the performance for p-i-n, n-i-p, and backside contact cells for several parameter sets. One parameter set reflects
existing, demonstrated technology with simple cell layouts. Others consider more exotic cell schedules and leading-edge parameters.
Chapter 2

A Detailed Modeling and Characterization Study of Phosphorus- and Boron-Doped Regions

2.1 Introduction

Passivated emitters are an important part of many high-efficiency solar cell designs [5,23,58,37,52]. An emitter at a semiconductor surface is said to be passivated if the surface has been treated in such a way as to reduce carrier recombination in the emitter. Such emitters can have an emitter saturation current density, $J_o$, that is an order of magnitude lower than that of an unpassivated emitter [58,35]. Moreover, the minimum $J_o$ of passivated emitters occurs for shallow, relatively lightly-doped diffusions, so the quantum efficiency of this type of emitter located on the sunward surface of a solar cell can be very high while maintaining low $J_o$. In contrast, the $J_o$ of unpassivated emitters decreases with increasing emitter thickness and surface dopant concentration [35,15], which compromises quantum efficiency. An oxide-passivated emitter in silicon also has some advantages over an oxidized silicon surface with the same doping density as the
substrate. For solar cells with a substrate in high-level injection, at low incident light intensities, recombination in a passivated emitter at the surface can be much lower than at an oxidized, undoped surface [37,38]. In addition, the recombination characteristics of passivated emitters have been found to be much more resistant to degradation by UV light than those of an oxidized, undoped surface [32].

Numerical modeling of these emitters is straightforward given the doping as a function of position; and the bandgap narrowing ($\Delta E_p$), minority carrier lifetime and mobility, and surface recombination velocity as a function of the doping level. Previous studies of the mobility, lifetime, and bandgap narrowing provide the necessary data for these parameters [15,60]. However, direct measurements of the surface recombination velocity as a function of the doping level for diffused regions were scarce. In many of the cases most relevant for solar cells, the recombination in the diffused emitter region is essentially proportional to this surface recombination velocity. Hence, the assumptions made for this function accounted for the greatest uncertainty in many modeling studies of diffused regions. We undertook this study primarily to determine this function so that more accurate predictions could be made.

In an initial study for phosphorus emitters, presented here, this data was determined from analyzing experimental recombination data with a numerical model using the best available values for the physical parameters. This allows a complete description for phosphorus-diffused regions. Measurements on boron diffusions at that time indicated that such a simple picture was not possible in that case. Inconsistencies appeared in the data analysis that could not be explained.

Subsequent work indicated that the case for boron was indeed more complex. In order to consistently describe the data obtained, a revision of the bandgap narrowing as a function of doping was required. In addition, a strong dependence of the Si-SiO$_2$ surface recombination velocity on the minority-carrier injection level complicated the analysis. These two facts necessitated a more detailed study. Hence, for boron, we present an extraction of both the surface recombination velocities and the bandgap narrowing as a function of the doping level.

The results from these studies of both phosphorus and boron can be used in solar
cell modeling at several different levels. First, they provide a data base of the emitter saturation current densities that result from a certain set of processing conditions. Several ambients and anneal schedules are studied in this regard and detailed physical characterization for each emitter is provided. Second, we fit the data with the best available physical models and parameters in order to provide graphs of modeling results for emitter saturation current densities, quantum efficiencies, and sheet resistances that would result from common dopant profiles as a function of the surface dopant concentration and the junction depth. Third, we provide new measurements for the several more fundamental physical parameters, namely the surface recombination velocities in phosphorus- and boron-doped silicon and the bandgap narrowing in boron-doped silicon. These measurements may improve the predictive accuracy when using complete numerical models such as PC-1D[3].

These data were obtained for the special case of doped-oxide diffusion sources. In a final section in this chapter, we provide data that indicate that essentially equivalent results can be obtained with POCl₃ n-type diffusions and BBr₃ p-type diffusions. A few Al diffusion schedules were characterized and found to decrease the base lifetime of the wafers and result in rather high emitter saturation current densities as well.

2.1.1 Previous work

Many workers have studied recombination at the oxidized silicon surface. Some of their contributions include: measurement of increasing density of interface states, \( N_{it} \), with increasing phosphorus, arsenic, boron, or gallium concentration in the silicon, and higher fixed oxide charge for boron doping than for phosphorus doping [57]; deep level transient spectroscopy measurements of the interface state density per unit energy, \( D_{it} \), and of electron and hole capture cross sections, \( \sigma_n \) and \( \sigma_p \), on nearly intrinsic silicon [18]; the decrease in the measured \( J_o \) of oxide passivated boron emitters with increasing oxidation temperature [5]; measurements of the \( J_o \) of oxide-passivated phosphorus and boron diffusions by contactless photoconductivity decay [35]; the \( \sigma_n/\sigma_p \) ratio of the interface traps that dominate recombination for lightly boron doped, oxidized surfaces [67]; and measurement of the decrease in \( s \) at a lightly boron doped Si/SiO₂ interface.
with increasing injected-carrier density [65,42].

Finally, several authors have measured the fundamental surface recombination velocity, \( s_o \), at oxidized, boron-doped silicon surfaces [34,20,60]. In principle, \( s_o \) can be used to predict the actual surface recombination velocity, \( s \), but, in practice, the predicted value of \( s \) is a very sensitive function of the surface potential and of the ratio \( \sigma_n/\sigma_p \). This leads to a large uncertainty in the value of \( s \) when calculated in this way. In addition, using \( s_o \) as a parameter to characterize recombination at the Si/SiO\(_2\) interface requires the assumption that \( D_{it}, \sigma_n, \) and \( \sigma_p \) are constant with respect to bandgap energy. These approximations become less valid as the fermi-level splitting becomes large, as in a passivated solar cell emitter.

### 2.1.2 Experimental method used in this work

Contactless photoconductivity decay [35,12] was used to measure surface and bulk recombination in this study. In this method, the sample to be measured is placed on a coil with an oscillating magnetic field. The coil couples inductively to the sample, and the measured signal output of the circuit containing the coil is proportional to the conductance of the sample. A pulse of light from a strobe lamp generates carriers in the silicon sample. After several transit times of the wafer have elapsed, the excess carrier concentration, \( n' \), has a nearly uniform distribution throughout the wafer. The decay of \( n' \) is then recorded as a function of time. The effective lifetime, \( \tau_{\text{eff}} \), of the sample as a whole is given by:

\[
\frac{1}{\tau_{\text{eff}}} = -\frac{1}{n'} \frac{dn'}{dt} .
\]

Both surface and bulk recombination components are included in \( \tau_{\text{eff}} \). Most of the samples consisted of a lightly-doped silicon substrate, that has identical planar dopant diffusions with thermal oxide passivation on both sides of the wafer. The substrate was in high-level injection during the measurement of \( \tau_{\text{eff}} \). The doped surfaces are in low-level injection. Since the substrate is highly injected, \( n' \) is almost exactly equal to \( n \), the total electron concentration, and \( \tau_{\text{eff}} \) depends on \( n \) according to the expression:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + 2J_o \frac{n}{q n_i^2 w} + C_A n^2 ,
\]
where $\tau_{\text{bulk}}$ is the bulk Shockley-Read-Hall (SRH) lifetime, $J_0$ is the emitter saturation current density of a single dopant diffusion, $w$ is the wafer thickness, and $C_A$ is the ambipolar bulk Auger coefficient [35]. When $(1/\tau_{\text{eff}}) - C_A n^2$ is plotted versus $n$, a straight line results which has a slope proportional to $J_0$. Thus this method yields a fairly direct measurement of $J_0$. The value of $C_A$ used for the highly-injected substrate was $1.66 \times 10^{-30}$ cm$^6$/s from [50], and was assumed to have an uncertainty of $\pm 10\%$. After the lifetime measurements, the oxide was stripped from the samples, the sheet resistance of each diffusion was measured, and the dopant profile was measured by secondary ion mass spectroscopy (SIMS).

In the low doping range, $\tau_{\text{eff}}$ was also measured for some uniformly doped substrates with oxidized surfaces. In this case, $\tau_{\text{eff}}$ is given by:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2}{w} s,$$

where $s$ is the surface recombination velocity. When several samples with identical doping and processing but different thicknesses are measured, $1/\tau_{\text{eff}}$ can be plotted versus $2/w$ to give a straight line with slope $s$ and a $(1/\tau_{\text{eff}})$-axis intercept of $1/\tau_{\text{bulk}}$.

### 2.2 Phosphorous diffusions

#### 2.2.1 Emitter saturation current density for diffusions.

Fig. 2.1 shows some of the measured values of $J_0$ at 300K for oxide-passivated phosphorus diffusions, and how they depend on $N_{D,\text{surf}}$, the surface phosphorus concentration, and $x_j$, the emitter thickness at which $N_D = 10^{16}$ cm$^{-3}$. The samples shown were processed in slightly different ways. Some were oxidized in an ambient containing trichloroethane (TCA). Some were not. Some were given a forming gas anneal (FGA) at 400$^\circ$C, others were given an aluminum anneal, in which both sides of the wafers were covered with sputtered aluminum, and annealed at 400$^\circ$C. For all samples, the dopant source was phosphorus-doped SiO$_2$, formed by atmospheric-pressure chemical vapor deposition at 400$^\circ$C.
Figure 2.1: Measured values of the emitter saturation current density for untextured, oxide-passivated phosphorus diffusions, after either a forming gas anneal or an aluminum anneal. The emitter thickness ($N_D = 10^{16}$ cm$^{-3}$) was determined by SIMS. The value of $J_o$, in units of $10^{-13}$ A/cm$^2$ is printed above each point.

From Fig. 2.1, it can be seen that increasing emitter thickness or increasing $N_{D,\text{surf}}$ tends to increase the $J_o$, as bulk recombination in the emitter dominates over surface recombination. $J_o$ is lowest for shallow, lightly-doped emitters. The $J_o$ remains small even for emitters with very low $N_{D,\text{surf}}$, in spite of the lower potential barrier between the surface and the bulk of the wafer that exists for such emitters. This is because $s$ decreases with decreasing $N_{D,\text{surf}}$, which tends to counteract the detrimental effect of the lower potential barrier.

Fig. 2.2 is a similar plot showing the experimental $J_o$ dependence on $N_{D,\text{surf}}$, for passivated emitters that have not received a forming gas anneal. Below $N_{D,\text{surf}} = 6 \times 10^{18}$ cm$^{-3}$, the higher $s$ of the samples without an FGA begins to impact the $J_o$ seriously.
Figure 2.2: Measured values of the emitter saturation current density, $J_o$, for untextured, oxide-passivated phosphorus diffusions, with no forming gas anneal. The value of $J_o$ in units of $10^{-13} \text{ A/cm}^2$ is printed above each point.
Figure 2.3: The emitter saturation current densities for textured wafers.

Since most high-efficiency silicon solar cells have a textured sunward surface, it is important to know what effect texturing has on the $J_o$. Fig. 2.3 shows measured values of $J_o$ for passivated emitters with a textured surface. $N_{D,\text{surf}}$ and $x_j$ could not be measured directly on the textured samples by SIMS, because of the rugged topography of the surface. Instead, the values of $N_{D,\text{surf}}$ and $x_j$ used in Fig. 2.3 are those measured on companion wafers that were processed identically, except that they were untextured. The value of $J_o$ for the textured emitters is typically higher than for the corresponding untextured emitter, but the same trends of lower $J_o$ with decreasing $N_{D,\text{surf}}$ and decreasing $x_j$ persist in the textured case.
2.2.2 The dependence of the surface recombination velocity on the doping level

Since the dependence of $J_0$ on $N_{D,\text{surf}}$ in the phosphorus emitters is determined at least in part by the dependence of $s$ on $N_{D,\text{surf}}$, it is possible to extract information about $s$ as a function of $N_{D,\text{surf}}$ from $J_0$ measurements. This was done by solving the carrier transport equations numerically, in the manner described by del Alaro [15]. To extract $s$ in this way requires well-known values of the properties that control carrier transport, such as minority-carrier lifetime, minority-carrier mobility, and bandgap narrowing, all as a function of $N_D$. Fortunately, these parameters are known with a high degree of confidence from previous experiments [15], with the possible exception of lifetime for doping lower than $N_D \approx 5 \times 10^{17} \text{cm}^{-3}$. Above $N_D \approx 4 \times 10^{18} \text{cm}^{-3}$, hole lifetime in the heavily phosphorus-doped emitter should be dominated by band-to-band Auger recombination. Since this process is fundamental, in that it does not depend on defect density in the silicon, the value of the Auger coefficient found in previous experiments should be quite applicable to the emitters in this study. In addition, the contribution of bulk recombination in the emitter to the measured $J_0$ can be minimized by using very thin emitters, improving the accuracy of $s$. The experimental uncertainty in bandgap narrowing is $\pm 9$ meV out of 81 meV at $N_D = 5.3 \times 10^{19} \text{cm}^{-3}$ [15].

Given the SIMS measurements of phosphorus concentration as a function of depth and the measured values of $J_0$, the numerical emitter model was used to find $s$ for each emitter. The results are shown in Fig. 2.4. Most of the emitters used to find $s$ were thin enough that the $J_0$ was dominated by surface recombination rather than bulk recombination, to make the measurement as sensitive to $s$ as possible. The extracted values of $s$ show a remarkable correlation with $N_{D,\text{surf}}$, especially for a parameter that is a process dependent as $s$. Note that the aluminum annealed samples have a consistently lower $s$ than those that received an FGA. Also, a 950°C oxidation seems to yield a somewhat higher $s$ than one at 1000°C.

For $N_{D,\text{surf}}$ greater than about $10^{18} \text{cm}^{-3}$, the increase in $s$ is approximately linear in $N_{D,\text{surf}}$. This is the behavior one would expect if the increased $s$ were due solely to an increase in interface states with a constant capture cross section, and if the
Figure 2.4: Surface recombination velocity, $s$, extracted from measurements of $J_o$ on oxide-passivated diffusions, using a numerical model. The value of $s$ for the starred points was measured using several thicknesses of wafers with uniform phosphorus doping.

* indicates that $s$ was measured on uniformly doped substrate
interface state density were proportional to the surface density of phosphorus atoms. This is an over-simplified explanation, since the cross section probably does depend on bandgap energy and the surface recombination rate is dependent on the quasi-fermi-level positions at the surface.

The points indicated by stars in Fig. 2.4 were measured on samples with uniform phosphorus doping throughout the wafer, using several different wafer thicknesses. This measurement does not require any assumption of the dependence of bulk lifetime on \( N_D \) and serves as a check on the values of \( s \) extracted from emitter measurements. It was found that the value of \( s \) is dependent on injection level in the uniformly doped substrate: \( s \) decreases with increasing excess-carrier concentration. Evidence for this phenomenon was also observed for the three emitters with \( N_{D,\text{surf}} < 3 \times 10^{17}\text{cm}^{-3} \). The \( (1/\tau_{\text{eff}}) - C_An^2 \) vs. \( n \) curves for these emitters were not straight lines as they were for all the other emitters in this study. Instead, they curve down as \( n \) increases, indicating that the recombination rate is lower than expected at high values of \( n \). This could be explained by an injection-level-dependent value of \( s \) that decreases as \( n \) increases. The \( J_0 \) values for these three samples were taken in the limit of low \( n \), where the \( (1/\tau_{\text{eff}}) - C_An^2 \) vs. \( n \) curves become nearly linear. The values of \( s \) found for the uniformly doped substrates were measured at \( n = 3.0 \times 10^{15}\text{cm}^{-3} \).

To show how small the contribution of bulk recombination in the emitter to the total \( J_0 \) is in these transparent emitters, the value of \( s \) extracted in the absence of bulk recombination is plotted in Fig. 2.5. In this case, all recombination is attributed to surface recombination, so these values of \( s \) are an upper limit given the bandgap narrowing and mobility measured by del Alamo, and the measured values of \( J_0 \). Comparison of the points calculated with and without bulk recombination shows that more than half of the recombination in the emitter takes place at the surface for most of the emitters.

2.2.3 Calculated performance for phosphorus emitters.

The experimentally determined dependence of \( s \) on \( N_{D,\text{surf}} \) from the last section can be combined with the lifetime, mobility, and bandgap narrowing data in [15] to gen-
Figure 2.5: Surface recombination velocity, $s$, extracted for both the standard case, in which the bulk recombination in the passivated emitter is accounted for, and the case in which there is no bulk recombination. The latter case gives an upper limit for $s$. 

* indicates that $s$ was measured on uniformly doped substrate.
erate a contour plot of $J_o$ for oxide-passivated phosphorus diffusions, as a function of both $N_{D,\text{surf}}$ and $x_j$. This has been done in Fig. 2.6, for diffusions with a gaussian phosphorus concentration profile. The $s$ vs. $N_{D,\text{surf}}$ data used was for samples with a 1000°C oxidation, no TCA during oxidation, and an FGA. The value of $s$ was found for a given $N_{D,\text{surf}}$ from the fit shown in Fig. 2.4. Since this contour plot was generated from $J_o$ data such as that shown in Fig. 2.1, it naturally agrees with that data. Because this contour plot is based on experimental $s$ values, it should be more useful for predicting the $J_o$ of oxide-passivated diffusions than emitter modeling based on an assumed value of $s$. In the previous absence of data on $s$ as a function of $N_{D,\text{surf}}$, a common practice was to use a constant value of $s$, e.g., 1000 cm/s, to predict the $J_o$ of passivated emitters. Fig. 2.7 is a contour plot of $J_o$ that assumes $s = 1000$ cm/s. A comparison between Figures 2.6 and 2.7 indicates that the inclusion of the doping dependence of $s$ fundamentally changes the trends in $J_o$. Most notably, for the doping range less than $10^{18}$ cm$^{-3}$, the use of an $s = 1000$ cm/s assumption leads to an order-of-magnitude overestimate of $J_o$. One can see that there is a large discrepancy between the values of $J_o$ predicted in this plot and those calculated using experimental values of $s$.

Another parameter of interest for solar cell design is the photogenerated current density lost due to recombination in the doped layer on the sunward surface, $J_{\text{lost}}$. $J_{\text{lost}}$ is defined to be the current density photogenerated within the volume of the emitter, minus the current density flowing out of the emitter into the substrate. In Fig. 2.8, contours of constant $J_{\text{lost}}$ are shown in the $N_{D,\text{surf}}, x_j$ plane for gaussian phosphorus diffusions on the sunward surface of a solar cell. The same fit of experimental $s$ vs. $N_{D,\text{surf}}$ data shown in Fig. 2.4 was used. $J_{\text{lost}}$ was calculated for the SERI AM1.5 direct normal solar spectrum [45] incident on the cell, normalized to have an incident intensity of 0.100 W/cm$^2$ (one sun), and for unity optical transmittance of the sunward surface. For reference, the photogenerated current density in 0.1 cm of silicon is 0.0415 A/cm$^2$ for this spectrum, using the absorption coefficient data in [26]. $J_{\text{lost}}$ is actually quite independent of $s$, except for deep emitters with low surface concentration.

Fig. 2.9 gives contours of constant sheet resistance, $\rho_\square$, of gaussian phosphorus diffusions on the same axes as the two previous plots, so that $J_o$ and $J_{\text{lost}}$ may be correlated with $\rho_\square$. The $\rho_\square$ contours were calculated using the majority-carrier mobility.
Figure 2.6: Contours of constant $J_0$ for oxide-passivated emitters with a gaussian phosphorus profile. The dependence of $s$ vs. $N_{D, surf}$ used is the fit shown in a previous figure, which was experimentally determined for emitters with an untextured surface, oxidized at 1000°C with no TCA, and with an FGA.
$J_0 \ (10^{-13} \ \text{A/cm}^2)$, using $s = 1000 \ \text{cm/s}$

Figure 2.7: Contours of constant $J_0$ for oxide-passivated emitters with a gaussian phosphorus profile assuming $s = 1000 \ \text{cm/s}$. The contours are labeled with the corresponding value of $J_0$, in units of $10^{-13} \ \text{A/cm}^2$. 
Figure 2.8: Contours of constant $J_{\text{lost}}$, the current density lost to recombination in the emitter, for oxide-passivated emitters with a gaussian phosphorus profile. The contours are labeled with the corresponding value of $J_{\text{lost}}$, in units of $10^{-3}$ A/cm$^2$. (SERI AM1.5 direct normal solar spectrum, normalized to 0.100 W/cm$^2$).
Figure 2.9: Contours of constant $\rho_p$ for emitters with a gaussian phosphorus profile, using the majority-carrier mobility data of Thurber. The contours are labeled with the corresponding value of $\rho_p$, in $\Omega/\square$.

data from [61]. Comparing Figures 8 and 9, it is evident that $J_{\text{lost}}$ depends mainly on $\rho_p$ (as the curves are roughly parallel), but that deeper emitters (when passivated) tend to have less photocurrent loss than shallower ones of the same sheet resistance.

Two solar cell design cases may illustrate how these plots can be put to use. In the case of a back-contacted cell in which the sunside diffusion is used mainly to reduce surface recombination, not to collect current, the optimum emitter is the one with the lowest $J_0$. For untextured surfaces, this corresponds to an emitter with $N_{D,\text{surf}} \approx 1 \times 10^{18} \text{cm}^{-3}$ that is as thin as possible. Fig. 2.3 shows an emitter with these specifications is probably near optimum in $J_0$ when it has a textured front surface, as well. Other considerations such as resistance to ultraviolet-induced degradation may play a dominant role in selecting the best emitter of this type [32].

The second case is that of the emitter on the sunward surface of a conventional solar cell contacted on both sides. From Figures 2.7, 2.8, and 2.9, one can see that if a value of $N_{D,\text{surf}} > 2 \times 10^{19}\text{cm}^{-3}$ is required for low contact resistance, a $J_0$ of $1 \times 10^{-13}\text{cm}^{-3}$ is desired, and $\rho_\Omega$ should be minimized, then this leads to an emitter with $N_{D,\text{surf}} = 2 \times 10^{19}\text{cm}^{-3}$, $x_j = 1.4\ \mu\text{m}$. This yields a value of $\rho_\Omega = 60\ \Omega/\square$. $J_{\text{lost}}$ for this emitter is $0.5\ \text{mA/cm}^2$, a tolerable loss out of the available $41.5\ \text{mA/cm}^2$.

2.3 Boron-doped emitters.

2.3.1 Introduction

The goal of this study is to experimentally determine the parameters which affect minority-carrier recombination in boron-diffused regions in silicon. Measured values of the emitter saturation current density, $J_0$, are reported for oxidized boron diffusions before and after a forming gas anneal (FGA), and for boron diffusions with Al:Si deposited directly on the silicon surface. It was found from both the oxide-passivated emitters and the Al:Si-coated emitters that previously reported values of the bandgap narrowing, $\Delta E_g$, in boron-doped silicon were too large to explain the data taken in this experiment. Accordingly, a new functional dependence of $\Delta E_g$ on boron concentration, $N_A$, was experimentally determined. This was accomplished by solving the carrier transport equations numerically in the manner described by del Alamo [14,15], using measured $J_0$ values, boron concentration profiles of the diffusions measured by secondary ion mass spectroscopy (SIMS), and experimental data on the dependence of minority carrier mobility and bulk lifetime on boron doping. The assumptions made in extracting $\Delta E_g$ from measurements of $J_0$, whether in bipolar transistors or in the planar diffusions studied in this experiment, are discussed in detail. Using the bandgap narrowing found here, the surface recombination velocity, $s$, at the boron-doped, Si/SiO$_2$ interface was also extracted from the measured $J_0$ values.

In the previous section, it was pointed out that $s$ depends strongly on the exact methods used to process the oxidized silicon samples for the case of phosphorus doping. The oxide growth conditions, anneal conditions, surface roughness, and contamination
can all have a dramatic effect on \( s \). In most device applications, it is desirable to make \( s \) as low as possible. This is particularly true for solar cells. So the oxidation conditions chosen for study were ones which yield a very low, stable, surface recombination velocity: dry oxidation at temperatures above 950\(^\circ\)C, with no trichloroethane (TCA) flowing while the wafers were in the furnace. The problem of contamination has been reduced as much as possible by using high-lifetime processing techniques.

The surface recombination velocity is also strongly dependent on surface potential, which can be altered by charge in the oxide, or by a voltage difference applied between the substrate and a conductive gate on top of the oxide. The case studied here is the situation in which there is no gate over the oxide to influence surface potential, and the fixed charge in the oxide is that obtained by the oxidation conditions described above. This is the surface potential found in practice in the oxide-passivated boron emitters of solar cells and many other devices. Therefore, the experimental values of \( s \) and \( J_0 \) reported here are directly applicable to the design of such devices.

### 2.3.2 Sample preparation

Boron was diffused into both sides of nearly intrinsic silicon wafers, from \( \text{SiO}_2 \) deposited by atmospheric-pressure chemical vapor deposition (APCVD). Four different concentrations of boron in the deposited glass were used. The samples were processed using three different drive-in and oxidation schedules: 1) a short drive-in and a short oxidation (with the APCVD oxide left on the wafer during the \( J_0 \) measurement); 2) the same short drive-in and oxidation, followed by stripping all oxide off of the wafers and reoxidizing; and 3) a long drive-in, followed by stripping all oxide and reoxidizing. Half of each wafer was given a forming gas anneal (FGA), while the other half was not. Further processing details are given in the Appendix.

On the samples that had Al:Si deposited on the surface to make \( s \) as high as possible, all oxide was stripped in 6:1 buffered oxide etch, and the samples were immediately placed in vacuum to prevent an interfacial oxide from growing in air. Approximately 74Å of 99% Al/1% Si was sputtered on one side, the samples were then flipped and about 32Å of Al:Si was sputtered on the other side. The 32Å layer was thin enough for
some light from a strong flash lamp to penetrate into the silicon during the $J_0$ measurement. It has been found previously [35] that the native oxide formed on bare silicon surfaces in air provides enough passivation to substantially decrease $s$. Depositing a metal which reacts strongly with oxygen, such as Al, on the surface causes $s$ to approach its maximum value. The samples in this experiment were given no heat treatment after Al:Si deposition.

Although the use of planar dopant diffusions requires the use of SIMS profiling to perform the most accurate extraction of $s$ and $\Delta E_g$ from the measured $J_0$, there are several strong advantages to using this type of doped layer. In addition to being a common device structure and being easier to fabricate than epitaxial layers, the defect density is generally lower in diffused layers than in doped layers formed by any other technique, such as epitaxy or ion implantation. This means that the bulk lifetime and minority-carrier mobility are likely to be near their highest possible values at a given doping, and are much more likely to be independent of processing details. The use of contactless photoconductivity decay to measure $J_0$ also means that the samples require only enough processing to form the emitter; no additional steps such as photolithography or contact formation are needed as they would be to form a transistor structure to measure $J_0$. This minimal processing schedule also increases the repeatability of the emitter parameters.

### 2.3.3 $J_0$ measurement

Contactless photoconductivity decay [35,12] was used to measure surface and bulk recombination in this study. In this method, the conductance of a sample is measured as a function of time by placing it on a coil which couples inductively to the wafer. A pulse of light generates an excess-carrier concentration, $n'$, in the sample, and the decay of $n'$ is monitored by the inductive coil. This yields an effective lifetime, $\tau_{\text{eff}}$, which is given by:

$$\frac{1}{\tau_{\text{eff}}} \equiv -\frac{1}{n'} \frac{dn'}{dt}.$$ 

Both surface and bulk recombination components are included in $\tau_{\text{eff}}$. In this experiment, the samples had identical, planar diffusions on each side of the wafer, and
lightly-doped substrates which were in high-level injection during the measurement of $\tau_{\text{eff}}$. The doped surfaces are in low-level injection. In this case, $n'$ is almost exactly equal to $n$, the total electron concentration in the substrate, and:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk,substrate}}} + 2J_0 \frac{n}{q n_{\text{io}}^2 w} + C_A n^2,$$

where $\tau_{\text{bulk,substrate}}$ is the bulk Shockley-Read-Hall (SRH) lifetime of the substrate, $J_0$ is the emitter saturation current density of a single dopant diffusion, $w$ is the wafer thickness, and $C_A$ is the ambipolar bulk Auger coefficient [35]. When $(1/\tau_{\text{eff}}) - C_A n^2$ is plotted versus $n$, a straight line results which has a slope proportional to $J_0/n_{\text{io}}^2$. Thus this method yields a direct measurement of $J_0/n_{\text{io}}^2$.

All values of $J_0$ reported here are the values at 300K, since the value of $n_{\text{io}}$ at 300K is used to find $J_0$ from the measured slope. The value of $n_{\text{io}}(300\text{K})$ used is $1.45 \times 10^{10}$ cm$^{-3}$. The sum of the electron and hole mobilities, $\mu_n$ and $\mu_p$, in highly-injected silicon was taken from the data of Dannhauser and Krause [13,43,59]. The accuracy of this data is $\pm 6\%$, and the value of $\mu_n + \mu_p$ approaches 1800 cm$^2$/Vs for $n < 10^{15}$ cm$^{-3}$. Dannhauser measured the value of $n$ by rapidly switching a p-i-n diode from forward to reverse bias, and essentially counting the carriers as they come out of the device. So the value of $n$ found using Dannhauser's measurements of $\mu_n + \mu_p$ does not depend on the value of $n_{\text{io}}$. The value of $C_A$ used for the highly-injected substrate was $1.66 \times 10^{-30}$ cm$^6$/s from [50], and was assumed to have an uncertainty of $\pm 10\%$. The carrier concentration $n$ was low enough ($< 1.5 \times 10^{16}$ cm$^{-3}$ for the oxidized samples and $< 1.5 \times 10^{15}$ cm$^{-3}$ for the Al:Si samples) that ignoring Auger recombination entirely (by setting the $C_A n^2$ term to zero) altered the measured value of $J_0$ by less than 10%. The value of $n$ was also low enough that the difference between the peak concentration halfway through the wafer thickness, and the concentration in the substrate at the edge of the surface diffusion, was usually less than 2.5%, and always less than 5%.

It should be emphasized that the parameter which is actually measured in this experiment is $J_0/n_{\text{io}}^2$. In contrast, measurements of the current-voltage characteristic of emitters, such as those found in [5,21], yield the value of the $J_0$ itself. The quantity $n_{\text{io}}(300\text{K})$ is a difficult one to measure, and the commonly accepted value is presently in flux. Although changing $n_{\text{io}}(300\text{K})$ from the value $1.45 \times 10^{10}$ cm$^{-3}$ used here to $1.08 \times 10^{10}$ cm$^{-3}$ suggested by Green [28] would change $J_0$ by a factor of 1.8, the value
of \( J_o/n_{1o}^2 \) is the same in either case, since this is the measured quantity. \( J_o/n_{1o}^2 \) is also nearly independent of temperature, and is the relevant parameter for calculating \( \Delta E_g \).

In Fig. 2.10, measured values of \( J_o \) are given for a wide variety of oxidized boron diffusions. The \( J_o \) of each emitter is shown next to a point which indicates \( N_{A,\text{surf}} \), the surface boron concentration of the emitter, and \( x_j \), the emitter thickness at which \( N_A = 10^{16} \text{ cm}^{-3} \). \( J_o \) data is presented for samples with and without a forming gas anneal. For the emitters thinner than 1 \( \mu \text{m} \), \( J_o \) has a broad minimum with respect to \( N_{A,\text{surf}} \), from about \( 3 \times 10^{18} \) to \( 2 \times 10^{19} \text{ cm}^{-3} \). For emitters thicker than 1 \( \mu \text{m} \), the minimum with respect to \( N_{A,\text{surf}} \) is narrower, and occurs at \( \sim 3 \times 10^{18} \text{ cm}^{-3} \) for samples with an FGA, and at \( \sim 1 \times 10^{19} \text{ cm}^{-3} \) for those without an FGA. For low \( N_{A,\text{surf}} \), the \( J_o \) decreases with increasing \( N_{A,\text{surf}} \) because the potential barrier between minority electrons in the bulk of the wafer and the surface increases. However, as \( N_{A,\text{surf}} \) becomes higher, \( J_o \) begins to increase. This is because \( \tau_{\text{bulk}} \) in the emitter decreases with increasing boron concentration, and because higher doping begins to have less effect on the potential barrier as bandgap narrowing sets in. In Fig. 2.10, the measurement error in \( J_o/n_{1o}^2 \) is less than 10\% for \( J_o \) values < \( 1 \times 10^{-13} \text{ A/cm}^2 \), and less than 20\% for higher values of \( J_o \). To find \( J_o/n_{1o}^2 \) from the \( J_o \) values given here or in the previous study of phosphorus diffusions [39], one simply divides by \( n_{1o}^2(300\text{K}) = (1.45 \times 10^{10} \text{ cm}^{-3})^2 \).

One emitter which was not profiled by SIMS has the lowest observed \( J_o \), at \( 0.52 \times 10^{-13} \text{ A/cm}^2 \pm 12\% \) after receiving an FGA. The processing of this sample was identical to that of sample C1G (see Appendix), except that the final oxide was grown for 120 min. instead of 210 min. The measured \( \rho_o \) of this emitter was 158 \( \Omega/\Box \), and by extrapolation from the SIMS profile of sample C1G, the emitter depth was \( \sim 1.4 \mu \text{m} \). This implies a surface boron concentration of \( \sim 5 \times 10^{18} \text{ cm}^{-3} \). The \( J_o \) of this sample is significantly lower than that of other emitters with similar \( x_j \) and \( N_{A,\text{surf}} \). This may indicate that oxidations as long as 210 min. degrade the emitter recombination properties significantly more than \( \sim 120 \text{ min.} \) oxidations. A wafer with a textured surface (selectively etched so that pyramids with sides that have (111) orientation cover the wafer surface) was processed alongside this low \( J_o \) sample. The measured \( J_o \) of the emitter with a textured surface is \( 3.3 \times 10^{-13} \text{ A/cm}^2 \pm 13\% \). This \( J_o \) is lower than that observed on other textured diffusions with comparable processing, which typically
Figure 2.10: Measured values of the emitter saturation current density for untextured wafers. The bracketed value was before an FGA, the unbracketed value is after. The emitter thickness ($N_A = 10^{16} \text{cm}^{-3}$) was determined by SIMS.
Figure 2.11: Emitter saturation current densities for the case of unpassivated diffusions, contacted by Al:Si.

have \( J_o \) values of \( \sim 10 \times 10^{-13} \text{ A/cm}^2 \).

Figure 2.11 is a plot similar to Fig. 2.10, showing the \( J_o \) measured for boron diffusions with an Al:Si layer contacting the silicon surface. The absolute value of \( J_o \) is higher for these diffusions than for the oxidized diffusions, because \( s \) is much higher at the Al:Si interface. The minimum \( J_o \) also occurs at a higher value of \( N_{A,\text{surf}} \), because the benefit of a high potential barrier between the substrate and the surface is more significant when \( s \) is so large. These measurements are useful for predicting the recombination in devices which have boron diffusions contacted by Al:Si, and will also be used to find the bandgap narrowing as a function of \( N_A \).

The profiles of boron concentration vs. depth were determined by SIMS. Fig. 2.12 shows the SIMS profile of a diffusion with \( N_{A,\text{surf}} = 2.6 \times 10^{19} \text{ cm}^{-3} \) and \( x_j = 0.50 \).
Figure 2.12: Boron profile of an emitter as determined by SIMS. In the profile used for modeling, the measurement artifact at the surface and the background noise have been removed.

\( \mu \text{m} \) (sample C1X). The sharp dip in concentration at the surface is a measurement artifact. Similarly, the background signal of \( \sim 3 \times 10^{15} \text{ cm}^{-3} \) is much higher than the true substrate doping. Both of these inaccuracies of the raw SIMS data were removed to find the profile used for modeling, as shown in Fig. 2.12.

The SIMS profiles were checked by comparing 4-point sheet resistance \( (\rho_{\Omega}) \) measurements of the diffusions with calculated values of \( \rho_{\Omega} \), using the fits to Thurber’s measurements of \( q\rho N_A \) vs. \( N_A \) and of \( \mu_{p,maz} \) vs. \( \rho \) [61], where \( \rho \) is bulk resistivity, and \( \mu_{p,maz} \) is the mobility of majority carriers (holes) in p-type silicon. The \( \rho_{\Omega} \) calculated in this way includes the effects of incomplete boron ionization as calculated by Li [44]. The discrepancy between the \( \rho_{\Omega} \) calculated using the SIMS profiles and the average \( \rho_{\Omega} \) measured on the two sides of the wafer was less than 10\% for all but
two samples. For these two samples, $N_{A,\text{surf}}$ is below $4 \times 10^{18} \text{ cm}^{-3}$, and the discrepancy between calculated and measured $\rho_\varnothing$ is less than 14\%. The calculated $\rho_\varnothing$ tended to be lower than the measured $\rho_\varnothing$. Given the large uncertainty in boron ionization fraction for $N_A$ near $3 \times 10^{18} \text{ cm}^{-3}$ [60], this degree of correlation seems reasonable. This difference between measured and calculated $\rho_\varnothing$ is incorporated into the error in $N_{A,\text{surf}}$ shown in the figures, as is the difference between the measured $\rho_\varnothing$ on the two sides of the wafer. As explained in the next section, all boron concentration axes for figures in this section refer to $N_A$, the total boron density, rather than $N_A^\text{+}$, which is the ionized boron density. It is assumed that all boron in the sample is on substitutional sites (no interstitial boron), so that every boron atom is ionizable, but some of the boron may be non-ionized. This is the common assumption used in work of this type [61,60,56,19].

### 2.3.4 Bandgap narrowing

It is always observed for boron emitters in silicon with dopant concentrations greater than about $10^{18} \text{ cm}^{-3}$, that the measured $J_\varnothing$ is higher than one would expect based on the measured doping, minority-carrier lifetime, and minority-carrier mobility in the emitter. It is believed that the equilibrium minority carrier concentration, $n_\varnothing$, is actually higher than $n_\varnothing^\text{+}/N_A$, where $n_\varnothing^\text{+}$ is the intrinsic equilibrium carrier density in the absence of bandgap narrowing, and $N_A$ is the total concentration of boron atoms on substitutional sites in the silicon lattice. Whether this effect is due to actual narrowing of the energy bandgap, a change in the density of states in the valence band, non-ionization of some of the boron atoms, or (as seems most likely) a combination of all three, the way it manifests itself physically is through a larger value of $n_\varnothing$ than would otherwise be predicted. This can be described mathematically by an *effective* or *apparent* bandgap narrowing, $\Delta E_g$, which is a function of $N_A$, and is related to $n_\varnothing$ through:

$$N_A n_\varnothing = n_\varnothing^2 e^{\Delta E_g/kT} \equiv n_{ir}^2$$

where $n_{ir}$ is called the *effective* intrinsic equilibrium carrier density, when bandgap narrowing is taken into account. Note that both $\Delta E_g$ and $n_{ir}$ are defined with respect to the total boron density, $N_A$, not the hole density, $p$, or the ionized boron density.
Several researchers have quantified the dependence of $\Delta E_g$ on $N_A$ experimentally [60,56,19]. These researchers all used npn bipolar transistors to perform their measurements of $\Delta E_g$. In one method, the $I_c$ vs. $V_{be}$ characteristic is measured as a function of temperature, and the value of $\Delta E_g$ is extracted from these measurements [56,19]. This is an attractive technique, since the absolute value of the minority-carrier (electron) mobility need not be known, only its temperature dependence. However, it requires the assumption that $\Delta E_g$ is independent of temperature. Swirhun has found that $\Delta E_g$ is a fairly strong function of temperature above 250K [60], so results from this type of experiment are difficult to interpret.

A more direct way to measure $\Delta E_g$ is to find the $J_o$ of the emitter-base junction in npn transistors from measurements of the $I_c$ vs. $V_{be}$ characteristic at a constant temperature. Slotboom and de Graaff [56] used transistor bases which were narrow enough that bulk recombination in the base could be ignored. The quantity which determines the $J_o$ of this type of structure is the product

$$\mu_{n,min} n_o = \mu_{n,min} \frac{n_{10}}{N_A} e^{\Delta E_g/kT}$$

where $\mu_{n,min}$ is the minority-carrier (electron) mobility in p-type silicon. So the extracted value of $\Delta E_g$ is strongly dependent on the choice of $\mu_{n,min}$ and of $n_{10}$. Both of these quantities are difficult to measure. In addition, the strong dependence of $n_{10}$ on temperature requires that the temperature of the device be measured very accurately. Slotboom and de Graaff assumed that $\mu_{n,min}$ at an acceptor concentration $N_A$ was equal to the majority-carrier electron mobility, $\mu_{n,maj}$, in n-type silicon with the same concentration of donor atoms. There is a fair amount of experimental evidence now that $\mu_{n,min}$ is two or more times greater than $\mu_{n,maj}$ for dopant concentrations greater than $5 \times 10^{18}$ cm$^{-3}$ [60,16]. Swirhun [60] performed an experiment in which $L_n$, the diffusion length of minority electrons, was measured in the same p-type epitaxial layers that formed the base of the vertical transistors used to measure $J_n$. The epitaxial layers were designed to have a thickness greater than $4L_n$, to make the measurement of $L_n$ more accurate. Unfortunately, this also magnifies the uncertainty in the extracted $\Delta E_g$, such that a 20% uncertainty in $L_n$ leads to an uncertainty in $\Delta E_g$ of 0.60$kT$. 

$N_A$.
The emitters used in the measurement of $\Delta E_g$ described here were not uniformly doped, which complicates the extraction of $\Delta E_g$ somewhat. In previous studies of bandgap narrowing in both n- and p-type silicon, $\Delta E_g$ has been found to depend on doping according to an expression of the form:

$$\Delta E_g = A \ln \left( \frac{N}{B} \right),$$

where $N$ is the total n- or p-type impurity concentration [15,60,56,19]. Note that $A$ is the slope of $\Delta E_g$ vs. $(\ln N_A)$, while $\ln B$ is the $(\ln N_A)$-axis intercept. For the extraction of $\Delta E_g$ using the full numerical emitter model, $\Delta E_g$ was assumed to have the above form. Then, for a given value of $B$, the value of $A$ that corresponds with the measured value of $J_o$ could be found. For each emitter studied, this resulted in a curve in the $A$ vs. $B$ plane along which the values of $A$ and $B$ yield values of $\Delta E_g$ that are consistent with the measured $J_o$.

These values of $A$ and $B$ were found by numerically solving the carrier transport equations for each emitter using the dopant profile measured by SIMS, the measured $J_o$, and the minority-carrier mobility in [60]:

$$\mu_{n,min} = (232 \text{ cm}^2/\text{Vs}) + \frac{(1180 \text{ cm}^2/\text{Vs})}{1 + (N_A/8 \times 10^{16} \text{cm}^{-3})^{0.9}},$$

which is based on the best data from studies by Dziewior and Silber [16], and Swirhun [60]. Unless explicitly stated otherwise, this is the assumed dependence of $\mu_{n,min}$ on $N_A$ used throughout this study. The minority-carrier lifetime in the bulk of the emitter, $\tau_{bulk}$, was assumed to be:

$$\tau_{bulk} = \frac{1}{(1350 \text{s}^{-1}) + (1.82 \times 10^{-14} \text{cm}^3 \text{s}^{-1})N_A + (9.9 \times 10^{-32} \text{cm}^6 \text{s}^{-1})N_A^2}.$$

This fit is dominated at high boron concentration by the Auger coefficient found for the e-h-h process in p-type silicon ($C_p = 9.9 \times 10^{-32} \text{ cm}^6 \text{s}^{-1}$) by Dziewior and Schmid [17], and at low concentrations by the Shockley-Read-Hall (SRH) lifetimes measured by Ciszek [9]. To place upper and lower limits on the bulk lifetime, $C_p$ was determined to be between $5.9 \times 10^{-32}$ and $1.66 \times 10^{-31} \text{ cm}^6 \text{s}^{-1}$ from the data in [17]. For many of the emitters in this study, bulk recombination is negligible compared to recombination at the surface.
Figure 2.13 shows the curves marking the upper limit of $A$ as a function of $B$, based on the measured $J_o$ of three different diffusions. For a given value of $B$, the upper limit of $A$ is taken to be the value which yields the upper limit of the measured $J_o$, when $s$ is set to zero, and the upper limit of $\tau_{\text{bulk}}(N_A)$ is used. These assumptions all conspire to make $A$ larger. For example, the oxidized emitter with $N_{A,\text{surf}} = 2.0 \times 10^{19} \, \text{cm}^{-3}$ and $x_j = 4.5 \, \mu\text{m}$ has a measured $J_o$ of $(3.57 \pm 0.11) \times 10^{-13} \, \text{A/cm}^2$ after an FGA. So the $J_o$ value used to find the upper limit of $A$ was $3.68 \times 10^{-13} \, \text{A/cm}^2$. $J_o$ measurements made on oxidized emitters that had received an FGA were used for establishing the upper limit of $A$, since this type of surface has the lowest technologically achievable $s$ (the value closest to the imposed condition of $s = 0$). Values of $A$ and $B$ above the upper limit curve for a given emitter would predict a negative value of $s$ for that emitter, which is clearly non-physical. Note that the fit $\Delta E_g = (0.0181\,\text{eV}) \ln(N_A/10^{17}\,\text{cm}^{-3})$, given by Swirhun to his data [60] and the data of Slotboom and de Graaff [56], has values of $A$ and $B$ which lie above the upper limit curves for emitters with $N_{A,\text{surf}} = 2.0 \times 10^{19}$ and $3.6 \times 10^{19} \, \text{cm}^{-3}$.

Figure 2.13 also shows the lower limit of $A$ as a function of $B$, found from the lower limit of the measured $J_o$ of diffusions with Al:Si deposited on the surface, by setting $s = \infty$, and using the lower limit of $\tau_{\text{bulk}}$. $J_o$ measurements made on emitters with Al:Si on the surface were used for finding the lower limit of $A$, since this surface has a value of $s$ which is close to the imposed condition of $s = \infty$.

When the dopant profiles are known, the surface recombination velocity and the bandgap narrowing may be extracted by comparing the $J_o$ measured on thick and thin emitters with the same surface boron concentration. The value of $s$ should be the same for two emitters with the same $N_{A,\text{surf}}$, even if $s$ is a function of $N_{A,\text{surf}}$. For a given value of $B$ in the fit of $\Delta E_g$ vs. $N_A$, analysis of carrier transport in the emitters [14] yields a system of two differential equations (one for each emitter) in two unknowns, $A$ and $s$. If two pairs of thick and thin emitters are used, for which $N_{A,\text{surf}}$ is the same for each emitter in a pair but the $N_{A,\text{surf}}$ of each pair is different, then a system of four independent equations results. In this way, all four unknown parameters ($A$, $B$, and the $s$ at the two values of $N_{A,\text{surf}}$) may be determined.

Al:Si-coated emitters with $N_{A,\text{surf}} = 3.4 \times 10^{18}$ and $2.8 \times 10^{18} \, \text{cm}^{-3}$ (samples A1X
Figure 2.13: Upper and lower limits of the parameter $A$ as determined by measured values of the $J_0$ of three boron diffusions, using the minority electron mobility measured by Dziewior and Silber, and Swirhun. $A$ and $B$ define the dependence of bandgap narrowing, $\Delta E_g$, on total boron concentration, $N_A$, through $\Delta E_g = A \ln(N_A/B)$. 
and C1G) were used to find \( s \) at their average value of \( N_{A,\text{surf}} = 3.1 \times 10^{18} \text{ cm}^{-3} \), by solving this system of equations numerically. Similarly, emitters with \( N_{A,\text{surf}} = 2.6 \times 10^{19} \) and \( 2.0 \times 10^{19} \text{ cm}^{-3} \) (samples C1X and B2G) were used to find \( s \) at the average value of \( N_{A,\text{surf}} = 2.3 \times 10^{19} \text{ cm}^{-3} \). These extracted values of \( s \) at the silicon surface contacted by Al:Si are shown in Fig. 2.14. The surface recombination velocity was found to be nearly the same at both of these surface concentrations, with an average value of \( 1.65 \times 10^{5} \text{ cm/s} \). Note that this is significantly lower than the maximum possible value of \( s \), \( \left( \frac{v_{th}}{4} \right) \approx 3 \times 10^{6} \text{ cm/s} \), where \( v_{th} \) is the average thermal velocity of electrons impinging on the surface. The uncertainty limits in \( N_{A,\text{surf}} \) in Fig. 2.14 includes the difference between the \( N_{A,\text{surf}} \) for the emitters in each pair, as well as the uncertainty in the measured \( N_{A,\text{surf}} \) for each emitter. The upper and lower limits of \( s \) were found by using the upper and lower limits of the measured \( J_{o} \) values, respectively.

These values of \( s \) were then used to generate \( A \) vs. \( B \) curves for each of the four emitters, as plotted in Fig. 2.15. The upper limit of \( A \) for each pair of emitters was calculated using the lower limit of \( s \), the upper limit of the measured \( J_{o} \), and the upper limit of \( \tau_{\text{bulk}} \), all of which tend to make \( \Delta E_{g} \) larger. Similarly, the lower limit of \( A \) was found using the upper limit of \( s \), the lower limit of measured \( J_{o} \), and the lower limit of \( \tau_{\text{bulk}} \). Because the recombination behavior of the emitters is dominated by the bandgap narrowing at the surface, the slope \( A \) becomes quite high for large \( B \) for the pair of emitters with low \( N_{A,\text{surf}} \). The measurements made here are consistent with the values of \( A \) and \( B \) that lie in the intersection of the uncertainty regions for each pair of emitters. The point at which the pair of curves for the emitters with low \( N_{A,\text{surf}} \) cross the pair of curves for high \( N_{A,\text{surf}} \) gives the fit of \( \Delta E_{g} \) vs. \( N_{A} \) which best agrees with the data taken in this study. This fit is:

\[
\Delta E_{g} = \left( 0.0178 \text{ eV} \right) \ln \left( \frac{N_{A}}{2.3 \times 10^{17} \text{ cm}^{-3}} \right).
\]

\( B \) must be between \( 1.9 \times 10^{17} \) and \( 2.9 \times 10^{17} \text{ cm}^{-3} \) at this value of \( A \) in order for \( A \) and \( B \) to lie with in the uncertainty limits of the emitter pair with high \( N_{A,\text{surf}} \).

Due to the non-gaussian, box-like shape of the emitter profiles (see Fig. 2.12.), the \( J_{o} \) depends very strongly on the value of \( \Delta E_{g} \) at \( N_{A} = N_{A,\text{surf}} \). This fact can be used in an alternative, approximate method for extracting \( \Delta E_{g} \) at the surface boron concentration. The real doping profile can be approximated by a profile with constant
Figure 2.14: Surface recombination velocity, $s$, extracted from measurements of $J_o$ on boron diffusions with Al:Si on the silicon surface. The value of $s$ was found from the measured $J_o$ by numerically solving the carrier transport equations, such that $s$ was the same for both thick and thin emitters that have nearly the same $N_{A,\text{surf}}$. 
Figure 2.15: $A$ vs. $B$ curves found from the measured $J_o$ values of four boron diffusions with Al:Si on the silicon surface. The value of $s$ at this surface was determined by comparing pairs of thick and thin emitters with similar surface boron concentrations. The point at which the curves cross gives the values of $A$ and $B$ which are most consistent with the data taken in this study.
concentration, \(N_{A,\text{surf}}\), and an effective thickness, \(w_{\text{eff}}\), such that the total boron dose is the same as for the real profile. This results in a change in the calculated \(J_0\) of less than 4% for all the emitters in Fig. 2.15, except for the emitter with \(N_{A,\text{surf}} = 2.6 \times 10^{19}\) cm\(^{-3}\) and \(x_j = 0.50\) \(\mu\)m, for which the change is 10%. For an emitter with a flat doping profile:

\[
J_0 = \frac{q n_{\text{io}}^2 e^{\Delta E_g/kT}}{N_{A,\text{surf}}} \left(\frac{D}{L}\right) \left(\frac{(sL/D) + \tanh(w_{\text{eff}}/L)}{1 + (sL/D) \tanh(w_{\text{eff}}/L)}\right),
\]

where \(D\) is the minority-carrier diffusion coefficient, and \(L\) is the minority-carrier diffusion length. For two emitters with flat dopant profiles and the same surface boron concentration, but different emitter depths, both the bandgap narrowing and the surface recombination velocity can be solved for in terms of the measured \(J_0\) values and effective thicknesses. Using this approximation, one pair of emitters was used to find \(s = 1.54 \times 10^5\) cm/s and \(\Delta E_g = 46\) meV at \(N_A = 3.1 \times 10^{18}\) cm\(^{-3}\), and the other pair was used to find \(s = 1.69 \times 10^5\) cm/s and \(\Delta E_g = 80\) meV at \(N_A = 2.3 \times 10^{19}\) cm\(^{-3}\). These points agree well with the fit of \(\Delta E_g\) vs. \(N_A\) found using the full numerical emitter model.

Fig. 2.16 compares the p-type bandgap narrowing values found in this work with those found by other researchers. The fit of \(\Delta E_g\) to \(N_A\) given by Swirhun [60], to his experimental data and the data of Slotboom and de Graaff [56], is about 16 meV above the fit found in this study, for all boron concentrations. The fit of \(\Delta E_g\) vs. \(N_D\) to the experimental data of del Alamo [15] for phosphorus-doped silicon is also shown, for comparison.

In addition, three data points for which the extraction of \(\Delta E_g\) was explicitly outlined in the paper by Slotboom and de Graaff [56] are plotted in Fig. 2.16, under three different sets of assumptions. Case A is the data as extracted by Slotboom and de Graaff, using the assumption that \(\mu_{n,\text{min}}\) equals \(\mu_{n,\text{maj}}\). The value of \(n_{\text{io}}\) that they used was \(\sim 1.19 \times 10^{10}\) cm\(^{-3}\) at 300K. In case B, the value of \(\mu_{n,\text{min}} n_{\text{io}}^2/N_A\) (the directly measured parameter) was found from the data given by Slotboom and de Graaff, and then the fit of \(\mu_{n,\text{min}}\) vs. \(N_A\) given by Swirhun was used to extract \(\Delta E_g\), using a value of \(n_{\text{io}} = 1.45 \times 10^{10}\) cm\(^{-3}\). Case C follows the same procedure for extracting \(\Delta E_g\) as case B, except the lower value of \(n_{\text{io}} = 1.08 \times 10^{10}\) cm\(^{-3}\) recently suggested by Green [28] is used. The data in case A cannot be compared to the data.
Figure 2.16: Comparison of the dependence of bandgap narrowing, $\Delta E_g$, on total boron concentration, as given by Swirhum and as found in this study. In addition, three data points that were explicitly tabulated by Slotboom and de Graaff are plotted, as they extracted them, and also for assumptions more consistent with those used in this study (see text).
from this study or the data taken by Swirhun for $N_A$ greater than about $10^{18}$ cm$^{-3}$, since $\mu_{n,\text{min}}$ differs significantly from $\mu_{n,\text{maj}}$ above this concentration. Case B, case C, the data in this study, and Swirhun's data can all be legitimately compared, however, because $\Delta E_g$ was extracted using Swirhun's $\mu_{n,\text{min}}$ fit for all of these data sets. For case C, which uses the most recently reported value of $n_{io}$, the bandgap narrowing is almost exactly zero at $N_A = 4 \times 10^{16}$ cm$^{-3}$, and $\Delta E_g$ at $N_A = 1 \times 10^{19}$ cm$^{-3}$ agrees fairly well with the data found in this study. The $\Delta E_g$ of case C is higher than that predicted in this study for $N_A = 3 \times 10^{17}$ cm$^{-3}$. This could be due to $\Delta E_g(N_A)$ approaching zero asymptotically as $N_A$ decreases.

One strong advantage of using contactless photoconductivity decay measurements to determine $\Delta E_g$ is that this method provides a direct measurement of $J_o/n_{io}^2$ rather than of $J_o$. From the expression for the $J_o$ of a flat profile emitter, it can be seen that the extracted $\Delta E_g$ depends only on $J_o/n_{io}^2$ when $s$, $L$, $D$, and $N_A,\text{surf}$ are known. The same is true for general emitter profiles. Measurement of the $I_C$ vs. $V_{be}$ characteristic of a bipolar transistor provides the $J_o$ directly, so some value of the difficult-to-measure $n_{io}$ must be used to find $J_o/n_{io}^2$, and hence to find $\Delta E_g$. This can result in considerable uncertainty in the value of $\Delta E_g$, as can be seen by comparing case B and case C of the Slotboom and de Graaff data in Fig. 2.16.

### 2.3.5 Surface recombination velocity

Using the dependence of $\Delta E_g$ on $N_A$ that was determined from these boron diffusions with metal contacts, the surface recombination velocity at the Si/SiO$_2$ interface was extracted for surface boron concentrations from $3 \times 10^{17}$ to $3 \times 10^{19}$ cm$^{-3}$, by finding the value of $s$ that corresponds with the measured $J_o$ of oxide-passivated emitters. This was done by numerical solution of the carrier transport equations, using the experimental dependences of $\mu_{n,\text{min}}$ and $\tau_{\text{bulk}}$ given earlier, and the measured SIMS profiles. The results are plotted in Fig. 2.17. For all of the emitters shown in Fig. 2.17, more than 50% of the recombination in the emitter takes place at the surface rather than in the bulk, and for most samples the surface recombination was more than 95% of the total. This makes the extracted $s$ fairly insensitive to the value of $\tau_{\text{bulk}}$. For the emitters
which are most transparent to minority carriers, the $J_0$ is simply $qS\tau \varepsilon^2 / N_{A,\text{surf}}$ [15], so that the extracted $s$ depends only on the bandgap narrowing. The error bars in $s$ shown in Fig. 2.17 reflect the uncertainty in $\Delta E_g$ and in the measured $J_0$.

For the emitters with a stripped, reoxidized surface that have received an FGA, and for the emitters with APCVD oxide both before and after an FGA, $s$ is very nearly constant with respect to $N_{A,\text{surf}}$. The average value of $s$ for these samples is 1640 cm/s. This constant value of $s$ contrasts strikingly with the strong dependence of $s$ on phosphorus concentration found previously [39]. Note that the $s$ of the stripped, reoxidized emitters with no FGA is more than 10 times higher than for the other processing conditions. The reason for this is unknown. One possibility is that the long oxidation received by these samples creates stress-related, positive charge in the oxide. This would tend to deplete the silicon of holes near the emitter surface, reducing the potential barrier to minority electrons, and thereby increasing the $J_0$. An anneal with aluminum covering the oxide (which generates hydrogen) has been found to reduce positive charge in oxide grown on boron-doped silicon [57], so it is possible that an FGA could also reduce the charge, causing the $J_0$ to return to normal.

The observed dependence of recombination rate on carrier density in the most lightly-doped emitter, with $N_{A,\text{surf}} = 2.5 \times 10^{17}$ cm$^{-3}$, was different than for the other samples: the $1/\tau_{\text{eff}}$ vs. $n$ curve is lower at high carrier densities than would be predicted by the $J_0$ found for low carrier density. This is consistent with a surface recombination velocity that decreases with increasing minority-carrier concentration at the surface, $n_s$. The $J_0$ value of this lightly-doped emitter that was shown in Fig. 2.10, and which was used to extract the value of $s$ plotted in Fig. 2.17, was the value found at low $n$ where the $1/\tau_{\text{eff}}$ vs. $n$ data approaches a straight line. This $J_0$ fits the data well when the $pn$-product is less that $\sim 10^{31}$ cm$^{-3}$, or up to a fermi-level splitting of $\sim 0.640$ V. The other emitters in the study had very straight $1/\tau_{\text{eff}}$ vs. $n$ plots. This indicates that for the more heavily-doped emitters, $s$ is independent of injection level. Several other authors have reported that $s$ at the boron-doped Si/SiO$_2$ interface decreases with increasing $n_s$ [36,65,42]. The values of surface recombination velocity in [36] were measured directly using uniformly-doped wafers of various thicknesses. At $N_A = 1.26 \times 10^{17}$ cm$^{-3}$, $s$ was measured to be $100 \pm 4$ cm/s, at an injected excess electron density of $2.5 \times 10^{15}$ cm$^{-3}$. This value of $s$ is significantly lower than the trend shown in Fig. 2.17, but since it was
Figure 2.17: Surface recombination velocity, $s$, extracted from measurements of $J_o$ on oxide-passivated boron diffusions, by numerically solving the carrier transport equations. For three of the four surface treatments investigated, $s$ is approximately independent of $N_{A,surf}$, and has an average value of 1640 cm/s.

Measured at a $pn$-product of $3.15 \times 10^{32}$ cm$^{-6}$, this is consistent with the observation that $s$ decreases with increasing $n_s$. When using the surface recombination velocity data in Fig. 2.17, it must be borne in mind that the injection level dependence of $s$ complicates matters considerably for oxide-passivated emitters with $N_{A,surf}$ less than $\sim 10^{18}$.

Another situation in which the surface recombination velocities of Fig. 2.17 must be applied with caution is the case of an oxide-passivated diffusion with a conductive layer over the oxide. Many authors have investigated recombination at the boron-doped Si/SiO$_2$ interface as a function of applied gate potential [60,34,20,67,22]. When this structure is encountered in a solar cell, the conductive layer is usually metal which is
electrically connected to the underlying diffusion over some fraction of its area. So to first order, the fermi level in the metal is the same as in the diffusion beneath the oxide. When the gate metal is Al, and the diffused layer is n-type, the presence of the metal tends to accumulate the surface very slightly, which could decrease $s$ to a small degree. In the Al/SiO$_2$/p-type Si system, however, the overlying metal tends to cause depletion or inversion at the silicon surface, which can alter $s$ dramatically. But it should be noted that there are many practical situations in which $N_{A,\text{surf}}$ is large, the interface charge in the oxide is small, or the oxide is thick enough that the metal layer does not affect the surface potential significantly.

### 2.3.6 Calculated performance of boron emitters

Using the average value of $s = 1640$ cm/s that was found for three of the four surface preparation conditions listed in Fig. 2.17, a plot of the contours of constant $J_0$ in the $N_{A,\text{surf}}$ vs. $x_j$ plane may be calculated for oxide-passivated boron diffusions. Fig. 2.18 shows such a plot, calculated for emitters with a gaussian boron profile, using the $\Delta E_g$ found in this study, and the experimental dependences of $\tau_{\text{bulk}}$ and $\mu_{n,\text{min}}$ stated earlier. Since this contour plot was generated from the $J_0$ data in Fig. 2.10, it naturally agrees fairly well with that data. The discrepancies which can be observed are due primarily to the non-gaussian shape of the actual boron diffusions measured in Figure 1.

Figures 2.19 and 2.20 are similar plots for metal-contacted boron diffusions. In Fig. 2.19, the value of $s = 1.65 \times 10^5$ cm/s that was found for Al-Si contacted diffusions is used. In Figure 2.20, $s$ was set to its maximum possible value: $(v_{th}/4) \approx 3 \times 10^6$ cm/s. Although both of these values of $s$ are very high, the difference between them still has a significant effect on the predicted $J_0$ for shallow boron emitters. For example, an Al-Si-contacted emitter with $N_{A,\text{surf}} = 1 \times 10^{19}$ cm$^{-3}$ and $x_j = 0.4$ $\mu$m should have a $J_0$ of $50 \times 10^{-13}$ A/cm$^2$, according to Figure 2.19. If the value of $s = 3 \times 10^6$ cm/s is assumed however, the predicted $J_0$ is 3 times higher, at $150 \times 10^{-13}$ A/cm$^2$.

An important parameter for the design of solar cells is $J_{\text{lost}}$, defined to be the current density photogenerated in the volume of the emitter on the sunward surface of
Figure 2.15: Contours of constant $J_0$ for oxide-passivated emitters with a gaussian boron profile. The value of $s$ used was 1640 cm/s, as shown in the previous figure. The contours are labeled with the corresponding value of $J_0$, in units of $10^{-13}$ A/cm$^2$. 

$J_0 \ (10^{-13} \text{ A/cm}^2), \text{ for } s = 1640 \text{ cm/s}$
Figure 2.19: Contours of constant $J_0$ for boron emitters with a gaussian profile. The value of $s$ used was $1.65 \times 10^5$ cm/s, independent of $N_{A,\text{surf}}$, which was experimentally determined for boron-doped surfaces with Al:Si sputtered on the silicon surface, with no subsequent heat treatment.
Figure 2.20: Contours of constant $J_o$ for boron emitters with a gaussian profile. The value of $s$ used was $3 \times 10^6$ cm/s, independent of $N_{A, surf}$. This is the approximate maximum value of the surface recombination velocity, $v_{th}/4$, where $v_{th}$ is the thermal velocity of electrons impinging on the surface.
a solar cell, minus the current density flowing out of the emitter into the substrate. In
Figure 2.21, contours of constant $J_{\text{lost}}$ are shown in the $N_{\text{A,sub}}$ vs. $x_j$ plane for gaussian
boron diffusions on an untextured, oxide-passivated surface. The experimentally deter-
mined value $s = 1640$ cm/s from Fig. 2.17 was used in the calculation. The spectrum
incident on the cell was assumed to be the SERI AM1.5 direct normal solar spectrum
[45], normalized to have an incident intensity of 0.100 W/cm² (one sun), with unity op-
tical transmittance of the sunward surface. The photogenerated current density in 0.1
cm of silicon is 0.0415 A/cm² for this spectrum, using the absorption coefficient data
in [26]. Fairly deep emitters can be placed on the sunward side before the photogener-
ated current loss becomes significant. For example, an emitter with $N_{\text{A,sub}} = 1 \times 10^{19}$
cm⁻³ and $x_j = 2.0$ μm has a $J_{\text{lost}}$ of only 0.0002 A/cm². This is less than 0.5% of
0.041 A/cm², a typical value of the current density that is photogenerated in the cell
as a whole. For reference, Figure 2.22 is a contour plot of the sheet resistance, $\rho_{s}$,
of gaussian boron diffusions, based on Thurber's p-type majority-carrier mobility data
[61].

2.3.7 Appendix: Processing details for boron diffusions.

Nearly intrinsic (>390 Ω·cm, n-type, phosphorus-doped) silicon wafers grown by the
float-zone method with (100) orientation were used in this experiment. They were
cleaned and ~15 μm of Si were removed from each side in an HNO₃:HF solution,
resulting in a final wafer thickness of ~260 μm. Boron-doped SiO₂ was deposited on
both sides of the wafers by atmospheric-pressure chemical vapor deposition (APCVD),
at 400°C. This was the boron doping source. Samples with labels beginning with 'A'
had boron-doped glass grown with a $B_2H_6$:SiH₄ ratio of 0.121, those beginning with
'B' had a ratio of 0.159, those beginning with 'C' had a ratio of 0.245, and samples
beginning with 'D' had a ratio of 0.410. Samples with labels ending in 'IX' were driven-
in for 10 min. in pure Ar, oxidized for 15 min. in pure O₂, then all O₂ was purged from
the furnace with Ar for 5 min., all at a temperature of 950°C. Samples with labels
ending in 'IG' received the same furnace steps, but afterwards, all oxide was stripped
from the wafers in 10:1 $H_2O$:HF, and the wafers were reoxidized for 210 min. in pure
$O_2$, followed by a 5 min. purge in pure Ar, both at 1000°C. Samples with labels ending
Figure 2.21: Contours of constant $J_{\text{lost}}$ for oxide-passivated emitters with a gaussian boron profile. The value of $s$ used was 1640 cm/s. $J_{\text{lost}}$ was calculated for the SERI AM1.5 direct normal solar spectrum incident on the cell, normalized to have an incident intensity of 0.100 W/cm² (one sun). The contours are labeled with the corresponding value of $J_{\text{lost}}$, in units of $10^{-3}$ A/cm².
Figure 2.22: Contours of constant $\rho_0$ for emitters with a gaussian boron profile, using the majority-carrier mobility data of Thurber. The contours are labeled with the corresponding value of $\rho_0$, in $\Omega/\square$. 
in '2G' were driven-in for 130 min. in pure Ar at 1120°C. The oxide was then stripped in 10:1 H₂O:HF, and they were given the same 210 min. oxidation and 5 min. purge (both at 1000°C) as the '1G' wafers. In all cases, wafers were pulled in pure Ar at a temperature below 800°C. After the final oxidation, each wafer was divided in two, and one half was given a forming gas anneal (FGA) in 10% H₂, 90% N₂ for 30 min. while ramping down from 400°C to ~350°C.

The furnaces were cleaned with a TCA getter immediately prior to these furnace steps, but no TCA was flowing when the wafers were in the furnace. This is an important point because it was found that the boron-doped Si/SiO₂ interface degrades if the oxide was grown in TCA, even when the samples are stored in the dark. No similar degradation in the dark has been observed for phosphorus diffusions oxidized in the presence of TCA, or for either boron or phosphorus diffusions oxidized without TCA.

### 2.4 Alternative doping sources: POCl₃, BBr₃, and Al.

It could be reasonably argued that the results from this chapter on the characterization of phosphorus- and boron-diffused regions are particular to the use of doped-oxide diffusion sources. An interesting study would be to see if similar results could be obtained with alternative sources. Two candidate alternatives are POCl₃ for n-type diffusions and BBr₃ for p-type diffusions. An additional p-type dopant that has proven successful is Al[25].

We have developed high-lifetime schedules for POCl₃ diffusions over the range of interest for the requirements of our solar cell technology. Doped layers with sheet resistances ranging from 10-1000 Ω/□ have been achieved repeatably with these schedules. The resulting recombination parameters have also been measured for these diffusions. The Figure 2.23 indicates the emitter saturation currents for three drive-in schedules. The best results (the lowest) are for deep diffusions at a given sheet resistance. The highest values are for the curve of shallow diffusions. The curve intermediate was for an intermediate diffusion drive-in. More importantly this curve was for POCl₃ doping.
The others were for doped oxides as reported in the first section of this chapter. The POCl₃ diffusions give the expected values of emitter saturation current, with no obvious difference from the case of doping from doped oxides. The resulting base lifetimes in the POCl₃ wafers in this experiment was typically 1.5-5 ms.

The boron diffusions are much less critical with respect to cell design parameters. The curves of oxide-passivated emitter saturation current vs. geometry indicate a broad optimum of surface concentrations and junction depths that all give about 1×10⁻¹³ A/cm² (Fig. 2.18). Also, the contact resistance behavior for boron is very tolerant. However, there was some question about whether BBr₃ was a lifetime killer. Over a matrix of experimental schedules, we obtained the target sheet resistances for the boron diffusions, with the expected 1-1.5×10⁻¹³ A/cm² emitter saturation currents that correspond to the expected values for diffusions with surface concentrations in the 10¹⁸-10¹⁹/cm³ doping range in Fig. 2.19 in the previous section of this report. So BBr₃ appears to be sufficient to obtain similar results to doped oxide. The final base lifetimes on these wafers were typically 0.5-5.0 ms.

We have also fabricated 35 cm² one-sun cells with a process schedule that utilized doping from BBr₃ and POCl₃. The resulting cell had the characteristic that would be expected from the similar cell fabricated with doped oxides, that is, about 21% efficiency at one sun.

The results from Al diffusions were not so promising. We took oxidized wafers with high lifetime, and etched the oxide off of one side. Al:Si was sputtered onto that side (4500 Å). The wafer was then annealed in nitrogen at 1100 °C for 30 min, followed by a forming gas anneal at 350 °C. It had an emitter saturation current density of 1×10⁻¹² A/cm². The wafer base lifetime was lowered to about 60 µsec. A control wafer, that went into the same tube simultaneously but without the oxide strip and Al deposition, maintained its high lifetime. The problem would seem to be in the low surface concentrations attainable for Al. The sheet resistance that resulted from this schedule was only 80 Ω/□. Even boron diffusions with this high of sheet resistance cannot attain emitter saturation current densities lower than 1×10⁻¹² A/cm² when Al-contacted. Ideally, surface concentrations greater than mid-10¹⁹/cm³ would be used to minimize this emitter saturation current density. The phase diagram for Al and Si
Figure 2.23: A comparison of phosphorus-doped diffusions from POCl₃ and from doped oxides. The upper curve is from doped oxides, with a shallow diffusion schedule. The central curve is from POCl₃ with a deeper diffusion. The lower curve is from doped oxide, and has the deepest diffusion. The trends are consistent with the doping methods being entirely equivalent.
indicates that only $2 \times 10^{19}/\text{cm}^3$ is possible, even at 1100 °C. These results are basically in agreement with the optimizations using open-circuit voltage reported by Green et al[25].

A more complete experimental matrix was done with even less encouraging results. Anneals of 45 min were performed at 900, 950, 1000 and 1100 °C as above, with two wafers at each temperature. No trends were seen. The lifetime on some of these wafers was killed to less than 50 μsec. This resulting lifetime differed even between wafers processed side by side. The emitter saturation current densities ranged from 2 to $4 \times 10^{-12}$ A/cm$^2$. Since Al diffusions are in fact more difficult to integrate into a high-efficiency process schedule than the other sources we have tried, there seems to be little to be gained in pursuing them. There may be cases where Al diffusion is natural to the process schedule. In these cases, our data indicate that emitter saturation current densities of about $10^{-12}$ A/cm$^2$ are attainable, but in the very brief outline of an experiment that we did, reproducibility and process control for this process was not obvious.

Significantly, the oxidation tube that we used for this experiment suffered no permanent damage. After an extended TCA getter, wafers could again be oxidized and shown to have lifetimes in excess of several ms.

2.5 Conclusions

In this chapter, we present extensive experimental and modeling data for phosphorus, boron, and Al diffused layers.

The main contribution of the work on phosphorus was the determination of the dependence of the surface recombination velocity on the doping level. Previous modeling studies for passivated emitters were limited in accuracy due to the assumptions made about this function. A full set of modeling results relevant to solar cells was generated from this new data and presented here. Additionally, the dependence of the recombination parameters for phosphorus-doped regions on the fabrication parameters was investigated. This included various temperature cycles, ambients, and surface
The same study was done for boron. In addition to the results above, more detail was provided in order to make as much sense as possible of the additional complexities. A new fit for the band-gap narrowing vs. dopant concentration was extracted as necessary to allow a consistent model for the data. A reduced band-gap narrowing from the commonly assumed functions is most consistent with the data presented here. The dependence of the surface recombination velocity on the dopant concentration was determined and found to be much less sensitive than in the case of phosphorus. Also, a strong dependence of the surface recombination velocity on the minority-carrier injection level was noted, as previously observed.

Similar experiments were performed in much less detail for several alternative dopant sources. POCl₃ and BBr₃ diffusions were found to be quite comparable to our baseline doped-oxide sources. Al diffusions proved to have quite high emitter saturation current densities (greater than $10^{-12}$/cm²), perhaps due to the range of rather low surface concentrations attainable. These Al diffusions also proved to be temperamental as well, decreasing the base lifetimes of wafers from values over a ms to tens of $\mu$s, with varied results from wafer to wafer in a single run.
Chapter 3

Simplified backside-contact solar cells

3.1 Introduction

Conventional solar cells have an apparent advantage in simplicity which implies lower fabrication cost. However, recent high-efficiency versions of these designs require increased complexity. High output voltages necessitate the use of oxide-passivated emitters. High currents require innovations such as a high-aspect-ratio gridline technology, buried grids, light-trapping features, prismatic cell covers, and double-layer antireflection coatings. A low metalization series resistance is an additional requirement that tends to compromise measures taken to optimize the photocurrent generation. The interactions between all these features can make the fabrication of these solar cells much more difficult than it may first appear. A discussion of many of these tradeoffs is included in the chapter on cells with frontside grids.

The inherent promise for a simple backside-contact cell design is that it decouples the classic series-resistance versus shadowing-loss compromise. The sunward side of the cell is optimized for optical performance (maximum photogeneration). Rather independently, the back surface can be optimized for electrical performance.
The sunward side of the high-efficiency backside solar cell is already quite simple, consisting of an oxidized, textured surface. The backside, however, is quite complex, generally requiring four to six mask levels to fabricate\[46,63\]. Here, we present new designs that reduce this fabrication complexity. The two features described that distinguish these designs from the previous high-efficiency backside cells are:

- The development of a self-aligned metalization technology.

- The optimization of heavily-doped compensated regions, so that the p+ and n+ diffusions need not be separated by a lightly-doped or undoped spacer region. Instead, the dopants are allowed to interdiffuse at their boundary.

Each of these new features allows the elimination of one photolithographic step. This permits the fabrication of high-efficiency cells with a process that involves as few as one photolithographic step.

Many of these concepts were presented in the final report from the previous contract[53]. At that time, promising results for many of the most basic elements in the design were presented, especially the self-aligned metalization process. However, the best performance achieved was for a cell at 40 suns, at only 15.4%. The optimism for the designs was based upon modeling results from several experiments on photo-conductivity lifetimes for proposed diffusion schedules that we thought constituted a successful demonstration of the most questionable features of the design.

In this chapter, we present the solar cell results from subsequent work. Initial success was for a 10-cm² one-sun cell at 22%. A study of the key compromises present in the choice of the emitter dopant profiles was done in order to determine how much would be compromised in an optimized design from the presence of the compensated regions at the boundaries between the stripes. In further work, 37.5-cm² cells were demonstrated that were 21% efficient. Application of several of the same concepts to concentrator cells resulted in efficiencies over 25% for soldered-down 0.64-cm² cells at 100 suns.
3.2 Device design

The proposed design is shown in Fig. 3.1. This is essentially an interdigitated backside contact solar cell with a fraction of the backside doped p+ with the remainder doped n+. The unique aspects of the design occur at the n+-p+ boundaries, as indicated by the inset. One set of the fingers, in this case the p+, is on a lower plane of silicon. In this way, the cell can be made with no alignments. A typical fabrication sequence might be:

1. Deposit an n+ doped-glass.
2. Etch a finger pattern in the glass and into the underlying silicon.
3. Deposit an p+ glass, and drive-in both dopants. This dopes the mesas n+ and the trenches p+.
4. Strip all of the oxides, and deposit a metal stack of Al:Si with a Ti capping layer.
5. Etch in Al-etch to clear the steps, isolating the metalization for the n+ and p+ regions. The Ti acts as a mask during this etch. However, this Ti is discontinuous over the step allowing the etch to attack Al and clear the step as indicated.

A complementary sequence can be used to obtain n+ in the trenches. Some previous work in optimizing this structure is described in [51].

The advantage of this sequence is that the entire process is self-aligned. In this respect, it is analogous to the laser-grooved solar cell process. The possible disadvantages are:

- The area of dopant diffusions is increased relative to point contact designs. This will have the effect of lowering the cell open-circuit voltage.
- The heavily-doped compensated regions may have excessive shunt leakage or poor reverse saturation current, Jsc, reducing the voltage further.
Figure 3.1: A backside-contact solar cell. Light enters from the bottom in this figure. The inset indicates a step that is introduced at an early stage in the process. With this step, a self-aligned process requiring no mask alignments has been optimized.
One option that partially addresses these problems is to cover the diffused regions with an oxide and etch contact windows prior to the metal deposition. In this way, the emitters are largely passivated. This provides an extra degree of freedom in the design, at the cost of an extra mask.

3.3 Some high-efficiency results.

A run of 10.5-cm$^2$ one-sun cells was fabricated in order to demonstrate this technology. The large dimensions of one sun cells simplify the characterization of the process as well as the testing of finished solar cells. These cells were fabricated on high-resistivity phosphorus-doped silicon wafers that were 130 $\mu$m thick. The sunward side was textured, and oxidized to a thickness of 1200 Å. The stripe dimensions consists of 60-$\mu$m-wide p$^+$ trenches separated by 140-$\mu$m n$^+$ mesas. For this process, an oxide was grown over these diffusions, and contact vias were opened prior to metalization, yielding a seven-percent metal-semiconductor contact area. Hence, this was a two-mask process. In addition, a light n$^+$ diffusion was made on the textured surface. This feature has been optimized in a previous study [37] and shown to improve the performance of textured high-injection solar cells operating at less than 10 suns of concentration. The three diffusions were 6 $\Omega$/□ for the n$^+$, 26 $\Omega$/□ for the p$^+$, and 400-500 $\Omega$/□ for the textured-side n$^+$. The run resulted in one solar cell on each of four wafers. A sporadic problem occurred to some degree on each wafer. The metal self-aligned on the contact-window steps in the passivation oxide as well as on the steps in the silicon, etching a line around the contact perimeter. Where this problem occurred, the metal line was almost entirely cut by the edge definition of the contact window. This may account for some of the subsequent scatter in the results due to excessive series resistance on some devices.

The results from the best cell are summarized in the illuminated current-voltage curve shown in Fig. 3.2. Under an AM1.5 Global spectrum, the best cell was found to be 21.9% efficient at one sun[4]. The four cells had efficiencies of 20.8, 21.1, 21.7 and 21.9%.
10.5 cm²  
$J_{sc} = 41.7 \text{ mA/cm}^2$  
$V_{oc} = 657 \text{ mV}$  
FF = 0.80  
$V_{mp} = 558 \text{ mV}$  
Efficiency = 21.9%  

Figure 3.2: The illuminated IV curve for a solar cell measured under 100 mW/cm² using an AM1.5 global spectrum (Sandia National Laboratories). Measurements were performed at 25°C.
Several aspects shown in Fig. 3.2 are of particular interest. First, the cell has a very high one-sun current density, 41.7 mA/cm². This is typical for backside-contact cells made on good quality material. It comes without any special attention, since no features mar the front surface of a backside-contact cell and the internal quantum efficiency is essentially unity. Second, the fill-factor of 0.80 is very high for a high-injection solar cell at one sun. This value could be as high as 0.84 as predicted for a cell with diffusions on all surfaces, and the open-circuit voltage of this cell[37]. This should be the case here. The difference is probably due to metalization series resistance. Notice that away from the active region of the cell, where a cleave or sawcut would be, the structure is n⁺-i-n⁺ to minimize edge effects. This is achieved without an additional mask since the one mask that defines the p⁺ trenched area can also insure that this region not extend to the sawcut.

Additional measurements were performed in order to assess the effects of the compensated regions in the device. For these devices, there are about 10 metres of compensated stripes. For the diffusion schedule and doping levels from the fabrication, these heavily-doped stripes are approximately 3 μm wide (the calculated width where both dopant densities exceed 10¹⁸/cm³). From the dark I-V curve, the reverse bias leakage at -1.0 volt was less than 1μA/cm². The reverse breakdown was very abrupt; 0.5 mA/cm² at -6.00 V increasing to 40 mA/cm² by -6.34 V. This data indicates that the compensated regions will not have any significant adverse effect upon the solar cell performance.

In addition to the one-sun efficiency measurements performed at Sandia National Laboratories, the cell with a measured efficiency of 21.7% was tested at lower intensities under artificial light. After duplicating the open-circuit voltage and fill-factor at the short-circuit current that corresponded to one-sun at Sandia, curves were taken at lower intensities. At 1/25 of one sun, the open-circuit voltage was 577 mV, and the fill factor 0.80, implying an efficiency of 19.0%. This high voltage and fill factor at very low illumination indicates very good junction characteristics. The open-circuit voltage, 577 mV, is 79 mV lower than at one-sun. This corresponds closely to the 84 mV expected from theory with an ideality factor of one. The fact that this was achieved in a solar cell with the substrate in high-injection indicates that recombination in the substrate does not contribute significantly to the solar cell characteristic even at this very low
intensity. Some heating of the cell relative to the 25 °C mount was observed under one-sun illumination since the cell active area was not in thermal contact with the mount during tests.

The fill factor peaked at 1/10 of 1 sun. This is an additional indication that series resistance limits the performance at one sun in this device. This need not be the case. The calculated resistance for the metalization pattern is 17 mΩ. The excess resistance was most likely due to a process problem described above that compromised some of the metal lines.

The 22% efficiencies demonstrated here are not the best that can be achieved for this device design. A logical practical limit would be given by the best demonstrated values for the three diffusions on the cell that determine its performance. The best front-surface passivation demonstrated is an n+ diffusion with an emitter saturation current density of $2.4 \times 10^{-14}$ A/cm²[41]. The combined emitter saturation current density for the backside diffusions can probably be reduced to $10^{-13}$ A/cm². This would be the case for a vanishingly small metal-semiconductor contact coverage fraction, reasonable at one sun. A total solar cell $J_o$ of $1.25 \times 10^{-13}$ (300 K) would allow an open-circuit voltage of 683 mV at 25 °C, and an efficiency of 24.3%. This assumes a photogenerated current density of 42 mA/cm². The one-mask process, with a full backside metal-semiconductor contact (part n+, part p+), would have a one sun efficiency of 23%, due to the backside emitter saturation current density of $4 \times 10^{-13}$ A/cm² for the unpassivated emitters (discussed below).

Currently, the best demonstrated one-sun solar cells are around 23% efficient[7,37]. One of these record cells has front grids. Although the authors foresee a simplified version of this design, the 23.2% 4 cm² demonstrated cell utilized 4 masks and 2 vacuum depositions during fabrication. Scaling the size upwards from the 4-cm² area will involve an increase in the metalization shadowing loss or a more complex grid process (high-aspect-ratio lines etc.) in order to maintain a low series resistance. The 22.7% backside point-contact solar cell involved four masks with three alignments[37]. Hence, the design presented here is simpler in fabrication complexity to these high-efficiency cells. The laser-grooved solar cell has an efficiency exceeding 20%, and a fabrication sequence that involves only one vacuum evaporation and laser patterning rather than
photolithography[66]. This laser-grooved design appears to be the most scalable of the frontside-grid designs, as already demonstrated in large-area cells. The backside cell designs are relatively easily scaled since half of the backside area can be devoted to each polarity of bussbar metalization, allowing a low series resistance.

3.4 The key optimization, the doped regions in the cell

The only uncertainties introduced by these new designs are in the performance of the doped areas on the cell backside, including any effects characteristic of the heavily doped and compensated regions. Consequently, most of the optimization for these designs consisted of detailed characterization of these doped regions.

Several issues that must be taken into account are:

- High doping levels lead to shorted junctions.
- Low doping will give poor contact resistance, or even Shottky diodes at the n⁺-Al contacts.
- The recombination in the doped regions should be minimized. This involves compromises between the optimum for regions that are n⁺ and p⁺, passivated and unpassivated, compensated and uncompensated.

The first two of these effects were evident from the first experiment[51]. The p⁺ doping was held fixed, at 17 ohms/□, and the n⁺ doping was varied from 5 to 4500 ohms/□. These junctions were very deep, about 5 μm. For n⁺ surface concentrations above mid-10⁻¹⁹ cm⁻³, the devices were shorted. At mid-10¹⁸ and below, Schottky barriers were formed rather than ohmic contacts. At intermediate concentrations, some devices showed reasonably good characteristics, although some shunting was observed as the n⁺ doping increased. This indicated that for this particular p⁺ doping, n⁺ surface concentrations should be in the narrow range between 1 and 4×10⁻¹⁹ cm⁻³. Since the
\( p^+ \) doping is less restricted by contact resistance concerns, it could be lowered in order to reduce the shunt effects. This was subsequently confirmed as discussed below.

In addition to these first two concerns, which can determine whether or not the cell functions at all, the doping concentrations need to be optimized to give the lowest possible emitter saturation current densities, \( J_o \). For cells with large, metal-contacted areas, as in the one-mask design, this requires deep diffusions. Difficulties in simultaneously optimizing all of the above factors led to an evolution toward the two-mask design. With two masks, the diffusions can be largely oxide-passivated with only small windows contacting them to the metalization. This passivation allows low \( J_o \) at lower dopant concentrations, virtually eliminating the problems arising from the compensated regions.

In addition to an optimization toward lower doping levels, widening the lines was found to improve the performance by minimizing the area of compensation (reducing the number of stripes). This simplifies the problem by reducing the number of regions that have shunt and recombination problems, as an alternative to finding the elusive optimum where these effects don’t occur. This was especially important in the case of unpassivated, but heavily compensated regions in the one-mask design. After these modifications had been implemented, good results were obtained for both the unpassivated emitter (one-mask) and passivated emitter (two-mask) processes.

The main trends evident in optimized schedules are shown in Table 1. A solar cell run of 10.5-cm\(^2\) cells was processed similarly to the one-sun cells described above. They were fabricated on thick, untextured substrates specifically in order to characterize the \( J_o \) as a function of process schedule and metalization contact-coverage fraction. Wafers with a drive-in schedule of 30 minutes at 1120 °C followed by a 45-minute oxidation had sheet resistances of 36/14 ohms/\( \Omega \) for the \( p^+/n^+ \), diffusions. A similar schedule at 1060 °C gave 87/46 ohms/\( \Omega \) for these \( p^+/n^+ \) diffusions. The emitter saturation currents were measured with an Open-Circuit-Voltage-Decay technique as previously described[50]. The cell with the more shallow diffusions has a very low \( J_o \), \( 1.5 \times 10^{-13} \) A/cm\(^2\), when only metal-contacted over 1% of the cell area. With 100% metal-Si contact area, this \( J_o \) increases to \( 6 \times 10^{-13} \) A/cm\(^2\). The heavier diffusion has a \( J_o \) of \( 2.3 \times 10^{-13} \) A/cm\(^2\) for the 1% contact area, increasing to \( 4 \times 10^{-13} \) when fully contacted. Surprisingly, these
<table>
<thead>
<tr>
<th>metal coverage</th>
<th>$J_o$ (1120 °C wafer)</th>
<th>$J_o$ (1060 °C wafer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>$2.3 \times 10^{-13} \text{A/cm}^2$</td>
<td>$1.5 \times 10^{-13} \text{A/cm}^2$</td>
</tr>
<tr>
<td>30%</td>
<td>$3 \times 10^{-13} \text{A/cm}^2$</td>
<td>$3 \times 10^{-13} \text{A/cm}^2$</td>
</tr>
<tr>
<td>100%</td>
<td>$4 \times 10^{-13} \text{A/cm}^2$</td>
<td>$6 \times 10^{-13} \text{A/cm}^2$</td>
</tr>
</tbody>
</table>

Figure 3.3: The emitter saturation currents (300 K, referenced to the total cell area) measured for two processing schedules, and a variety of metal-to-diffusion contact area fractions. The cells processed at 1120 °C had $p^+/n^+$ sheet resistances of 36/14 ohms/□. The 1060 °C wafer had 87/46 ohms/□.

values for the emitter saturation currents are very near those expected in the absence of any effects due to the compensated regions.

3.5 Continued process development and more solar cell runs.

After the demonstration of the 22%-efficient one-sun cell, the major issues in the device physics concerning the operation of this cell design were confirmed. Additional process development continued along several lines.

1. Research on the self-aligned metalization technique.
2. Demonstration of the lowest possible total backside emitter saturation current density.

3. Alternative process schedules for obtaining the structure described in the section on the 22% cell.

4. Demonstration of the design on larger cells with better optimized mask layouts.

5. Adaptation of the design to concentrator cells.

Research on the self-aligned metalization techniques proceeded slowly. The sputtering machine in our laboratory is a general use machine. Half a dozen targets are swapped around between two target slots. Hence, each experiment typically involves a recalibration of the fundamental deposition conditions (such as the deposition rate, etc.) prior to the intentional experiment. We found that the Ti/Al process was not entirely repeatable under these conditions. At times, it would work for an entire run, over entire wafers. A good demonstration of this was one run of 37.5-cm² one-sun cells. That the self-aligned metalization works for this device size indicates a tolerant process. In this case, 15 metres of adjacent lines separated by about 5 µm must exist with no shorts. This defect density would be difficult to match with a conventional photolithographic technique.

Three weeks later, the same process didn't work on a single wafer out of a run of nine wafers.

Similar results were obtained for a selection of other metal overlayers used as a self-aligned mask in this process. 600 Å of tungsten works fairly well. 500 Å of silicon worked extremely well....once. A second time it did not. This area of investigation could use more work. It would proceed much more smoothly if a dedicated sputtering machine were available. Having shown that it could work, we soon abandoned the use of self-aligned metal on experimental runs except for those specifically designed to investigate this topic. Photolithography is more work, but it is also somewhat more predictable at this stage.

Process optimization of the diffusion parameters resulted in one run of one-sun solar cells with a total backside emitter saturation current density of $10^{-13}$ A/cm². This
demonstration indicates that the cell design is quite capable of efficiencies exceeding 24%.

Much of the continued process development of actual cell processes was tested on one-sun cells under investigation for another Sandia contract no. 66-2878. These results will probably be reported there. In summary, the basic device design has been implemented on a number of cell runs. A number of different process schedules were investigated for accomplishing this.

For example, one run of 37.5% cells was fabricated entirely with doped oxides, deposited in three separate depositions. This allowed an independent choice of the surface concentration and emitter depth for the front n+, back n+ and back p+ diffusions. This run was completed with the self-aligned metalization technique using Ti/(Al:Si). The resulting efficiency (measured at Sandia) was 21%. The open-circuit voltage was 674 mV, the short-circuit current density was 40 mA/cm² and the fill factor was 0.78.

Another process schedule was developed that used BBr₃ and POCl₃ dopant sources. Designed for simplicity, the phosphorus diffusions on the front and back sides are the same (one doping step determined both). This 35 cm² cell has (Stanford measurements) an open-circuit voltage of 646 mV, and a fill-factor of 0.80. Assuming the same 40 mA/cm² in lieu of a proper calibration, this implies an efficiency of 20.7%.

A more recent run used a combination of B-doped oxide and POCl₃ to good advantage. The process schedule was:

1. Deposit B-doped oxide and densify it.
2. Texture the wafer in a random-texture solution. The B-glass masks the one side from the texture solution.
3. Pattern the B-glass and trench the silicon.
4. Dope with POCl₃ creating both front and back n+ regions.
5. Strip the oxide, reoxidize.
6. Pattern contact windows in the oxide.
7. Deposit Al and pattern it.

Twenty wafers were processed with this schedule. One broke. The other 19 had virtually identical characteristics. Sandia measurements indicate open-circuit voltages of 670 mV, and fill factors of 0.77. The cells were designed to be encapsulated and have no antireflection coating at all (200 Å of SiO₂). Their resulting low currents were about 36 mA/cm². Since the wafers are textured, it is reasonable to assume that this will improve substantially when encapsulated, and possible result in efficiencies of about 20-21%. The total emitter saturation current density measured for these cells from open-circuit voltage decay was \(2.7 \times 10^{-13}\) A/cm². The phosphorus diffusions on both sides were about 60 Ω/□. From Chapter Two, the expected emitter saturation current density from this diffusion on the textured frontside is about \(7 \times 10^{-13}\) A/cm². On the planar backside, the phosphorus diffusion would have an emitter saturation current density of \(1 \times 10^{-13}\) A/cm². The boron diffusion on the back would also have \(1 \times 10^{-13}\) A/cm². Weighting by the appropriate area fractions covered by each, the results of Chapter 2 would predict a total emitter saturation current density for this cell of about \(3 \times 10^{-13}\) A/cm², in good agreement with the measured value.

### 3.6 Application to concentrator cells.

This simplified backside contact design has also been applied to concentrator cells. In one of the first successful runs of concentrator devices, cells with an active area of 0.64 cm² were fabricated on high-resistivity 150-μm-thick n-type substrates. They had a textured front surface that was doped n⁺ to improve the stability after extended high-concentration sunlight exposure[30,31].

These cells had all the features of the one-sun cell (Fig. 3.1), complete with the trenches and compensated regions. However, this particular run was done with conventional photolithographic patterning of the Al since Ti was unavailable in the laboratory at the time. This detail should have little effect upon the experimental performance of the finished devices.
For this concentrator cell, 40-μm-wide trenches were doped n+ (6 Ω/□) and 120-μm-wide mesas were doped p+ (18 Ω/□). Compared to the previously described 2-masks fabrication sequence for the one-sun cell, some additional processing was added in order to allow the cell to be soldered to a substrate. The structure described here is particularly well suited to cells intended for direct mounting. The p+ mesas were defined to be only in the cell active area, and the n+ trenches traverse this area and account for the entire periphery of the die. After patterning of the 3.5 μm-thick Al layer, an SiO2 layer was deposited over the entire device. Contact windows were opened to the mesas in the active area, and to the trenches in the perimeter region. In this way, the active area mesa metalization could be soldered directly to a positive electrode that provided both electrical and thermal contact. The perimeter trench metalization was soldered to a negative electrode. This soldering was accomplished after Ni- and Au-plating the Al that had been exposed by the contact windows in the SiO2 over the metalization.

Since the p+ metalization is soldered directly to the substrate, it contributes virtually no series resistance. The n+ trenches are arranged in a chevron pattern through the 8 mm active area in order to take advantage of the lower series resistance of an approximately radial grid in transporting the current to the cell perimeter. A sectional view of the cell is shown in Fig. 3.4.

Cells soldered to substrates were tested at the Stanford facility as previously described[11]. For an absolute reference, cells recently measured at Sandia National Laboratories were used (the one-sun cells described above). The efficiencies for a cell under concentrated sunlight are shown in Fig. 3.5. It was 24% efficient at 2 W/cm², (20 suns, 25°C), and 25% for a range between 4 and 10 W/cm². The efficiency dropped off at higher concentrations to 24% at 20 W/cm².

The presence of the frontside n+ diffusion is largely responsible for the loss of efficiency at high concentrations. It is likely that a diffusion with an emitter saturation current of $1 \times 10^{-13}$ A/cm² is necessary on the cell frontside to achieve an efficiency that does not degrade after exposure to highly concentrated light [31]. For concentrator cells, this diffusion is not as effective at passivating the surface as the undoped oxides on previous backside-contact cells, before extended exposure to concentrated light. This
Figure 3.4: A cross-section of a portion of the cell indicating the 140-μm-wide p-type mesas that are subsequently soldered directly to the substrate. The metalization in the 40 μm wide trenches extends out to the perimeter of the die, where electrical contact to that level is made.
Figure 3.5: The efficiency for a 0.64 cm² cell under concentrated sunlight.

decreases the attainable starting efficiency from the 28% levels previously reported for those devices[51]. The loss in efficiency due to front surface recombinaton at this diffusion is approximately linear in the concentration ratio and quadratic in the substrate thickness. The dependence on concentration demonstrated by the high-concentration performance of the cell is shown here. The measured total series resistance, 4.7 mΩ, accounts for less than half of the 3% loss in efficiency that occurs between 10 W/cm² and 40 W/cm². A frontside emitter saturation current density of $6 \times 10^{-14}$ A/cm² can explain the additional loss in efficiency.

About forty of these cells from a subsequent run were delivered to Sandia National Laboratories for use in modules. Results from the Sandia flash tests for one of these is provided in the following table. These cells were thinner than those described above, about 85 μm thick, and had significantly lower series resistance, about 2 mΩ·cm². These cells had a very light frontside phosphorus diffusion, 300 Ω cm. This is higher than our target and may not be as stable as desired.

A curve of the results for these cells from Stanford's outdoor facility is shown in
Table 3.1: Efficiency vs. incident power density, measured at Sandia National Laboratories under a 0.365 cm² aperture. Voltages are 16 mV low due to the small aperture, hence the efficiencies are understated by about 0.6% absolute, compared to the case of illuminating the full 0.64 cm² design area.

Fig. 3.6.

At one-sun, the cells were 20.8% efficient, with an open-circuit voltage of 668 mV, and a fill-factor of 0.81. These results are essentially equivalent to the very large one-sun cells, indicating the commonality of design.

At the time of this writing, early module results indicate a module efficiency of 19%, at operating temperature, implying 20-21% at 25°C. This is despite an unoptimized optical path in the lens and secondary with an estimated 81% transmission[8].

Cells from this run were also fully characterized using open-circuit-voltage decay. These data are shown in Fig. 3.7. From these data, the total emitter saturation current density for the cell is $2.44 \times 10^{-13}$ A/cm², and the substrate lifetime is longer than 360 $\mu$s. These results are quite consistent with the value for the total emitter saturation current density extracted from the dark current-voltage curve ($2 \times 10^{-13}$ A/cm²) and from the illuminated characteristics shown in the table ($1.7 \times 10^{-13}$ A/cm²).

Many hundreds of cells similar to those shown here were fabricated for use in Electric Power Research Institute 500X modules. A detailed on-sun characterization of about 300 such cells at 500X (36 W/cm²) illumination is given in reference[55]. About two thirds of those cells were nominally 23% efficient at this intensity. Most of the remaining cells suffered from various degrees of shunting, some of which was present
Figure 3.6: The efficiency of a run of 0.64 cm² cells measured under concentrated sunlight at Stanford University.
Figure 3.7: The open-circuit-voltage decay for a 0.64-cm² solar cell. This technique is referred to many times in this report as a method for assessing the recombination parameters for finished cells. This data is in good agreement with dark IV and illuminated IV measurements.
after fabrication but most of which was due to the soldering procedure.

When the self-aligned metalization patterning is used, the fabrication of these cells to a stage suitable for mounting requires three masks. This is significantly simpler than previous designs for mounted backside contact cells that utilized six to eight masks and a double-level metalization[63]. The efficiencies achieved at this early stage of development were already comparable to those previous results. With the previous backside point-contact cells, efficiencies of 27.2% were measured at 15 W/cm². The level of complexity for this new design is comparable to the front-gridded cells that have similar efficiencies at these concentrations. When the details, such as prismatic cover-glass application and overall design rules for the different cell fabrication processes, are considered, these initial results for a simplified backside-contact concentrator cell show a great deal of promise.

Both the one-sun and the concentrator cells reported here have backside emitter diffusions that are very deep. In further optimizations, total emitter saturation currents for the cell backside of about $1 \times 10^{-13}$ A/cm² have been achieved in test devices[54]. The incorporation of these better emitters could provide an additional 20 mV to the cell voltage at the lower concentrations. Initial attempts to fabricate optimized 100X cells with these lighter diffusion schedules failed. It proves to be difficult to obtain the very low emitter saturation current densities for the n⁺ diffused regions, requiring low surface concentration, simultaneously with good contact resistance, requiring high surface concentration. This is quite well known, and accounts for the fact that high-efficiency cells with frontside n⁺ diffusions generally resort to using a heavy n⁺ diffusion under the metal contacts and a lighter diffusion elsewhere, despite the obvious increase in complexity[6]. This same double diffused emitter schedule could be applied to the back n⁺ diffusion in a backside cell in order to test the true efficiency limits of the device. In this case, the emitter saturation current density for the entire back surface could be reduced to well below $10^{-13}$ A/cm².

Several subsequent runs failed for various reasons, leaving the optimized 100X cell largely to the imagination. 27% cells with stable front-surface passivations are not outside of the realm of possibilities. Detailed modeling results are reported in a subsequent comparison of backside and two-side cells in the next chapter of this report.
Chapter 4

Sandia Baseline 3 Cells: Experiments in cells with frontside grids

4.1 Introduction

The difference in performance between backside contact solar cells and cells with frontside grids is almost entirely due to the grid-shadowing vs. series resistance compromise. Recent results with prismatic covers have allowed cells with frontside grids to attain very comparable efficiencies to backside contact solar cells in the range of incident power densities around 10 W/cm². The group from the University of New South Wales has achieved 25% at 12.5 W/cm². They fabricated and delivered large quantities of nominally 24% cells to Sandia National Laboratories. These cells were tested in several different module configurations leading to impressive efficiency records such as a combined lens/cell efficiency of 21%[29].

It is possible that cells with frontside grids may be more easily fabricated and applied in module applications than backside-contact cells. Certainly the fabrication, testing, and mounting for module use of simple cells of this type is quite straightforward.
However, upon close inspection, the steps necessary to improve a nominally 22%, 1.56 cm² cell of the type required for the Sandia Baseline 3 module to 25% present quite a challenge. In the best demonstrations to date of the cell operating behind a Fresnel lens (above), it is estimated that the cell is operating at 23.5% at 20 °C, significantly less than its efficiency indoors (25%) based upon normal-incidence light. This is attributed to acceptance-angle problems with the prismatic covers as mounted on these cells. A complete assessment of this cell design for concentrator module applications needs to take into account not only the ease of fabrication of the cells themselves, but the ease of all of the subsequent procedures necessary to give them high performance in the module. Even the cell fabrication itself for these cells is rather complex, requiring three vacuum depositions, four photolithographies, two dopant diffusions, antireflection coating deposition, and grid electroplating.

We chose to follow a different, but complementary research path to the one described above. Rather than design our own front-gridded cells dependent upon the prismatic coverglass concept, we decided to investigate designs in which the grid losses due to shadowing and resistance were minimized at the cell level, without complex external elements. Essentially, this folds the optical complexity back into the initial cell design and fabrication on the wafer as opposed to mitigating the optical losses at a later stage.

In this chapter, we present results from numerous different approaches we tried to optimize in order to achieve 25% efficiencies on front-side solar cells. The most successful design reached 26% at 90 suns. Several designs exceeded 24% in efficiency. In addition, we discuss the effects of taking into account the necessity for front-surface passivation stability on the cell design. We also describe some experiments on very simple fabrication schedules that may be able to reach moderate efficiencies with no mask alignments whatsoever. Finally, a modeling study is presented indicating the relative performance of several cell designs. This comparison keys upon the differences between p-i-n, n-i-p, and backside-contact solar cells. The parameters used in this study were firmly based upon our experience from all of the various experiments presented in this final report. Considerations taken into account in this study include realistic estimates for the metalization series resistance, emitter performance, and surface passivation stability.
The number of cells of many different configurations presented an opportunity for a study of the short-circuit responsivity for $p-i-n$ and $n-i-p$ cells. This is included as an appendix to this chapter. A listing of experimental Sandia Baseline 3 cells is also given.

4.2 Early results: trying to push a simple design to 25%.

In the final report for the last contract period[53], we reported two distinct cell designs. The first was a simple design with point-contacts front and back in which the grids on the front were haphazardly superimposed upon the textured surface, Fig. 4.1. One run of these cells had been processed that had 23% efficiency at the Sandia module design point of 12.5 W/cm$^2$. A second design puts the metal grids on sloped runways which traverse the textured surface, Fig. 4.3. The intention of this design is that the light which strikes the metalization is deflected downwards onto the texturized region of the cell. In our initial work on this new contract, we tried to extend the results from the first, more simple design, in the most obvious ways.

The distinguishing feature of this cell design is that it requires only one mask alignment, the one that aligns the front metal grid to the contact windows. The fabrication sequence is given below.

1. Oxidize some wafers.
2. Strip the oxide from one side.
3. Texture the front side.
4. Strip the oxide and grow a new one.
5. Pattern contacts photolithographically, front and back (simultaneously). Open these contacts with a wet etch.
6. Deposit APCVD $p^+$-doped glass front, $n^+$ back.

7. Drive the dopant in.

8. Strip the oxide until the contact windows are open, leaving the original mask oxide (tuned to be the correct thickness for antireflection).

9. Deposit metal and pattern a frontside grid aligned to the contact openings.

The 23% result was limited primarily by the series resistance of the metal lines which were 4-μm thick and traversed some very rough terrain. In the first subsequent run, cells were processed using this same schedule except that the frontside Al thickness was 7 μm. These wafers turned out to be somewhat of a nightmare to pattern. Photore sist coverage across the wafer, alignment, exposure, development, and wet-etching thick Al over this topography proved to be extremely difficult and irreproducible. This last step was a learning experience that resulted in a motley bunch of wafers, with line widths varying from 0 μm up to a maximum of about 10 μm. This provided the experiment shown in Fig. 4.2. Here, the performance of the original run is compared.
Figure 4.2: The performance of three cells from the run Sandia 7 compared to the original run of this same cell type.
to a variety of the wafers from the new run. The wafer with thin lines, 7-3-2, had a very high current density, due to the small shadowing losses. In fact, this cell was a record one-sun cell for its size, (for a few days anyway) at 21.7%. The skimp lines on 7-3-2 couldn’t handle much current though, so the performance dropped off steeply at significant power densities. However, in the region between 5 and 20 suns, the 25% efficiencies were clearly a record for anything except our own backside point-contact cells.

At the design point power density of 12.5 W/cm$^2$, the best cell was 7-4-1. This cell was from the last wafer completed, and as a result it had the best etch optimization, keeping almost 10-μm-wide lines. This cell had an efficiency just under 24% at the design point.

The next enhancement we wanted to try was to make some thin cells of the same type. All of the previous cells were 200-μm thick. Sandia run 8 was about 110-μm thick. We chose to return to a more conservative 4 μm of Al for this test. These cells had grid series resistance problems. They showed 14 mΩ of series resistance. The very high responsivities, about 38.4 mA/cm$^2$, indicated that these high resistances probably were due to thin gridlines. The efficiencies peaked at 22.7% at 50 suns, dropping to 21.9 by 100 suns.

Hence, for this process, it appears that design-point efficiencies around 23% are straightforward to achieve, and 25% can be approached, but not without great difficulty and irreproducibility. Due to the simplicity of this runsheet, we returned to it frequently as a baseline process from which to try variations (a listing of runs is given in an appendix to this chapter). This schedule forms the basis for all of the subsequent runs that have point diffusions. The only major difference between runs is the original form of the substrate (textured, planar, patterned with v-grooves and inverted pyramids, etc.).

In particular, run 23 was a closely related variation. Rather than texturing the entire frontside, flat mesas were left where the metal lines and busbars would eventually lie. The rest of the front surface was randomly textured. This allowed an improved metalization series resistance at the cost of this one additional mask and the subsequent
alignment of the contacts to these flat mesas. Cells from this run were measured at Sandia to be 24.5% efficient at the design point. Twenty of these cells were gold plated. After the plating, which produced a widening of the metal fingers, the efficiency decreased to 23.5%. There was some hope that a cover glass could possibly recover a part of the light reflected by the metal gridlines. A quick experiment showed that the increase in responsivity produced by the cover glass was only about 1.5%.

4.3 More carefully optically engineered cells

The second type of two-sided cell, Fig. 4.3, has proven to be difficult to implement. The scheme here is to run the metal lines down ridges patterned into the silicon. In this way, light that strikes the metal will reflect down onto the cell.
A similar idea was previously implemented in the V-groove solar cell[4], in which the metal covered only a portion of one of the two slopes of each inverted V. A more recent attempt[62] was to metalize a portion of the two slopes of some of the grooves; this produced a high responsivity but not a complete demonstration of the concept, including series resistance and efficiency. Compared to these two previous approaches in which the surface topography consisted of an array of ridges the present cell consists mostly of pyramids, the number of ridges being strictly restricted to what the metal grid requires. This is a superior light-trapping configuration.

The pattern sculpted into the silicon that all of the subsequent lithographies and etches must deal with consists of 10-μm-high peaks and ridges. Photoresist coverage, alignment and exposure, successful resist development, and finally etching of complex patterns over this topography have all proven to be tedious exercises in process development. In addition to the obvious problems, one problem that was unanticipated is that the very optical reflections that these cells are designed to utilize have very detrimental effects during lithographic exposures. With Al on the wafer, light reflections from this mirrored surface during the photoresist exposure wreak havoc with the patterning. Initial attempts proved that the solutions to these problems would not be easy. Although many different attempts were made to surmount the various problems, our final assessment is that they seem to be largely intractable. It may not be possible to develop a reproducible process that gives uniform results from wafer to wafer and even across single wafers using the geometry of Fig. 4.3.

Several runs were completed during the development. The first (processed in parallel with the thin wafers discussed above) consisted of some wafers that had been processed up to the fateful last step. They looked good after the Al etch, but didn’t work. In the run Sandia 9, the wafers had planar diffusions front and rear. The sheet rhos were below the targets, 30 Ω/□ for the front p⁺ and 14 for the back n⁺. They had low currents (33.9 mA/cm²), low voltages (614 mV), and low efficiencies (15.5%). At 100 suns, they were 21%.

The run Sandia 10 showed infinitely more promise. This run consisted of wafers 115-μm thick. The experiment was split into two types, one with line diffusions (3% coverage), and the other with point diffusions (5% coverage). The sheet resistances
were 8 and 7 Ω/□ for the p- and n-type diffusions, respectively. The Al was 4.4 μm thick.

A visual inspection of the silicon ridges indicated lines that were 22 μm wide. A 7-8 μm wide flat spot was left on the top of each line. After the Al deposition and etch, the lines appeared to have 9-10 μm flat spots and 25 μm wide bases. The flat spot on the top of the lines is considered to be the limiting factor in the performance of these cells since it places a rather low upper limit on the amount of current that can be generated. In fact, the currents achieved were about 36.1 mA/cm². While this is high given the 20% grid coverage of the lines, it is anticipated that this current can be increased by reducing the flat spot on the top of the lines. This flat spot accounts for a loss of about 3 mA/cm². Additionally, the oxide thickness on the textured surface was found to be too thin at the end of the process, accounting for some of the additional loss in current.

The performance of these cells equaled the best result from the run Sandia 7. If placed on the figure of efficiencies for run 7 (Fig. 4.2), it traces out the same curve as 7-4-1. The one-sun efficiency was 19.5% with a fill factor of 0.79 and open circuit voltage of 692 mV. The efficiencies under concentration were about 24.2% at 50 suns and 23.2% at 200 suns. This was the best performance that we obtained from the design with this surface topography. It was a bit disappointing that it was not significantly better than what we could get from the simpler schemes. In subsequent runs, several attempts were made to reduce the “flat spot” area on top of the gridlines by isotropically etching the silicon after the anisotropic etching, and by using off-axis anisotropic etching to controllably undercut the oxide mask. Each of these “solutions” introduced its own problems into the already complicated subsequent photolithographic and wet-etch steps. The net result is that although one aspect, such as the flat spot area, could be improved in any one run, it always caused more problems somewhere else so that the efficiency was never improved beyond that achieved for run 10.
A dramatic improvement in the processing problems for these designs came from an apparently simple variation. By using inverted pyramids rather than upright pyramids (Fig. 4.4), much better, more reproducible results were obtained. This seems to be because the structure of the inverted pyramids holds a uniform layer of resist much better than the upright pyramids do. In addition, the patterning of the metal lines in this case occurs in a V-groove, for which the reflected light from the opposite V-groove wall during the photolithographic exposure is not nearly so problematic as the reflections from upright pyramids (that create a corrugated pattern). This enabled, finally, a demonstration of the main concepts for these cells.
4.4.1 Cell structure

The internal structure of the cell is shown in Fig. 4.5. It consists of an undoped (or moderately n-type) substrate with imbedded point p+ and n+ islands. The silicon oxide used to mask the boron and phosphorus diffusions passivates the undoped surfaces and also acts as an antireflection coating. The front p+ regions are lined in rows separated 60 μm, and they are 30 μm apart. The back n+ regions are created through 5x5 μm² windows in a 40x40 μm² pitch. Considering the lateral diffusion, the surface coverage fraction, relative to a horizontal plane, is about 10% for the p+ and about 20% for the n+ highly-doped regions. Note that the percentage of silicon (horizontal) area to be contacted is only about a 0.8% for the p+ and about 1.6% for the n+. This is the fractional area corresponding to the diffusion windows, which are re-opened for contact using a self-aligned process described earlier in [53]. In this process the boron and phosphorus doped glasses used as dopant sources are etched off in HF; at the same time the oxide thickness is adjusted to obtain reasonable anti-reflection properties. The metal grid is arranged in a chevron pattern that aligns on the triangular ridges. It covers about 17% of the cell's active area of 1.56 cm². To obtain the original topography in the silicon, we utilized pure ammonium hydroxide as an anisotropic etchant because it is better suited to a contamination-free environment than other alkaline etchants.

4.4.2 Cell performance

Table 4.1 compares the one-sun performance of selected cells from a high-resistivity (100-200 ohm cm), 165μm-thick wafer and from a low resistivity (0.2-0.3 ohm cm), 240μm-thick wafer. Both wafers are n-type, (100)-oriented, float-zone silicon. The best cell has an efficiency of 21.7% under direct AM1.5 spectrum and 22% under a global AM1.5 spectrum, as measured by Sandia National Labs. The efficiency of the best low-resistivity cell is only 20.7% because its responsivity is lower. These results are nearly the same as the corresponding ones for both high- and low-resistivity backside, point-junction cells reported recently [38]. The fact that the present front-gridded cells show nearly as high a responsivity as cells with no front grid (the current densities under global AM1.5 spectrum are 40.1 mA/cm² and 40.6mA/cm², respectively, for a
high-resistivity substrate; 35.2 mA/cm² and 35.6 mA/cm² for a low resistivity one) is particularly striking and provides an excellent demonstration of the sloped gridline concept.

Optical photographs of the cell front surface are shown in Fig. 4.6. This grid occupies a significant amount of area on the front surface. We can estimate the loss in current due to the presence of this front metal grid by comparing their measured responsivities to the maximum one that can be theoretically expected. Considering a 110-nm-thick silicon dioxide layer on the front-textured surface (reflectivity 0.018), a polished back surface with a reflectivity of 0.95, and a thickness of 165 μm, the short-circuit current theoretically achievable is 41.62 mA/cm² for the AM1.5 G spectrum. The measured responsivities of 38.24-39.66 mA/cm² then imply that the metal grid is causing a 5%-8% loss even though it covers 14%-20% of the surface. The fact that there is still a 5%-8% loss can be understood by realizing that in an important fraction of the surface the light bounces only once and therefore it is subject to a 13.5% reflection corresponding to the silicon dioxide coating. This occurs in the area covered by the
Table 4.1: One-sun performance (AM1.5 D, 25°C) of point-junction cells made on a high-resistivity substrate and on a low-resistivity substrate.

<table>
<thead>
<tr>
<th>Resistivity (Ω.cm)</th>
<th>Cell #</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (mV)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-200</td>
<td>3-5</td>
<td>39.66</td>
<td>703</td>
<td>0.781</td>
<td>21.74</td>
</tr>
<tr>
<td></td>
<td>3-6</td>
<td>39.65</td>
<td>696</td>
<td>0.775</td>
<td>21.39</td>
</tr>
<tr>
<td></td>
<td>3-7</td>
<td>38.41</td>
<td>704</td>
<td>0.781</td>
<td>21.10</td>
</tr>
<tr>
<td></td>
<td>3-8</td>
<td>39.64</td>
<td>703</td>
<td>0.771</td>
<td>21.47</td>
</tr>
<tr>
<td></td>
<td>3-10</td>
<td>39.52</td>
<td>701</td>
<td>0.774</td>
<td>21.45</td>
</tr>
<tr>
<td></td>
<td>3-11</td>
<td>38.24</td>
<td>703</td>
<td>0.781</td>
<td>20.97</td>
</tr>
<tr>
<td>0.2-0.3</td>
<td>6-3</td>
<td>34.58</td>
<td>699</td>
<td>0.826</td>
<td>19.95</td>
</tr>
<tr>
<td></td>
<td>6-4</td>
<td>34.27</td>
<td>698</td>
<td>0.827</td>
<td>19.90</td>
</tr>
<tr>
<td></td>
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<td>0.837</td>
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<td>0.827</td>
<td>20.39</td>
</tr>
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<td>700</td>
<td>0.839</td>
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<tr>
<td></td>
<td>6-13</td>
<td>35.23</td>
<td>701</td>
<td>0.839</td>
<td>20.73</td>
</tr>
</tbody>
</table>
metal grid (17%) and also in the regions adjacent to the metal lines (another 17%). The resulting estimate for the current loss, 4.5%, is in good agreement with the measurements. It therefore appears that the responsivity of some of the cells is as high as can be expected for this design. Note that there is significant room for improvement in the antireflection coating. The use of a coating material with a higher refractive index than silicon dioxide should reduce the effective shadowing to 1-2%.

The performance under concentrated light for a high-resistivity cell from a different wafer is given in Table 4.2. The efficiency is 26% at 90 suns (direct AM1.5, 25°C) and 25% at the design point of 15 W/cm². These results account for a sublinearity of the short-circuit current of 0.8%-1.5% in the range of interest. This performance relative to the earlier runs is shown in Fig. 4.7.
Table 4.2: Performance of a high-resistivity cell under concentrated light, 25°C.

<table>
<thead>
<tr>
<th>Irradiance (W/cm²)</th>
<th>Responsivity (mA/0.1W)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>38.7</td>
<td>698</td>
<td>0.791</td>
<td>21.4</td>
</tr>
<tr>
<td>5.0</td>
<td>38.7</td>
<td>802</td>
<td>0.847</td>
<td>26.3</td>
</tr>
<tr>
<td>8.8</td>
<td>38.6</td>
<td>811</td>
<td>0.830</td>
<td>26.0</td>
</tr>
<tr>
<td>12.9</td>
<td>38.3</td>
<td>817</td>
<td>0.807</td>
<td>25.3</td>
</tr>
<tr>
<td>17.4</td>
<td>38.1</td>
<td>823</td>
<td>0.781</td>
<td>24.5</td>
</tr>
</tbody>
</table>

Figure 4.7: Conversion efficiency vs. irradiance for front-gridded point-junction cells showing the historical evolution of the research. In cells S/3 and S/7 the metal fingers run haphazardly over a field of small pyramids. In cells S/10 and S/22 the metal fingers are on top of triangular ridges.
The 26% efficiency achieved by the present design is higher than the highest previously reported[2] for a silicon cell having a front metal grid, including those that make use of a microprism cover[68]. It has only been surpassed by the back-point-contact cell, which attained 28.2% for a 0.15-cm² device[64] and 27.2% for a 0.64-cm² cell[48]. The present cell is larger, with an area of 1.56 cm². A light-trapping scheme consisting of inverted pyramids and a back surface reflector together with placement of the metal grid lines on top of sloped ridges has produced responsivities as high as 39.7 mA/cm², despite a 17% grid obscuration. Restricting the emitters to points and using a high lifetime material and a silicon dioxide surface passivation has led to open-circuit voltages over 700 mV at one sun. The performance at concentrations around the design point of 15 W/cm² is limited by a decreasing fill factor. Current crowding near the point-like junctions and the metal grid series resistance are the principal reasons for this decrease. The use of a better antireflection coating than silicon dioxide is probably the most straightforward way to boost the efficiency.

The precise results for the low-resistivity cell under concentration deserve further attention. The one-sun responsivity for this cell was low. The explanation for this is that the front surface recombination velocity is high, since the substrate is doped at $2 \times 10^{16}$/cm³. When the front surface high-injects, this surface recombination should be the same as for the high-resistivity substrate. In other words, we expect that the low-resistivity substrate short-circuit current should be superlinear with concentration, and the current density should approach the same value as for the high-resistivity cell. In fact, such a superlinearity was observed during the measurement, but was thought to be spurious. This effect was 5-10%, and if taken into account would imply that the low-resistivity cells actually have an efficiency at 150 suns of 25%, equivalent to the best high-resistivity cell. Subsequent experiments done at Sandia confirmed this superlinearity several months later, but on a cell for which the grid was poorly defined. The OCVD from the finished low-resistivity cell indicated an effective lifetime of 400 μS, including both bulk and surface recombination. So the hypothesis that the front surface determines the rather low one-sun responsivity is quite consistent with all of the available data.
4.5 The issue of stability in $p-i-n$ cells

In the front-gridded cell design discussed in the previous section, most of the surface is covered by an undoped silicon-silicon dioxide interface. Because of this it suffers similar degradation problems as those that have been found in the back-point-contact cell[32]. After a 2-hour exposure to natural sunlight concentrated 100 times a Point-Junction $P-I-N$ cell degraded both in voltage and responsivity. The cell passed from being dominated by emitter recombination, with a total saturation current density of $J_0=5\times10^{-14}$ A/cm$^2$ at 27 °C to be dominated by recombination at the undoped surface, with a surface recombination velocity of $S=425$ cm/s. The short-circuit current measured at 100 suns decreased by 10%.

4.5.1 Cells with Adjacent $P^+$-Point and $N^+$-Planar Diffusions

To address the stability problem we incorporated into the cell fabrication a step believed to yield a reasonably stable silicon-silicon dioxide interface; it consists of a front phosphorus diffusion[33]. The resulting device structure is quite uncommon, with the collecting $p^+$ points being imbedded in a floating $n^+$ region (see Fig. 4.8). This is similar to the most recent, simplified implementation of the backside-contact and does not hurt the cell performance in that case. The compensated regions produce a relatively low reverse breakdown voltage, 6 V, as compared to the 350-400 V measured in cells that do not incorporate the front phosphorus diffusion.

We used two different front diffusion schedules and also two different optical designs for the cells. As expected, the front diffusion resulted in an improved stability. Upon a 2-hour exposure to concentrated light from a xenon lamp, the saturation current density increased between 1.6 and 3 times depending on the phosphorus diffusion process. The final saturation current density measured for the heaviest of the two diffusions, about $3\times10^{-13}$ A/cm$^2$, is still quite low. Table 4.3 summarizes the stability tests that were performed both in terms of saturation current (measured by illuminated OCVD) and of short-circuit current. The stability improves as the sheet resistivity of the front diffusion decreases, but it is not yet fully optimized.
Figure 4.8: Cross-sectional view of a "stable" point-junction $p-i-n$ cell. Note the presence of a floating n-type region at the front surface adjacent to the "point" p-type regions.
The planar phosphorus predeposition was done early in the fabrication process and received the high-temperature cycles needed to form the point boron and phosphorus emitters and to grow the passivating silicon dioxide. This resulted in a relatively deep diffusion with a relatively low surface concentration. The instability found for these particular diffusions was quite surprising at first because other diffusions with similar sheet resistivities had been found at Stanford to be stable. The dopant concentration at the front surface rather than the sheet resistivity seems to be the critical parameter that determines the stability. A further optimization of the cell fabrication should aim at shallow front diffusions with a higher surface concentration.

Two different surface configurations were formed using different chemical etchants. Ammonium hydroxide was used to form inverted pyramids (Fig. 4.5). A solution of potassium hydroxide was used to create a field of random pyramids in between the grid fingers (Fig. 4.9). We did not notice any difference between both topographies with respect to stability, at least for this size of pyramids (about 10 μm).

The performance of cells with and without a front floating diffusion is shown in Table 4.4. The design in which the metal fingers are on top of flat mesa runways (Fig. 4.9) gives a much lower short-circuit current than the sloped-gridline approach.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Front Diff.</th>
<th>$\rho_{\text{sheet}}$ ($\Omega$)</th>
<th>$J_{\text{sc}}$ (Acm$^{-2}$)</th>
<th>$J_{0}$ ($10^{-13}$Acm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
</tr>
<tr>
<td>22-1-1</td>
<td>$\infty$</td>
<td>2.71</td>
<td>2.44</td>
<td>0.5</td>
</tr>
<tr>
<td>25-7-7</td>
<td>165</td>
<td>2.69</td>
<td>2.43</td>
<td>2.7</td>
</tr>
<tr>
<td>26-1-4</td>
<td>85</td>
<td>1.8</td>
<td></td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 4.3: Stability of front-gridded point-junction cells as a function of the sheet resistivity of a front surface phosphorus diffusion. The dark saturation and short-circuit current densities were measured at 27 °C before and after a two hour exposure to concentrated light.
Figure 4.9: Same cell structure as the 26% cell but with a different, more conventional optical design. The size and location of the pyramids are random and the metal gridlines are on flat runways.
Table 4.4: Performance of front-gridded point-junction cells with and without a front-surface stabilizing diffusion and having the metal grid on top of either flat mesa runways or triangularly shaped ridges. The temperature was 25 °C and the light spectrum was the standard Direct AM 1.5.

(Fig. 4.3), while the latter is more prone to have series resistance problems because of difficulties in the patterning of the metal grid. The best cells with a front diffusion from either design reached only 21% efficiency at 125 suns mainly because of a low fill factor. The whole batch of cells showed very scattered fill factors, possibly because of a poor metal-to-silicon contact. Scattered fill factors have been common in all the runs. For example, most cells from the run that produced one cell with a 25.3% efficiency at 125 suns had efficiencies in the range 22.4%-24%. We realized later on that the mask set used to fabricate the inverted-pyramid cells had a slight misplacement that made it impossible to make a good alignment of the metal fingers to the triangular ridges across the whole wafer. The usual consequence of a misalignment was, besides a loss in responsivity, an overetching of the metal lines.

The results for cells with a floating diffusion presented here should be considered as preliminary, since the fabrication process was not yet fully optimized and only two runs were processed. Both runs were flawed with metallization problems. They are good enough to demonstrate the feasibility of a cell structure where $p^+$ and $n^+$ regions touch and produce a compensated region. This cell structure is reasonably stable and could be optimized for full stability while maintaining high performance. A prediction
of its performance is presented in the next section of this chapter.

4.6 Planar junction \( p-i-n \) and \( n-i-p \) cells

A planar diffusion appears to be necessary to obtain a stable front surface. Because of this consideration \( p^+-i-n^+ \) and \( n^--i-p^+ \) planar-junction devices are a logical alternative to point-junction cells. Several runs of \( p-i-n \) cells were processed using several different fabrication sequences. The resulting surface finishes included upright pyramids, inverted pyramids, random pyramids (as produced by an unmasked texturing etch) and just the original mirror polished surface of the wafers. Fig. 4.10 shows the internal structure of a \( p-i-n \) cell with inverted pyramids. Most of the doped front and back surfaces are covered by a thermally grown silicon dioxide. The diffusions are only moderately doped so recombination at the surfaces has to be kept low. The metal contact area fraction is about 1% on the front surface and 2% on the back.

Notice that since the diffusions extend beneath the bus bars the total dark saturation current of this cell design is unnecessarily high. However when it operates under concentrated light, the effective junction area can be expected to effectively shrink, thus decreasing the saturation current. The dark diode that is in parallel with the active cell actually presents a very high series resistance because it is contacted only at the inner edge of the bus-bar. At high currents a lateral voltage drop develops in the region beneath the bus-bar that tends to turn it off. Recombination at the saw cuts should at the same time become irrelevant.

A run of cells (S/9) with upright pyramids and far from optimum diffusions (30 \( \Omega/\square \), for the boron one) had a 21\% efficiency between 100 and 200 suns. Both the current and voltage were too low, although the fill factor was satisfactory. Another run (S/29) with inverted pyramids and a 50 \( \Omega/\square \) boron diffusion showed a 6\% improvement in responsivity and a similar open-circuit voltage at one sun. 620 mV. Several additional runs were processed with polished wafers. These cells were used to test deviations from linearity in the dependence of the short-circuit current with the irradiance. Significant differences were found in this respect between the \( p-i-n \) and the \( n-i-p \) structures.
Figure 4.10: Structure of a planar junction $p-i-n$ cell with a sophisticated optical design.
The latter are significantly more sublinear than the former. These data are presented in the second appendix to this chapter.

4.6.1 "Low-Tech" $p-i-n$ Cells

One of the major assets of the conventional $p-i-n$ cell structure is its simplicity. But when a complex faceting of the surface such as the sloped gridline-inverted pyramids scheme is used, the simplification introduced by the planar diffusions is almost irrelevant in the overall fabrication process. In a search for simplicity we have demonstrated a simple process [49] that utilizes only one photolithographic masking step. No mask alignment is necessary. The process is based on the difficulty of coating with photoresist the pyramids that constitute a randomly textured surface. Spinning photoresist or a similar light-insensitive coating material on a textured wafer is a simple way to cut contact holes (the uncoated peaks of the pyramids) in the passivating oxide.

1. Maskless texturing of the wafers, both sides.
2. APCVD oxide depositions, B-doped on front, P-doped on back.
3. Dopant drive-in.
4. Photoresist spinning, both sides.
5. Oxide etch of the exposed pyramid peaks.
6. Metal deposition.
7. Patterning grid on front.

Both $p-i-n$ and $n-i-p$ planar structures fabricated using this process exhibited a similar performance, with an efficiency of 20% at 10-20 suns. The premature roll-off in efficiency is due to the fact that the metal layer deposited in this experiment was too thin; the sheet resistivities of the boron and phosphorus regions were 80 $\Omega/\square$ and 60 $\Omega/\square$, respectively. These are nearly optimal for emitters that must be transparent and
have about 10% of their surface de-passivated. A disadvantage of this process is that the contacts are opened everywhere, including the areas covered by the metal bus-bars, and this makes the total junction area about two times higher than the illuminated area. Because of this the measured open-circuit voltages show an apparent \( J_0 \) of about \( 1.6 \times 10^{-12} \) A/cm\(^2\). We also observed a marked edge effect after scribing the wafer into individual cells. The effective lifetime in the base region dropped from 1.1 ms to 0.46 ms, and the open-circuit voltage at one sun from 640 mV to 620 mV. This effect was magnified by the fact that 365 μm thick wafers were used in the experiment, which gives an edge to active-area ratio of 8% for an individual cell.

The results from photoconductivity decay and OCVD are summarized in Table 4.5. The OCVD-measured total emitter saturation current density of about \( 5 \times 10^{-13} \) A/cm\(^2\) indicates the potential for this very simple process that requires no alignments. The use of thinner wafers, a relocation of the bus-bar so that the metal does not extend to the edge and a minimization of the bus-bar area should suppress the edge parasitic, improve the output voltage and make the sublinearity of the short-circuit current in \( n-i-p \) cells less severe. The technology seems especially appropriate for low concentration applications. The basic idea of pyramid-peak de-wetting can be used to form point diffusions (in the peaks of the pyramids), which in some circumstances can provide a boost in performance. This is a sensible thing to do if the cell stability is not compromised.

Since both \( n-i-p \) and \( p-i-n \) cells were fabricated simultaneously here, it provided an interesting test of the linearity under illumination. Since the cells were thick, trans-

<table>
<thead>
<tr>
<th>Sample</th>
<th>fraction of bared surface</th>
<th>( \tau_{eff} ) mS</th>
<th>Total ( J_0 ) (Amps/cm(^2) 300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished test</td>
<td>0%</td>
<td>2</td>
<td>( 2 \times 10^{-13} )</td>
</tr>
<tr>
<td>Textured test</td>
<td>0%</td>
<td>2</td>
<td>( 4.4 \times 10^{-13} )</td>
</tr>
<tr>
<td>Cells (on wafer)</td>
<td>10%</td>
<td>1.1</td>
<td>( 3.5 \times 10^{-13} )</td>
</tr>
<tr>
<td>One cell (1.8×1.8 cm die)</td>
<td>10%</td>
<td>460 μs</td>
<td>( 4.0 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

Table 4.5: Recombination parameters extracted from photoconductivity decay (on wafers prior to metalization) or open-circuit-voltage-decay (for finished solar cells).
port effects across the base should be quite pronounced in these cells. The measured responsivities are shown in Fig. 4.11. The curves are for PC-1D simulations of the sublinearity. Agreement can be obtained for the $n-i-p$ using an emitter saturation current density of $4.8\times10^{-12}$ A/cm$^2$. For the $p-i-n$ cell, agreement is not possible, even if the entire measured emitter saturation current $1.6\times10^{-13}$ A/cm$^2$ is attributed to the p-type emitter. The ill-defined geometry makes it difficult to attribute these discrepancies to anything in particular.
4.7 A modeling comparison of \( p-i-n \), \( n-i-p \), and backside contact solar cells.

The 21% efficiency of experimental "stable" \( p-i-n \) cells presented in the previous sections gives a pessimistic idea about the potential of this design due to the early stage of this experimental optimization. In this section, we model the performance that we should be able to attain. We assume a cell structure of moderate complexity, like that shown in Fig. 4.10, with a planar diffusion at the back side. Both the structure and the fabrication process of this \( p-i-n \) cell and of the latest, simplified design of the backside-contact cell are very similar.

4.7.1 Terms of the comparison

The modeling of concentrator solar cell performance is commonly done by assuming a certain cell size and a variable irradiance. This implies that the lens that produces the desired irradiance changes in size. We have opted for a different basis of comparison, the lens size is kept constant and the area of the cell is varied to achieve the desired sunlight concentration factor. This approach decouples to a great extent the optimization of the optical and structural components of the system from that of the active device. As representative of a new generation of concentrators we consider the case of a 10x10 cm\(^2\) lens. Optical losses together with the fact that only direct sunlight can be concentrated bring the 10 W of sunlight incident on the lens in standard conditions down to about 8 W at the cell.

Since the cell size decreases as the geometric concentration ratio increases, the output current is always about 3.15 A and the optimization of the front metal grid leads to the same total power loss for all the cell sizes (for all the irradiances). Following the design rules described in [2] we have estimated the shading loss to be 5.6%, the series resistance 9 mΩ and the total power loss 10%. The assumptions were a chevron pattern, an aluminum thickness of 3.5 μm, an emitter sheet resistivity of 70 Ω/□, and a ratio between the output current and the output voltage of 4.8. A different set of
technological choices would of course lead to a different optimization. For example, a thicker layer of metal or the use of silver instead of aluminum would reduce the losses. Also, it is possible to dissociate to some extent the resistive and the shadowing losses by using sophisticated concepts such as sloped gridlines, textured cover glasses, or reflective cavities[48]. These concepts could possibly reduce the total power loss to 5% or even less at the cost of greater complexity. Series resistance losses are also present in the back-junction cell, although they are not subject to optical constraints and can be reduced more easily to negligible levels. The measured series resistance of a 0.64 cm² cell is about 4 mΩ, including the resistance of the mount. Accordingly we have assumed a 2% relative power loss for the BJC in our comparison.

### 4.7.2 Solar cell models

To analyze the $p-i-n$ and $n-i-p$ cell structures we have used both the numerical program PC-1D [3] and a very simple analytical model developed at Stanford. The type of back-junction cell that we consider here has adjacent phosphorus and boron diffusions in the back surface, typically covering 25% and 75% of its area, respectively[54]. The cell also incorporates a floating, light phosphorus diffusion at the front surface to provide a stable passivation. To study this structure we have use the model previously developed for backside point-contact cells[47]. With this model the best representation of the actual cell structure is to assume a 25% fractional area for each diffusion type and double the assumed emitter saturation current density for each type. For diffusion stripe widths comparable to or less than the device thickness, the two-dimensional effects are very small at these large emitter coverage fractions, and the geometrical details have virtually no effect upon the modeled results. The computer code, [47], assumes the sum of a delta function of generation at the front of the cell and a uniform generation, which gives a correct average generation depth. The $p-i-n$ code assumes a delta function of generation at an average generation depth that is dependent on the cell thickness. The total photogeneration was adjusted in both codes to agree with PC-1D. A textured front surface with zero reflection loss and a polished back surface with a 95% reflectivity have been assumed as representative of an ideal light-trapping scheme.
4.7.3 Recombination parameters

The SRH lifetime typically measured in high resistivity, float-zone silicon is of the order of 1-3 ms. This makes SRH recombination a minor concern in most cases. At high carrier injection levels Auger recombination can be important, especially when the most recent data for the ambipolar Auger coefficient, $1.66 \times 10^{-30}$ cm$^6$/s [50], is used. For the saturation current densities that characterize recombination in the heavily doped regions we have selected reasonable values based on available experimental data such as that presented in Chapter 2 of this report.

The emitter saturation current densities that can be obtained for textured surfaces, with surface concentrations sufficiently high for contact resistance concerns will be assumed to be $1.4 \times 10^{-13}$ and $2.8 \times 10^{-13}$ A/cm$^2$ for phosphorus and boron respectively. These are the key parameters for the evaluation of $p-i-n$ and $n-i-p$ solar cells with single front diffusions. The back diffusion parameters have much less influence upon the results. Also, they can be on planar surfaces, allowing lower emitter saturation current densities. For the backside-contact solar cells, the backside total emitter saturation current density will be assumed as $2.5 \times 10^{-13}$ A/cm$^2$. The frontside $n^+$ diffusion can be better than in the case of the $n-i-p$ cell because the surface concentration need not be so high since it is not contacted; we conservatively assumed $1 \times 10^{-13}$ A/cm$^2$.

The best way to reduce emitter recombination in $p-i-n$ and $n-i-p$ cells is to use two diffusions for the front emitter to separately optimize the regions beneath the metal contacts and beneath the passivating oxide. A boron emitter with a $J_o$ of $1.6 \times 10^{-13}$ A/cm$^2$ covering a 10% of the front surface together with a floating phosphorus diffusion with $5 \times 10^{-14}$ A/cm$^2$ and a back-surface phosphorus diffusion with $8 \times 10^{-14}$ A/cm$^2$ would give a total recombination current of about $1.4 \times 10^{-13}$ A/cm$^2$ for a $p-i-n$ cell. Devices with this structure not yet optimized have shown a total saturation current of $1.8 \times 10^{-13}$ A/cm$^2$. Analogously, one can reasonably assume a front $J_o$ of $5 \times 10^{-14}$ A/cm$^2$ and a back one of $1.6 \times 10^{-13}$ A/cm$^2$ for an advanced $n-i-p$ cell having a doubly diffused front emitter. Some of the $n^+p$ cells fabricated at UNSW have shown a total $J_o$ of about $8 \times 10^{-14}$ A/cm$^2$. The simplified back-junction cell with 75% of its surface diffused with boron and 25% with phosphorus would present a total recombination current at the back surface of $1.4 \times 10^{-13}$ A/cm$^2$, approximately and $5 \times 10^{-14}$ A/cm$^2$ at the front.
surface. These optimized parameters have already been demonstrated separately in test devices. This second set of parameters will be referred to as "advanced" cells, indicating that some degree of speculation exists in projecting these values, and the stability of the light diffusions assumed here that allow very low front-surface recombination.

4.7.4 Performance of BJC, n–i–p and p–i–n Cells

The behaviour of the short-circuit current with the incident power density determines to a great extent the overall cell performance. Silicon cells made with high resistivity material frequently show a sublinear responsivity. The effect can be very important in the cases of the back-junction cell and the n–i–p cell, especially if they are relatively thick and/or if the recombination rate at the front emitter is relatively high. The effect is far less severe for p–i–n cells, and this is their major asset compared to the other two structures. The modeled responsivity for the two sets of assumptions regarding the recombination parameters are shown in Figs 4.12, 4.13, 4.14, 4.15, 4.16.

Recombination at the front emitter is the main reason for the sublinearities predicted by our modeling. Previously, in the point-contact solar cells with an undoped front surface, the sublinearities were caused by Auger recombination in the base. However, with the front emitter apparently necessary for stability (for the time being, at least) this Auger recombination is relatively unimportant. The trends are as expected given the frontside recombination parameters and the relevant diffusion coefficients. p–i–n cells are most linear, back-junction cells show significant sublinearity, and n–i–p cells are the worst of all. These curves are discussed in detail here for reference.

Fig. 4.17 indicates the performance expected from the three types of cells, using the first set of assumptions concerning the design and parameters. Under these conditions, with a single front diffusion for the case of the p–i–n and n–i–p cells, the backside-contact cell appears to be superior in performance in a range up to 40 W/cm².

Fig. 4.18 shows the performance that can be envisioned for optimized cells. The parameters assumed here are for the "advanced" cells, that is, in all three cases the majority of the front surface is assumed to be covered by the same referred passivation.
Figure 4.12: The responsivity for backside-contact solar cells using demonstrated parameters.
Figure 4.13: The responsivities for advanced backside-contact cells.
Figure 4.14: The responsivities for $n-i-p$ solar cells.
Figure 4.15: The responsivities for advanced $n-i-p$ solar cells.
Figure 4.16: The responsivities for $p-i-n$ solar cells.
of relatively-lightly-doped phosphorus. Hence the recombination parameters for the three cases are almost identical. The efficiency of the backside-contact cell is about 1-2 absolute percent higher than that of the \( n-i-p \) and \( p-i-n \) cells in the range of irradiances 10-20 W/cm\(^2\). The main reason for this is the 10% relative power loss caused in these cells by the front metal grid, compared with the 2% loss that occurs in the BJC. Thanks to its nearly linear responsivity the \( p-i-n \) cell outperforms the BJC at very high irradiances. The \( n-i-p \) cell is always worse than the \( p-i-n \), yet it is quite acceptable for irradiances in the vicinity of 10 W/cm\(^2\). For the back-junction cell, efficiencies over 27% appear to be achievable in the range 10-20 W/cm\(^2\). The actions that can lead to this improved performance are the use of a thin substrate, the reduction of the recombination currents of its three diffused regions, especially the front one, and the use of an antireflection material better matched than the customary silicon dioxide. Although 75 \( \mu \)m-thick wafers (routinely processed at Stanford with a reasonable yield) have been assumed, there is little penalty in the range 10-20 W/cm\(^2\) for using a 100 \( \mu \)m substrate. The optimization of the front emitters of conventional \( p-i-n \) and \( n-i-p \) cells appears to be comparatively more difficult considering that they have to have a good quantum efficiency, provide good ohmic contacts and be formed on textured surfaces.

A significant reduction of emitter recombination may require the use of double-diffusion schedules to form a heavily doped region beneath the contacts and a lightly doped one in the rest of the surface, but this makes the fabrication process very complex. The best option for this type of sophisticated cell is to form a boron diffusion beneath the contacts and a light phosphorus diffusion elsewhere. Efficiencies around 26% are achievable with a \( p^+/n-i-n^+ \) structure (about half an absolute per cent point less for a \( n^+/n-i-p^+ \) structure), in the range 10-20 W/cm\(^2\). The front metal grid offers substantial room for the improvement of \( p-i-n \) and \( n-i-p \) cells. With a sophisticated front metal grid a \( p^+/n-i-n^+ \) cell could achieve in the range 10-20 W/cm\(^2\) an efficiency of about 27%, as high as that predicted for the BJC. The most remarkable advantage of \( p-i-n \) cells is that they can be relatively thick, as thick as 250 \( \mu \)m with no efficiency loss at 20 W/cm\(^2\). The \( n-i-p \) cell should not be thicker than 150 \( \mu \)m and the BJC should be less than 125 \( \mu \)m thick. The thickness constraints are much tighter for less optimized diffusions.
Figure 4.17: A comparison of basic $p-i-n$, $n-i-p$, and backside cells.

One last figure, Fig. 4.19, indicates the performance comparison for the case where the total shadowing/grid-resistance loss for the two-sided cells is reduced to 5%. In this case, the distinction between cell geometries virtually disappears into the noise, except at very high concentrations where the transport properties of electrons across the base are preferred. Keep in mind, however, that achieving 5% total shadowing/grid-resistance loss is not easy with the gridline geometries and acceptance angle requirements of cells operating under these high concentrations. At the lower concentrations, this comparison is more realistic since prismatic cover-glasses have been demonstrated with this type of performance for use in this range.
Figure 4.18: "Advanced" P-I-N, N-I-P and backside-contact cells. Each of these cells has the majority of the front surface covered by the same low-recombination n+ diffusion.
Figure 4.19: A comparison of advanced backside cells, \( n-i-p \), and \( p-i-n \) cells, with one further assumption; that the total of the shadowing and grid resistance losses in the two-sided cells can be reduced to 5%.
4.8 Appendix: Listing of Sandia Baseline 3 1.56-cm$^2$ cell runs

Run S/3. Date:
Number of wafers:
Purpose. Uniform field of very small pyramids. Line-diffusions at the front and point-diffusions at the back.
Results. 23% peak efficiency at 50-100 suns.

Run S/7. Date:
Number of wafers:
Purpose. Uniform field of very small pyramids. Line-diffusions at the front and point-diffusions at the back.
Results. 25% efficiency at 10-20 suns for a cell with overetched metal fingers. 23.5% cells at the design point.

Run S/8. Date:
Number of wafers:
Purpose. Uniform field of very small pyramids. Line-diffusions at the front and point-diffusions at the back. Thin wafers, 110μm thick.
Results. High series resistance due to overly thin metal lines (14 mΩ). Peak efficiency, 22.7% at 50 suns, 21.9% at 100 suns.

Run P1 Date: 10-88
Number of wafers: 7
Purpose: Point-diffusions with no photolithography. Diffusion windows were opened in the peaks of the pyramids of a textured wafer, both sides, by spinning photoresist at 5000 r.p.m. The doped glasses were selectively etched (with no mask) and aluminum was deposited.
Results: OCVD gave a base lifetime of about 0.5 ms and a total $J_0 = 3 \times 10^{-13}$ Acm$^{-2}$. The devices did not work, probably because of shorts between the peak diffusions and the intrinsic substrate.
Date. 11-88.

Number of wafers. 7.

Purpose. Contact holes with no photolithography. Similar to the previous run but with planar diffusions.

Results. Bad lifetimes and $J_o$. No devices.

Run P3. Date. 11-88.

Number of wafers. 8.

Purpose. Planar-junction p-i-n cells. Photolithographic surface faceting, with upright pyramids and ridges.

Results. The $\rho_{\text{sheet}}$ were out of target. Photoresist coating was a nightmare for the 20 $\mu$m-wide, 14 $\mu$m-high features of the wafer surface. We could measure $J_{\text{sc}} = 31.4 \text{ mA/cm}^2$ and $V_{\text{oc}} = 610 \text{ mV}$ in an untextured test wafer.

Run P4. Date. 12-88.

Number of wafers. 8.

Purpose. Planar-junction p-i-n cells. Similar to the previous run. Emphasis on photoresist coating problems.

Results. $\rho_{\text{sheet}} = 220 \Omega/\square$ for the front boron diffusion. Total $J_o = 2 \times 10^{-13}$ Acm$^{-2}$. Two different photoresists and many different coating schedules were tried with relatively acceptable results for the cells in the center of the wafer. The final mask, the metal-patterning one, poses still greater difficulties, since the very thick layer of photoresist that fills the valleys of the surface topography has to be exposed and developed away. This threatens the need for maintaining in good shape the unexposed resist that defines the metal fingers. Some of the finished devices exhibited $J_{\text{sc}} = 38.2$ mA cm$^{-2}$ and $V_{\text{oc}} = 620$ mV.


Number of wafers: 5.

Purpose. Planar-junction p-i-n with upright pyramids and ridges. Similar to the previous two runs.
Results. The sheet resistivities were too low, 30 Ω/□, for the boron layer. This probably helped to give low series resistance (about 3mΩ), which led to a nearly flat efficiency behaviour between 50 and 200 suns of about 21%. This indicated that the patterning of a 4 μm aluminum layer was successful. The one-sun responsivity was low, at 34.5 mA cm⁻².

Run S/10. Date: 12-88.
Number of wafers: 5.
Purpose. Point-junction and linear-junction p-i-n cells. The use of doped oxides allowed to form simultaneously the p⁺ and the n⁺ point-like regions. After the drive-in these oxides were carefully etched off while keeping the undoped oxide that protected most of the surface, thus saving one masking step. Still, the number of masks used was four, including that used to etch the surface.

Results. Precisely this first mask was responsible for the low responsivity of the finished cells, 36.2 mA/cm². An insufficient knowledge of the mechanisms of silicon etching (orientation-dependent) had led to an inadequate design of the mask. The metal-line runways resulted in trapezoids rather than triangles, with a width of the top side of about 7-8 μm (10 μm after the metal deposition, producing a 12% shadowing). A high VOC = 690 mV led to nearly 20% efficiency at one sun. The series resistance was about 6 mΩ and the efficiency under concentration dropped from 24 % at 50 suns to 23 % at 200 suns. These results are nearly identical to those obtained with Run S/7, made with a different process. We did not observe a significant difference between line-junction (8% diffused area) and point-junction (5% diffused area) devices.

Run S/11. Date: 1-89.
Number of wafers: 8.
Purpose. Improve run S/10 modifying the surface features by means of a mild isotropic etch. The hope was that the ridges could be sharpened and that the height of the pyramids could be reduced and their peaks softened.

Results. The flat top of the ridges was decreased to about 3-5 μm (6-8 μm after metal deposition). Simultaneously a narrower, 20 μm mask was used
to pattern the metal. This led to very narrow metal fingers, restricted in many cases to the flat top of the ridges. Some fingers do not meet the busbar. This was in spite of a double-layer photoresist process (first thick layer, flood exposure, second layer, patterning). A high responsivity resulted, 39.3 mA/cm²; $V_{oc} = 675$ mV was reasonable, but the series resistance was too high.

Run S/12. Date: 1-89.

Number of wafers: 8.

Purpose. Replicate the results of Run S/7, with small 4μm-high pyramids and metal lines running over them. To improve series resistance the metal runways were smoothed with an isotropic etching step that produces a shallow trench in which the metal fingers are partially buried.

Results. Photoresist coating did not pose any problem but the cells did not work, probably because of metal shorts between the line-emitters and the base.

Run S/13. Date: 2-89.

Number of wafers: 6.

Purpose. To obtain sharp ridges by means of an off-axis crystalographic etch. A thorough bibliographic search together with a set of controlled experiments provided the know-how needed to carve in the silicon the desired features. The best that could be done with the available mask was to rotate it 26° relative to the flat of the (100) wafer. This permitted to undercut the 10 μm lines used in this mask to define the ridges.

Results. Ridges with a perfectly sharp inverted V shape were obtained. However, some flat spots appear at the intersections between the pyramid bases, and also, the total surface relief increased to about 20 μm. The photoresist coating problems persisted (spray developing was tried, as well as double layer processes). Some cells could be finished, showing a responsivity between 38 and 40.7 mA/cm² depending on the amount of metal remaining in the slopes of the ridges, from too much to nearly nothing. The voltage of these cells was very scattered, from zero to 630 mV.
Run S/14. Date: 2-89.

Number of wafers: 2.

Purpose. Off-axis silicon etching (similar to the previous run). Include a floating front phosphorus diffusion for stability.

Results. Photolithography on the sharp ridges was again very difficult. The self-aligned etching back of the doped oxides was not well controlled and this probably resulted in metal shorts between the p⁺ points and the floating n⁺ planar diffusion.

Run S/15. Date: 2-89.

Number of wafers: 6.


Results. Processed along with Run S/14, this one suffered similar problems, with scattered results and many shorted cells. Some of them did have a good voltage though, around 675 mV, demonstrating the feasibility of this cell structure in which the p⁺ emitter is imbedded in a n⁺ planar region. The responsivity was low, about 32 mA/cm² because of a badly tuned ARC but also because of the inherent limitation of the grid shadowing in this design.

Run S/16. Date: 4-89.

Number of wafers: 6.

Purpose. "Low-tech" p – i – n cells. Opening of contact holes without photolithography. Similar to experiment P/2. After simultaneous front and back planar diffusions contact holes are cut in the peaks of the pyramids of these maskless-textured wafers. These peaks remain bare after spin-coating the wafers with photoresist.

Results. After a prolonged effort we finally got a reliable schedule for maskless texturing the wafers. The planar B and P diffusions were on target (60-75 Ω) and the $J_0=5\times10^{-13}$ A/cm² was satisfactory for emitters that are transparent and have a significant portion of their surface de-passivated. The $V_{oc}$ was 640 mV on the wafer and 615 mV after sawing the devices out. The efficiency peaked at 10-20 suns because the
metal layer was thin and not carefully patterned. Both \( p-i-n \) and \( n-i-p \) devices showed a 20\% efficiency and a markedly different sublinear responsivity.

Run S/17. Date: 4-89.

*Number of wafers:* 17.

**Purpose.** Polysilicon-emitter cells. Apply the techniques developed by J.Y. Gan to full, working devices. Explore different options for integrating the polysilicon depositions in the cell process.

**Results.** Although a good amount of work was put in this run, none of the wafers reached the end, in many cases because of the customary photore sist coating problems. It was a shame because the total \( J_0 \) measured in a test wafer was \( 2 \times 10^{-14} \text{ A/cm}^2 \). In passing, we observed a self-aligned opening of linear contact holes on top of the ridges that could be used for future process simplifications.

Run S/18. Date: 4-89.

*Number of wafers:* 8, four inch.

**Purpose.** Process development using a new mask set, emphasis on surface faceting and photoresist coating and patterning. Evaluate inverted pyramids as an alternative to upright pyramids.

**Results.** The silicon etching experiments done earlier permitted the design of new masks that should give sharp ridges. Also, the critical feature dimension, the height of the pyramids, was decreased by a factor of 2 to facilitate the photolithography. A combination of a KOH etch followed by a mild isotropic etch gave satisfactory results. The inverted pyramid scheme was found to be superior in terms of tolerance to overetching and of photoresist coating uniformity. Also, it can be done with ammonium hydroxide.

Run S/19. Date: 4-89.

*Number of wafers:* 8, MCZ.

**Purpose.** Evaluate magnetically-grown CZ silicon for concentrator cells.

**Results.** The run was not finished.
Run S/20. Date: 5-89.
Number of wafers: 12.


Results. Ammonium hydroxide, a cleaner alternative to KOH suggested by J.Y. Gan, works very well for inverted pyramids but cannot be used for upright pyramids. The self-aligned contact opening (doped oxides etch-back) failed in this run.

Run S/21. Date: 5-89.
Number of wafers: 6, 4 inch.

Purpose. Upright pyramids with KOH.

Results. The smaller pyramid size, 7 μm made the photolithographies more manageable. In spite of an excessive rounding of the peaks the responsivity was 38.5 mA/cm² in one of the cells. V_oc was between 645 and 685 mV. The concentration performance was not measured.

Run S/22. Date: 5-89.
Number of wafers: 7, 4 inch.

Purpose. Inverted-pyramid cells. Comparison between low and high resistivity substrates.

Results. This was the most successful run, with 22%-25% efficient cells at the design point. Described in two papers.

Run S/23. Date: 5-89.
Number of wafers: 8.

Purpose. Deliver solderable, working cells. Use a more reliable process based on maskless texturing the areas between metal fingers, which run on top of flat mesas.

Results. Successful run that produced about two dozen cells that were 24.5% efficient before plating and 23.5% after the nickel-gold plating. The grid shadowing was about 15% before plating. The responsivity increased only 1.5% with a cover glass.

Run S/24. Date: 6-89.
Number of wafers: 8, 4-inch.

Purpose. Fabricate and deliver inverted-pyramid cells.

Results. The run was finished but the cells did not work. The cell active area was protected from the nickel-gold plating using adhesive tape. A LPCVD silicon dioxide mask was attempted without success.

Run S/25. Date: 7-89.
Number of wafers: 12.

Purpose. Stable cells with a floating phosphorus diffusion. Inverted pyramid topography.

Results. Improved stability, yet not perfect. Scattered results, mostly because of the difficulty of perfectly aligning the metal mask to the 10 \( \mu \text{m} \)-wide ridges. Metal is frequently overetched and lost in one of the slopes. Modest 21\% efficiency at the design point. Demonstration of the cell structure with adjacent \( p^+ \) and \( n^+ \) regions (like run S/15). Selective gold plating and delivery of 39 cells.

Run S/26. Date: 7-89.
Number of wafers: 10.


Results. Reasonable yield at one sun but not under concentration. The mesas emerged too much from the sea of pyramids, and photoresist coating was impaired in some areas of the wafer. The efficiency reached 21\% at the design point. The stability provided by a front 85 \( \Omega/\square \) diffusion was found to be much better than that of a 165 \( \Omega/\square \) diffusion, although none of them was optimized in terms of dopant surface concentration. 20 cells were plated and delivered.

Run S/27. Date: 9-89.
Number of wafers: 6.

Purpose. (Planar)\( N^+ \)-I-(Point)\( P^+ \) cells. Since a front phosphorus diffusion is needed for stability the idea in this run was to use a single planar front
diffusion relatively thin and highly doped. The back boron diffusion was restricted to points to improve the voltage, given the high saturation current that boron emitters usually have. The surface was inverted-pyramid etched.

Results. Problems with the back oxide led to metal shorts of the $p^+\text{-}i$ junction and to voltages in the range of 300-400 mV. An alternative explanation is the formation of a Schottky contact. Only a few cells worked, with a $V_{oc} = 610$-630 mV.

Number of wafers: 6.
Purpose. Identical to the previous run.
Results. Same problems.

Run S/29. Date: 11-89.
Purpose. Planar-junction $p\text{-}i\text{-}n$ cells. Inverted pyramid topography (similar to run S/9, with upright pyramids). This run should serve to answer the questions about the stability of a boron diffusion. The simple cell structure should be robust with respect to the metal shorts found in some runs with point diffusions. The emphasis is now in the stability, in the responsivity and in the series resistance, precisely the most difficult qualities to achieve.

Results. Diffusions out of target. Customary metal patterning problems; some fingers have metal in only one of the slopes. Responsivity around 36 mA/cm$^2$, voltage 620 mV. Concentration performance not measured.

Run S/30. Date: 11-89.
Number of wafers: 6.
Purpose. $p\text{-}i\text{-}n$ and $n\text{-}i\text{-}p$ cells. Polished surface, several different thicknesses.
Results. This run and also a part of the previous one produced $p\text{-}i\text{-}n$ and $n\text{-}i\text{-}p$ cells to test the different sublinear behaviour of their responsivities.
4.9 - Appendix: The sublinearity of p-i-n and n-i-p cells.

The wide variety of structures that resulted from this work, as summarized in this chapter and in the last appendix, provides fodder for a nice study of the sublinearity for the different cells as a function of the cell thickness, doping, and design. Here are presented the beginnings of such a study. The responsivity for a number of cells was measured at Stanford using an indoor xenon flashlamp. This is shown Table 4.20. The cells were then sent to Sandia for confirmation of the measurements. A comparison of the measured results is shown.

For small deviations from linearity, the sublinearity should be proportional to:

1. The incident power density.
2. The cell thickness.
3. The front-surface total emitter saturation current density.
4. The inverse mobility squared of the carrier of the opposite type to the front junction. (i.e. n-i-p cells should be 9 times more sublinear than p-i-n cells, if the front-surface emitter saturation current density is the same in both cases.

Each of these trends is clearly evident in the data. However, the Sandia data are considerably more sublinear than the Stanford data. It would be nice to fully investigate the details of the experiment and the analysis in order to make sense of all of this, but it has not been done to date.
Fraction of one-sun responsivity at 100 and 200 suns

<table>
<thead>
<tr>
<th>Cell type</th>
<th>Stanford measurement</th>
<th>Sandia Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>point-contact p-i-n, 165 μm</td>
<td>99.5%/98.5%</td>
<td>93%/87%</td>
</tr>
<tr>
<td>planar n-i-p cell, 520 μm</td>
<td>62%/52%</td>
<td>64%/52%</td>
</tr>
<tr>
<td>planar p-i-n cell, 510 μm</td>
<td>95%/91%</td>
<td>88%/81%</td>
</tr>
<tr>
<td>planar p-i-n cell, 110 μm</td>
<td>99%/98%</td>
<td>96%/92%</td>
</tr>
</tbody>
</table>

Figure 4.20: Examples of the measured responsivities at 200 suns for various types and thicknesses of solar cells as determined from xenon flash measurements at Stanford and at Sandia National Laboratories.
Chapter 5

Conclusions

This report covers several different topics. The first chapter contains fundamental information on the characteristics of diffused emitters. This can be used at several levels. The modeling plots can be referenced as a sort of solar cell design handbook. Emitters with the desired characteristics for a particular design can more or less be chosen directly from these plots. At another level, the fundamental data from this chapter on the dependence of surface recombination velocity on process variables and doping levels, and some new data on bandgap narrowing could be useful for in numerical modeling programs.

The second and third chapters present data from development efforts in both backside contact solar cells, and cells with front grids. Much detail is given on successful and unsuccessful process development. Both efforts resulted in very high-efficiency cells. The 26% 1.56-cm² cells with frontside grids are the most efficient cells of their type, even slightly better than similar cells with prismatic covers. The 26% module-ready backside cells fabricated with the simplified schedules are also state-of-the-art.

A modeling study in the third chapter summarizes the short-term prospects for the cell designs for which we have experience. This study makes full use of the new data presented in this report, in order to give realistic predictions for the attainable efficiencies taking series resistance, measured recombination parameters, the passivation stability of the critical surfaces, and the differences between p-i-n, n-i-p, and backside cells into account. Under these assumptions, stable
module-ready concentrator cells with 27% efficiency at 10-60 W/cm² seem to be an attainable goal.
Bibliography


N.B. The calculated $J_o$ in Fig. 7 of this paper is incorrect due to a computational error, and should be disregarded. The experimental data in Figures 2-6, however, is still valid.


[41] Richard King, To be published, Stanford University, Stanford CA.


Specialists Conf. (Las Vegas, NV), 1985, pp. 43-49.


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