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Citation: *Journal of Applied Physics* **89**, 3821 (2001); doi: 10.1063/1.1350633

View online: <http://dx.doi.org/10.1063/1.1350633>

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# Surface recombination velocity of phosphorus-diffused silicon solar cell emitters passivated with plasma enhanced chemical vapor deposited silicon nitride and thermal silicon oxide

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(Received 27 October 2000; accepted for publication 3 January 2001)

The emitter saturation current density ( $J_{0e}$ ) and surface recombination velocity ( $S_p$ ) of various high quality passivation schemes on phosphorus-diffused solar cell emitters have been determined and compared. The passivation schemes investigated were (i) stoichiometric plasma enhanced chemical vapor deposited (PECVD) silicon nitride (SiN), (ii) forming gas annealed thermally grown silicon oxide, and (iii) aluminum annealed (alenealed) thermal silicon oxide. Emitters with sheet resistances ranging from 30 to 430 and 50 to 380  $\Omega/\square$  were investigated for planar and random-pyramid textured silicon surfaces, which covers both industrial and laboratory emitters. The electronic surface passivation quality provided by PECVD SiN films was found to be good, with  $S_p$  values ranging from 1400 to 25 000 cm/s for planar emitters. Thin thermal silicon oxides were found to provide superior passivation to PECVD SiN, with the best passivation provided by an alenealed thin oxide ( $S_p$  values between 250 and 21 000 cm/s). The optimized PECVD SiN films are, nevertheless, sufficiently good for most silicon solar cell applications. © 2001 American Institute of Physics. [DOI: 10.1063/1.1350633]

## I. INTRODUCTION

Emitter passivation is an important aspect of high efficiency solar cells.<sup>1,2</sup> Not only must the passivating layer reduce the surface recombination at the  $n^+$ -diffused surface to acceptably low levels, it must also be compatible with anti-reflection coatings to maximize the photogenerated current within the silicon substrate. In the highest efficiency laboratory cells, this is achieved by appropriately annealing a thin, high temperature thermal oxide, and subsequently depositing ZnS/MgF<sub>2</sub> antireflection coatings.<sup>3</sup> For commercial solar cells, a promising technology with which to simultaneously provide surface passivation and an effective antireflection coating is plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN).<sup>4</sup> PECVD SiN films have the additional benefits that they are deposited at low temperature ( $\leq 400$  °C) and are thus compatible with many other commercial fabrication processes like screenprinted metal contacts.<sup>5</sup>

In this work, we present a systematic study of phosphorus-diffused emitter passivation achieved with optimized PECVD SiN layers and thin high temperature thermal oxides. Values of the emitter saturation current ( $J_{0e}$ ) are reported for both planar and textured emitters that are suitable for laboratory and commercial solar cells (sheet resistivities ranging from  $\approx 30$  to 430  $\Omega/\square$ ). After measuring the phosphorus doping profiles of the planar samples by means

of the stripping Hall technique, device simulation was used to determine the surface recombination velocity ( $S_p$ ) at the highly doped  $n$ -type silicon interface.

## II. PREVIOUS WORK

Comprehensive experimental studies for oxide passivated  $n^+$ -diffused emitters have been carried out by King *et al.*,<sup>1</sup> by Cuevas *et al.*<sup>6</sup> and by Glunz *et al.*<sup>7</sup> In general, all three studies show increasing  $J_{0e}$  and  $S_p$  as the surface phosphorus concentration increases. The effect of postoxidation anneals using either forming gas anneal (FGA) or aluminum (a so-called aleneal) is to lower the  $S_p$  for a given surface phosphorus concentration ( $N_s$ ), the lowest surface recombination velocities being obtained for the alenealed condition. Typical values for the  $S_p$  of planar emitters are about 800 cm/s for  $N_s = 1 \times 10^{19}$  cm<sup>-3</sup> following an FGA and about 400 cm/s following an aleneal.<sup>5</sup> Textured emitters have typically shown an increase in  $J_{0e}$  by a factor of 2–3 with the increase in  $J_{0e}$  being attributed to the increase in surface area of the emitter and the possibility of increased surface recombination on the  $\langle 111 \rangle$  oriented silicon planes.

Experimental data for PECVD SiN passivated  $n^+$  emitters are less available in the literature. Ruby *et al.*<sup>4</sup> and Chen *et al.*<sup>8</sup> deposited high frequency direct PECVD SiN films onto  $\approx 100$   $\Omega/\square$  emitters and obtained  $J_{0e}$  values of 80 and 220 fA/cm<sup>2</sup>, respectively. Lenkeit *et al.*<sup>9</sup> have published  $J_{0e}$  data for 40 and 100  $\Omega/\square$  emitters for different PECVD methods and concluded that remote and high frequency direct PECVD give the best results. Moschner *et al.*<sup>10</sup> also published  $J_{0e}$  data for PECVD SiN passivated emitters with

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sheet resistances of 40 and 90  $\Omega/\square$  and investigated both planar and textured emitters. Consistent with the studies of oxide passivated emitters, the PECVD SiN studies showed increasing  $J_{Oe}$  for increased emitter doping, and increased  $J_{Oe}$  on textured surfaces. There does not appear to be  $J_{Oe}$  data for SiN passivated emitters at other sheet resistances, particularly for lightly doped emitters ( $>100 \Omega/\square$ ). Further, there appear to be no data on the extracted  $S_p$  for the highly doped  $n$ -type silicon/PECVD SiN interface.

Data comparing conventional furnace oxide passivation and PECVD SiN passivation for  $n^+$  emitters have been published by Aberle<sup>5</sup> and by Moschner *et al.*<sup>10</sup> for 40 and 90  $\Omega/\square$  emitters, respectively. Both concluded that the passivation achieved by the best PECVD SiN films is comparable to that of a thermal oxide.

### III. EXPERIMENTAL DETAILS

The  $n^+pn^+$  test structures used to investigate emitter passivation were prepared using shiny etched, 50  $\Omega\text{cm}$   $p$ -type, (100) oriented float zone (FZ) wafers. Texturing was performed in a mixture of KOH and isopropanol to produce random pyramids which are  $\approx 10 \mu\text{m}$  in size. All diffusions were performed in a quartz tube at temperatures between 840 and 925  $^\circ\text{C}$  using liquid  $\text{POCl}_3$  as the dopant source. After stripping the phosphorus glass, the samples were oxidized at 900  $^\circ\text{C}$  for 30 min. This produced a thin oxide layer ( $\approx 13 \text{ nm}$ ) and simultaneously drove in the diffusion. The  $J_{Oe}$  of the samples was then measured for the as-oxidized condition following a FGA and following an aneal. The thin oxide layers were then stripped in dilute hydrofluoric acid (HF). Optimized SiN layers were deposited on both sides, and the  $J_{Oe}$  was remeasured (both the planar and textured surfaces). The low temperature used for the PECVD depositions (400  $^\circ\text{C}$ ) should not result in significant redistribution in the phosphorus doping profile and so direct comparison of the data for oxide passivated and SiN passivated emitters is valid.

The SiN films used in this work were fabricated in a high frequency (13.56 MHz), direct PECVD reactor. Ammonia ( $\text{NH}_3$ ) and 4.5% silane in nitrogen ( $\text{SiH}_4:\text{N}_2$ ) were used as the process gases. Optimized deposition parameters were determined using statistical methods, with the results reported elsewhere.<sup>11</sup> The optimized SiN films have a refractive index of  $n \approx 1.9$ , indicating that they are approximately stoichiometric in composition. It is important to note that for this work we consider the optimal SiN films to be those with the lowest  $J_{Oe}$ . These are not necessarily the best films for solar cell applications. While higher refractive index SiN films may not offer quite as good a  $J_{Oe}$  (see Ref. 11), they are suitable for the first layer of a double layer anti-reflection coating (DLARC) or as a single layer anti-reflection coating for glass encapsulated solar cells. Thus, higher refractive index SiN films may result in a net increase in cell efficiency due to increased photogeneration compared to the lowest  $J_{Oe}$  films. We do not consider this trade-off any further in this work, although more detailed measurements of the refractive index and absorption coefficient of these SiN films can be found in Ref. 12.

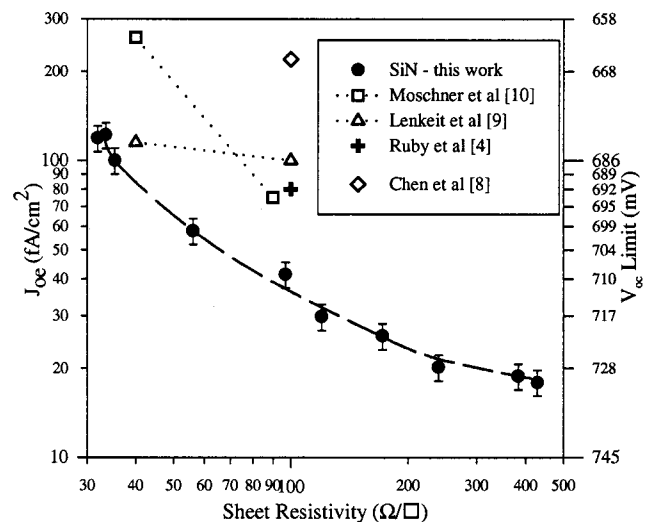


FIG. 1. Effect of sheet resistance on the  $J_{Oe}$  of SiN passivated phosphorus-diffused emitters with a planar surface.

The emitter saturation current density ( $J_{Oe}$ ) was determined using the quasisteady-state photoconductance method<sup>13,14</sup> with the samples in high injection ( $\Delta n > 1 \times 10^{15} \text{ cm}^{-3}$ ). The  $J_{Oe}$  determinations were made at a temperature of 25  $^\circ\text{C}$  using an intrinsic carrier concentration of  $8.65 \times 10^9 \text{ cm}^{-3}$ . Following  $J_{Oe}$  measurements on the passivated samples, the SiN layers were etched in dilute HF and the emitter sheet resistance determined using a four-point probe (the sheet resistance for the textured samples was measured on the actual sample). The electrically active phosphorus doping profile for the planar samples was determined using the stripping Hall technique. The semiconductor device simulation program PC1D (Ver. 5.3) was then used to extract the  $S_p$  at the passivated, heavily doped  $n$ -type silicon surface by adjusting the  $S_p$  values in the model so that the measured and calculated  $J_{Oe}$  coincided.

A second set of  $n^+pn^+$  samples was prepared using the same diffusion and drive-in conditions. For these samples the oxide layers formed during the diffusion drive in were etched in dilute HF and the  $J_{Oe}$  of the unpassivated samples measured. A thin transparent layer of aluminum ( $\approx 30 \text{ \AA}$ ) was then evaporated onto the rear side of the samples only and the  $J_{Oe}$  remeasured. From these measurements, the  $J_{Oe}$  of the unpassivated and metallized diffusion can be determined.

## IV. RESULTS AND DISCUSSION

### A. $J_{Oe}$ measurements for planar SiN passivated samples

The effect of sheet resistance on the  $J_{Oe}$  of SiN passivated, phosphorus-diffused emitters is shown in Fig. 1. The range of sheet resistances covered is from 30 to 430  $\Omega/\square$ . This covers (i) emitters which can accommodate screen-printed contacts ( $\approx 40 \Omega/\square$ ); (ii) high efficiency homogeneous emitters suitable for evaporated contacts ( $\approx 100 \Omega/\square$ ); and (iii) transparent, lightly doped emitters as would occur at uncontacted sections of a selective emitter structure ( $>150$

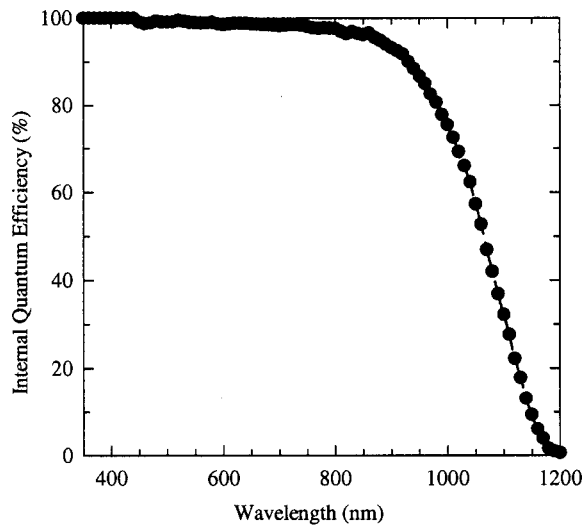


FIG. 2. Internal quantum efficiency of an all-SiN passivated PERC cell measured at Sandia National Laboratories. The front surface was planar, with a homogeneous emitter.

$\Omega/\square$ ). The error bars in Fig. 1 represent an estimated error of  $\pm 10\%$  in the  $J_{Oe}$  value. The dashed line is included as a visual guide.

As expected, the  $J_{Oe}$  increases as the sheet resistance decreases.  $J_{Oe}$  values as low as  $\approx 20 \text{ fA/cm}^2$  have been measured for lightly doped emitters and  $\approx 100 \text{ fA/cm}^2$  for industrial like emitters. Assuming a short circuit current density of  $40 \text{ mA/cm}^2$ , these  $J_{Oe}$  values limit the open circuit voltage of a solar cell to 727 and 686 mV, respectively (not including recombination at the contacts). The surface passivation of these PECVD SiN films is clearly very good. It is worth mentioning that emitter passivation provided by the PECVD SiN films was not altered by either a forming gas anneal for 30 min at  $400^\circ\text{C}$  nor by an anneal in nitrogen gas for 30 min at  $400^\circ\text{C}$ .

Included in Fig. 1 are data for other PECVD SiN passivated solar cell emitters obtained from the literature. While the diffusion profiles, PECVD deposition parameters, mode of plasma excitation, and method for measuring  $J_{Oe}$  may be different for some of these data, the  $J_{Oe}$  values of our optimized films compare favorably with those of other SiN films.

To confirm the excellent emitter passivation of our SiN films, we have fabricated all-SiN passivated simplified passivated emitter and rear cells (PERCS) with a planar front surface and homogeneous emitter (see Ref. 15 for details). The emitter of these cells was fabricated in the same way as for the  $n^+pn^+$  test structures and had a sheet resistance of approximately  $100 \Omega/\square$ . The internal quantum efficiency (IQE) for one of these cells is shown in Fig. 2. The IQE is approximately 100% between the wavelengths of 350–650 nm, demonstrating the excellent passivation provided by the front SiN layer. Further details of the electrical performance and characteristics of these cells can be found in Ref. 16.

**B.  $J_{Oe}$  measurements for planar thin oxide passivated samples**

The effect of sheet resistance on the  $J_{Oe}$  of planar, thin oxide samples is shown in Fig. 3. The data for the SiN pas-

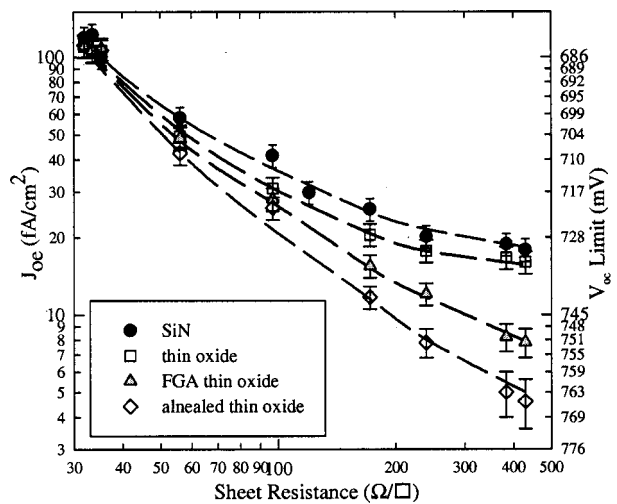


FIG. 3. Comparison of the  $J_{Oe}$  of phosphorus-diffused, planar emitters passivated with PECVD SiN and thin thermal oxides.

sivated samples are included for comparison. Again, the  $J_{Oe}$  increases as the sheet resistance decreases as expected. Further, while the SiN films offer good passivation, it can be seen that a thin oxide offers superior passivation, particularly when the oxide is FGA or annealed. Indeed, for the annealed oxides,  $J_{Oe}$  as low as  $5\text{--}10 \text{ fA/cm}^2$  has been measured for sheet resistances above  $200 \Omega/\square$ . The very low  $J_{Oe}$  values measured for lightly doped emitters with an annealed thin oxide are comparable with the values published by King *et al.*<sup>1</sup> and by Cuevas *et al.*<sup>6</sup>

At lower sheet resistances, where the emitters are more opaque, there is a minimal difference in the passivation quality of the SiN films compared to that in any of the oxide films. This is a significant result, since it indicates that, on industrial like emitters, PECVD SiN films are capable of passivating the surface as well as the best solid film passivation schemes available.

Another highly effective passivation scheme is the thin oxide/SiN stack used by Moschner *et al.*<sup>10</sup> We have shown previously that the  $J_{Oe}$  of emitters passivated with an annealed thin oxide or a thin oxide/SiN stack are practically identical,<sup>11</sup> independent of whether stoichiometric SiN ( $n \approx 1.9$ ) or Si-rich SiN ( $n \geq 2.1$ ) is used in the stack. This suggests that the effect of the SiN layer on the thin oxide is similar to that of an annealed aluminum layer and it is therefore likely that atomic hydrogen in the SiN layer is diffusing to the silicon/SiO<sub>2</sub> interface and passivating dangling bonds.

It is interesting to compare the relative passivation quality of PECVD SiN layers and thermal oxides on  $p$ -type and  $n$ -type surfaces. The results above show that thin oxides (with no annealing) and FGA oxides both offer better passivation of the  $n^+$ -diffused surface than SiN layers. However, on undiffused  $p$ -type surfaces, SiN layers offer significantly better surface passivation than FGA oxides.<sup>12</sup> Assuming that doped and diffused surfaces are similar, it follows that there should be a doping level where the passivation quality of SiN and thermal SiO<sub>2</sub>, under low injection conditions, is similar.



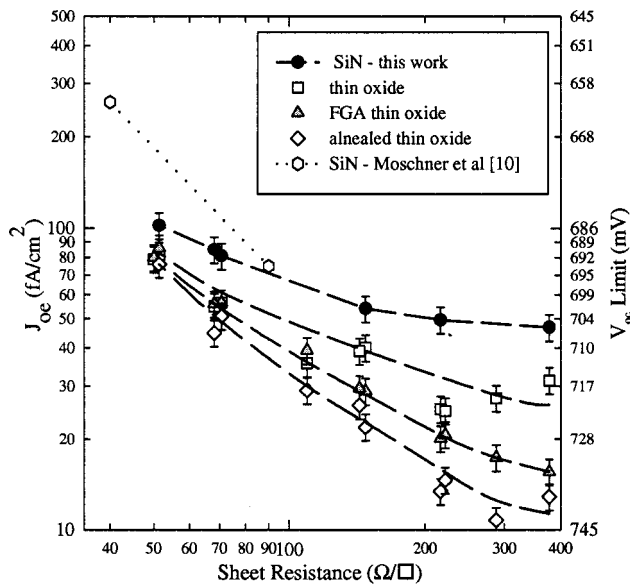


FIG. 4. Comparison of the  $J_{Oe}$  of phosphorus-diffused, textured emitters passivated with PECVD SiN and thin thermal oxides.

### C. $J_{Oe}$ measurements for textured samples

The measured  $J_{Oe}$  values for random pyramid textured samples passivated with SiN layers and thin thermal oxides are shown in Fig. 4. For the SiN passivated emitters, the  $J_{Oe}$  values range from 47 to 105 fA/cm<sup>2</sup> as the sheet resistance decreases from 380 to 50 Ω/□. Again, this emitter passivation is very acceptable, with the open circuit voltage limited to between 685 and 705 mV, depending on the emitter sheet resistance. Comparison of the data in Figs. 3 and 4 for SiN passivated emitters indicates that the  $J_{Oe}$  increases by a factor of 1.5–2.5 when going from a planar to a textured surface. This is similar to the increase measured by Moschner *et al.*<sup>10</sup> and is consistent with the increase in surface area by a factor of 1.73 compared to a planar surface.

The data in Fig. 4 for oxide passivated emitters again show that thin oxide passivation is superior to SiN passivation. Similarly, an annealed oxide is superior to a FGA oxide, which is superior to the as-oxidized samples. The lowest  $J_{Oe}$  measured for textured samples (the annealed oxide) was ≈12 fA/cm<sup>2</sup> for sheet resistances above 300 Ω/□. The increase in  $J_{Oe}$  when comparing textured and planar oxide passivated samples was a factor of 1.5–2.5, the same as that for the SiN samples. It appears that the ratio of  $J_{Oe}$  for a textured emitter to  $J_{Oe}$  for a planar emitter of the same sheet resistance increases as the sheet resistance increases.

### D. $J_{Oe}$ measurements for planar unpassivated samples

The effect of sheet resistance on the  $J_{Oe}$  of unpassivated and metal coated, phosphorus-diffused emitters with a planar surface is shown in Fig. 5. It can be seen that, without a passivating layer, increased sheet resistance results in increased  $J_{Oe}$ . This is opposite behavior to that of passivated emitters, and is consistent with the results of other studies.<sup>6</sup> The increase in  $J_{Oe}$  with sheet resistance for unpassivated emitters results from the fact that only the electric field as-

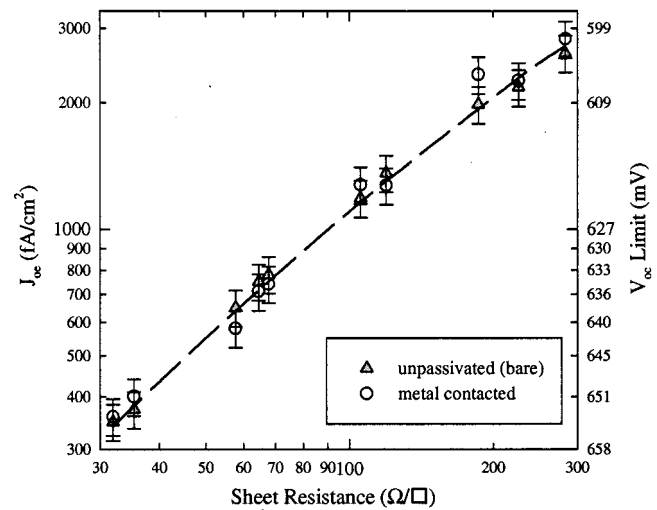


FIG. 5. Effect of sheet resistance on the  $J_{Oe}$  of unpassivated and metal coated, phosphorus-diffused emitters with a planar surface.

sociated with the gradient of the dopant profile is acting. The more heavily doped emitters provide a greater barrier to the diffusion of holes to the  $n^+$ -doped surface and therefore show lower  $J_{Oe}$ .

It can also be seen from Fig. 5 that there is little difference in the recombination properties of the unpassivated and metal contacted emitters. Further, a comparison of Figs. 3 and 5 shows that even for the more heavily doped emitters ( $N_{\text{surf}} > 2 \times 10^{20}$  cm<sup>-3</sup>), a SiN or thin oxide passivating layer still results in a significant reduction of the  $J_{Oe}$  ( $J_{Oe \text{ pass}} \approx 120$  fA/cm<sup>2</sup> cf.  $J_{Oe \text{ unpass}} \approx 400$  fA/cm<sup>2</sup>). If the SiN films relied solely on fixed positive charges near the Si/SiN interface for surface passivation, then it is unlikely that SiN films would be able to passivate heavily diffused samples well. Because the SiN films do passivate heavily doped emitters quite well, we conclude that the SiN films must derive a significant proportion of their surface passivation by reducing the density of interface traps (chemical passivation). This conclusion is in good agreement with the more fundamental study of Schmidt and Aberle.<sup>17</sup>

### E. Electrically active phosphorus profiles

The electrically active phosphorus profile of nine planar samples was determined using the stripping Hall technique. The profiles for some of the samples are shown in Fig. 6. The phosphorus surface doping concentration of the profiles ranged from  $N_s = 7.5 \times 10^{18}$  to  $1.8 \times 10^{20}$  cm<sup>-3</sup>, with the junction depths ranging from ≈0.25 to ≈0.8 μm, respectively. In general, the emitter sheet resistances determined by integrating the electrically active phosphorus profiles agree well with the values determined using the four-point probe. The largest discrepancies between the two measurements of emitter sheet resistance are found for the lightly doped emitters, where the four-point probe data gives a lower sheet resistance (for the lightest doped emitter, the four-point probe gives 430 Ω/□ while the integrated dopant profile gives ≈470 Ω/□).

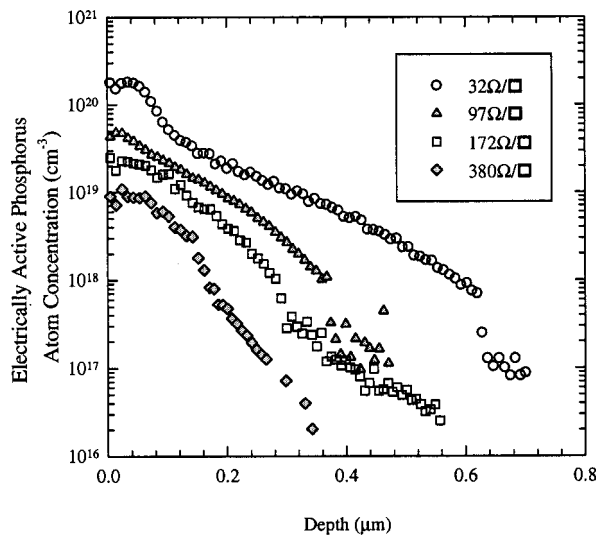


FIG. 6. Electrically active phosphorus profiles of some of the planar emitter samples used in this study.

**F. Band gap narrowing (BGN) parameters for PC1D**

The  $S_p$  determined from the measured  $J_{Oe}$  data is dependent on the model used for the BGN, since the model determines how the recombination losses in the emitter are divided between the bulk of the emitter and the surface. The semiconductor device simulation tool PC1D uses a simplified band gap narrowing model, while more sophisticated models are possible in three-dimensional modeling programs such as those used by Altermatt *et al.*<sup>18</sup> An important aspect to using the model in PC1D is to obtain a self-consistent data set for the BGN parameters and the extracted  $S_p$ . To achieve a self-consistent data set, we adjusted the BGN parameters in PC1D such that the measured  $J_{Oe}$  of the unpassivated, metalized emitters resulted in a  $S_p$  of  $1 \times 10^7$  cm/s, which is the thermal velocity limit for silicon.<sup>18</sup>

In Fig. 7 we show the apparent band gap narrowing used in this work as a function of doping concentration. The

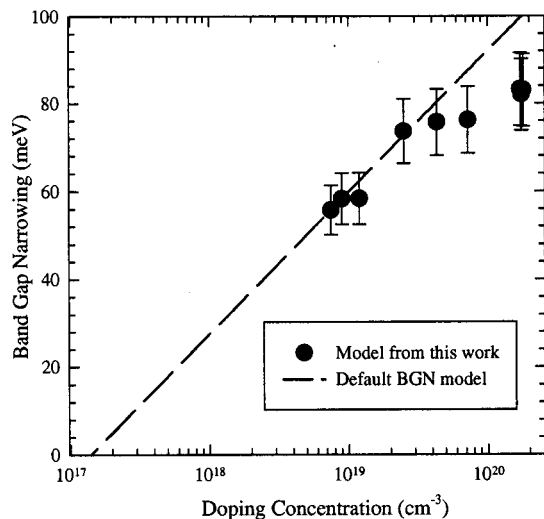


FIG. 7. Apparent band gap narrowing model determined for the emitters of this work and the default BGN model of PC1D.

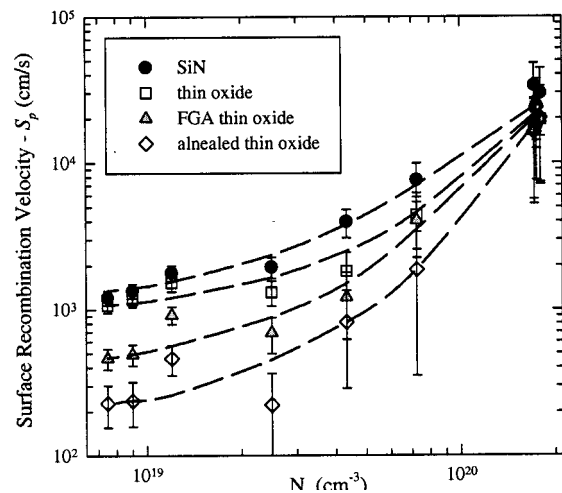


FIG. 8. Extracted  $S_p$  for the different passivation schemes as a function of phosphorus surface concentration ( $N_s$ ) for a  $\langle 100 \rangle$  oriented planar silicon surface.

straight line in Fig. 7 is the default BGN model in PC1D and was taken from Cuevas *et al.*<sup>2</sup> It can be seen that, for the lightly doped emitters, the default BGN model and the model used in this work agree. However, for the more heavily doped emitters, the model used in this work diverges from the default. The effect of this divergence is to reduce the amount of recombination occurring within the bulk of the emitter and therefore the  $S_p$  extracted using this modified BGN model will be higher than if the default model had been used.

**G. Extracted  $S_p$  for passivated emitters**

Figure 8 shows the  $S_p$  determined for each of the planar emitter samples for the different passivation schemes. Consistent with other studies,  $S_p$  increases as the surface doping concentration increases. For SiN passivated emitters,  $S_p$  increases from about 1400 to 25 000 cm/s as  $N_s$  increases from  $7.5 \times 10^{18}$  to  $1.8 \times 10^{20}$   $\text{cm}^{-3}$ . As expected from the  $J_{Oe}$  data, the  $S_p$  at the Si/SiN interface is higher than that at the Si/SiO<sub>2</sub> interface for a given surface doping. The lowest  $S_p$  as obtained for an annealed thin oxide passivation with  $S_p$  ranging from 250 to 21 000 cm/s. The values for the oxide passivated emitters (FGA and annealed) are in reasonable agreement with the data reported by Cuevas *et al.*<sup>6</sup> and by King *et al.*<sup>1</sup> (the results of King *et al.* need to be revised to account for the new value of  $n_i$ ).

**V. CONCLUSION**

A systematic comparison of phosphorus-diffused solar cell emitter passivation achieved with thin, high temperature thermal oxides and optimized PECVD SiN layers has been made.  $J_{Oe}$  values for emitters passivated with PECVD SiN layers ranged from 20 to 120  $\text{fA}/\text{cm}^2$  (47–105  $\text{fA}/\text{cm}^2$ ) as the sheet resistance decreased from 400 to 30  $\Omega/\square$  (380–50  $\Omega/\square$ ) on planar surfaces (textured surfaces). These  $J_{Oe}$  values correspond to a  $S_p$  value at the heavily doped  $n^+$ -Si/PECVD SiN interface of between 1400 and 25 000 cm/s.

The  $J_{\text{Oe}}$  and  $S_p$  values for thin oxide passivated emitters were consistent with other studies. The best passivation was provided by an annealed oxide with  $J_{\text{Oe}}$  values between 5 and 100 fA/cm<sup>2</sup> and  $S_p$  values ranging from 250 to 21 000 cm/s. For lightly doped emitters, thin oxide passivation was found to be superior to SiN passivation, while for industrial like solar cell emitters ( $\sim 40 \Omega/\square$ ), the  $J_{\text{Oe}}$  values for SiN passivated emitters and the various oxide passivated emitters are very similar. The  $J_{\text{Oe}}$  values for textured surfaces were a factor of 1.5–2.5 times greater than those for planar surfaces.

## ACKNOWLEDGMENTS

The authors would like to thank C. Jagadish and H. Tan for making it possible to use the PECVD reactor at the Electronic Materials Engineering Department of The Australian National University. Many thanks go to D. S. Ruby of Sandia National Laboratories for providing the IQE data. This work was supported by funding from the Australian Research Council. One of the authors (J.S.) gratefully acknowledges the support of a Feodor Lynen fellowship by the Alexander von Humboldt Foundation of Germany.

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