

# Oxidation Enhanced Diffusion of Phosphorus in Silicon in Heavily Doped Background Concentrations

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## ABSTRACT

An experimental study investigates the oxidation-enhanced diffusion of phosphorus in silicon in both heavily doped boron and arsenic backgrounds at 900 and 1100°C. This data can be modeled using the interstitial charge state levels to control the equilibrium concentration as a function of doping. The interstitials are assumed to be composed of only positive, negative, and neutral interstitial defects. The same values for the charge states are used to model previously published investigations of boron oxidation-enhanced diffusion under extrinsic isoconcentration conditions. This indicates that these effects are not strongly dependent on the value of the fractional interstitiality, since two different dopants exhibit similar behavior.

Understanding oxidation enhanced diffusion is important for modern process fabrication technology. The use of the lightly doped drain (LDD) MOS devices for channel lengths below 2  $\mu\text{m}$  is critical for reliability concerns. One final step in a typical LDD process involves the anneal of the  $n^+$  source/drain in dry oxygen to regrow the oxide on the silicon surface. Only through the complete understanding of the processes involved can optimization of the device structure be done. Controlling the junction depth can influence such factors as the diffusion spread under the masks and the depletion capacitance in the well.

Shockley and Last<sup>1</sup> derived relationships for the thermal equilibrium concentration of charged defects in semiconductors. These relationships are

$$C_i^+ = C_i^o \frac{p}{n_i} \exp\left(\frac{-\frac{E_g}{2} + (E_{i^+} - E_v)}{kT}\right) \quad [1]$$

$$C_i^- = C_i^o \frac{n}{n_i} \exp\left(\frac{-\frac{E_g}{2} + (E_c - E_{i^-})}{kT}\right) \quad [2]$$

where  $E_g$  is the bandgap as a function of temperature,  $C_i$  is the concentration of interstitials with the superscript +, o, - refer to the positive, neutral, and negative charge states, respectively,  $E_{i^-}$  and  $E_{i^+}$  are the negative and positive charge state levels, and  $E_c$  and  $E_v$  refer to the conduction and valence band energies. In thermal equilibrium the total concentration is given by the sum of all the concentrations in the various charge states, and is dependent on the electron concentration. During oxidation, interstitials are injected from and recombine at the surface. Hu<sup>2</sup> derived the surface boundary condition for interstitials during oxidation

$$g_i = k_r(C_i - C_i^*) - D_i \frac{dC_i}{dx} \quad [3]$$

where  $g_i$  is the surface injection,  $k_r$  is the surface recombination rate,  $D_i$  is the interstitial diffusivity, and  $C_i^*$  is the interstitial thermal equilibrium concentration. Both  $g_i$  and  $k_r$  can depend on the oxidation rate. No evidence exists for the doping dependence of  $g_i$  and  $k_r$  and here they are assumed to be functions only of the oxidation rate. The oxidation rate was adjusted to include doping effects by matching the measured oxide thickness. If the diffusion term is neglected, the surface concentration of excess interstitials is

$$\frac{C_i}{C_i^*} = 1 + \frac{g_i}{k_r C_i^*} \quad [4]$$

This equation indicates that the surface excess interstitial concentration depends on the value of the equilibrium interstitial concentration, which in turn depends on the interstitial charge states.

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The phosphorus diffusion flux in an isoconcentration background is given by

$$J_p = D_p \left( \frac{D_{PI}}{D_p} \frac{C_i}{C_i^*} + \frac{D_{PV}}{D_p} \frac{C_v}{C_v^*} \right) \nabla C_p \quad [5]$$

where  $D_p$  is the total phosphorus diffusivity measured during thermal equilibrium conditions and depends on both temperature and the Fermi level, and  $D_{PI}$  and  $D_{PV}$  are the components on that diffusivity with either interstitials or vacancies as indicated by the subscript. The diffusivity ratio,  $D_{PI}/D_p$ , is normally referred to as the fractional interstitiality,  $f_i$ .  $D_p$  has a neutral, negative, and double negative component<sup>3</sup>

$$D_p = D_p^0 + D_p^- \left( \frac{n}{n_i} \right) + D_p^{2-} \left( \frac{n}{n_i} \right)^2 \quad [6]$$

Both the interstitial and vacancy component of the diffusivity may have the same dependence on the Fermi level. The fractional interstitiality therefore can have a complicated dependence on the Fermi level depending on the charge states of the interstitial- and vacancy-phosphorus pairs. In intrinsic conditions, the fractional interstitiality of phosphorus is equal to one.<sup>4</sup>

## Isoconcentration Experiment

An isoconcentration experiment was designed to investigate the dependence of phosphorus enhancement on background doping. Ten  $\langle 100 \rangle$  silicon wafers with five different background doping levels of boron and arsenic were used ( $4 \cdot 10^{20}$ ,  $3 \cdot 10^{19}$   $\text{cm}^{-3}$  B, and  $2 \cdot 10^{14}$ ,  $1 \cdot 10^{19}$ ,  $3 \cdot 10^{19}$   $\text{cm}^{-3}$  As). A capping oxide was grown for 30 min at 900°C in dry  $\text{O}_2$ , and phosphorus was implanted at 150 keV with a  $5 \cdot$

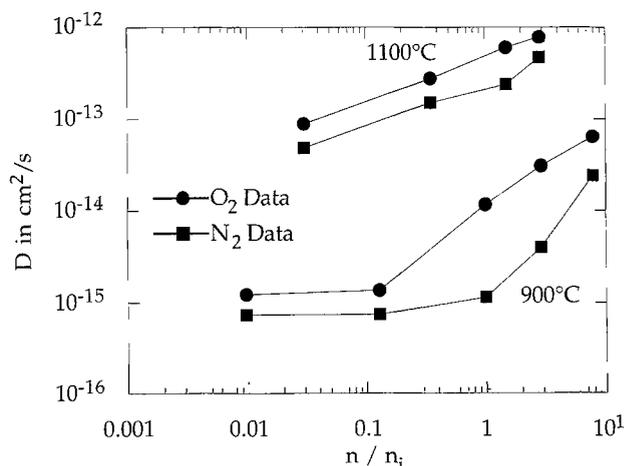


Fig. 1. Measured phosphorus diffusivity at 900 and 1100°C for dry oxygen and nitrogen ambients plotted vs.  $n/n_i$ .

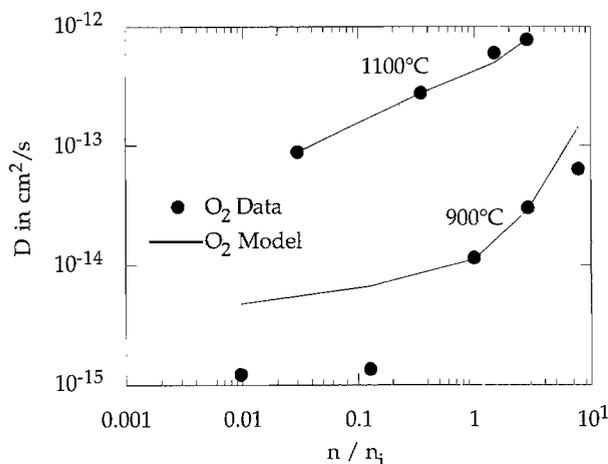


Fig. 2. Measured phosphorus diffusivity compared to the predicted diffusivity at 900 and 1100°C for dry oxygen ambient plotted vs.  $n/n_i$ .

$10^{13}$  cm $^{-2}$  dose. The wafers were halved and one-half of each wafer had nitride deposited with a 850°C, 50 min heat cycle. The other half of each wafer was annealed at 850°C for 50 min in nitrogen. This heat cycle also served as the damage anneal for the phosphorus implant. At this point the wafers were quartered and SIMS was performed with a CAMECA 4F system using a 14.5 keV Cs $^+$  beam to measure the initial profiles before the main diffusion. The wafers were annealed at 1100°C for 30 min in dry O $_2$  or at 900°C for 60 min in dry O $_2$ . The samples that were covered in nitride grew no oxide and were effectively diffused at thermal equilibrium of the point-defect concentrations. SIMS was performed again to obtain the final profiles for all the samples.

Figure 1 shows the measured diffusivities plotted vs.  $n/n_i$  for both 900 and 1100°C. The plots show a smaller OED for smaller  $n/n_i$  (p-type silicon). Also, the 900°C data show a greater proportional increase in the diffusivity due to the OED. The diffusivity in an inert ambient exhibits the standard concentration dependence $^3$  as first described by Fair. $^3$

### Modeling and Discussion

Since phosphorus diffusion is dominated by an interstitial mechanism in intrinsically doped material, a starting point for analysis is to assume that it is dominated by an interstitial mechanism at all doping levels. This assumption is examined in more detail later. Additionally, the dependence on velocity for the defect injection rate and defect surface recombination rates is used. $^6$  Parameters for the defects other than the charge states is assumed to be constants independent of the Fermi level, and is the same values that are used in fitting both intrinsic OED and Si implant damage. $^7$  The vacancy charge states are those measured by Watkins using electroparamagnetic resonance. $^8$  The only parameter remaining to be extracted from the measured enhancements is the interstitial charge levels.

Simulations of the diffusion of phosphorus were performed using SUPREM-IV. The diffusivity as measured in an inert ambient is used in the simulations. The starting profiles were measured in the experiment and used as the initial conditions for the diffusion profile. The oxide growth rate was adjusted so that the simulation accurately predicted the measured oxide thicknesses, which were larger than that predicted by the Deal-Grove model by no more than 20%. The best fit negative level for the interstitials was 0.11 eV below the conduction band, and the best fit positive level was 0.17 eV above the valence band.

Figure 2 compares the measured enhancements in an oxidizing ambient with those simulated. The fit is good at 1100°C, but is limited because of the limited range of  $n/n_i$  available in the study. At 900°C, the fit differs for the heaviest n-type and p-type samples. Because the diffusivity of

phosphorus is small at 900°C in p-type material, the error in the diffusivity produces small differences in the profiles. Figure 3 shows the junction depths (simulated and experimental) plotted vs.  $n/n_i$  for 900 and 1100°C. These figures show that the diffusivity has been modeled accurately for both temperatures. The junction depth fit at 900°C is better than the diffusivity fit suggests, and all the junction depths agree to within about 10%. The profiles also match well and are in some cases better matched than the junction depth indicates.

Miyake has examined the OED of boron in extrinsic material. $^9,10$  In his experiment, phosphorus and  $^{11}$ Boron were implanted into n-type, <100> silicon wafers at a high dose and driven in for 4 h at 1150°C. This produced nearly iso-concentration conditions, since at the region near the surface, the concentration of phosphorus and  $^{11}$ Boron was nearly constant. The implants were tailored to obtain two heavily doped n-type backgrounds, two heavily doped p-type backgrounds, and an intrinsically doped background wafer.  $^{10}$ Boron then was implanted at 150 keV at a  $5 \cdot 10^{13}$  cm $^{-2}$  dose and annealed at 900°C to remove the damage. Finally, the wafers were annealed at 1000°C for 30 min; half in nitrogen and half in dry oxygen ambient. Several problems exist with this experiment that make analysis difficult. Miyake showed that transient damage enhancement of the boron diffusivity was observed during the damage anneal, however, no initial SIMS profiles previous to the main 1000°C diffusion were available for analysis. Therefore, assumptions have to be made about the initial location of the  $^{10}$ Boron profiles. This complicates analysis as the inert diffusivity is not well controlled. Giles modeled this experiment $^{11}$  and used analytic formulas to extract the charge state values, which were larger than those obtained from the phosphorus experiment. The boron experiment is more difficult to analyze analytically because boron has a finite diffusion component via vacancies.

For Miyake's experiment, SUPREM-III's empirical model which includes channeling effects was assumed to be the correct starting profile. To account for the damage anneal, these starting profiles were given a longer anneal time. The other assumptions used in modeling the phosphorus experiment were used. The simulations used the boron diffusivity dependence on doping from Barbuscia *et al.* $^{12}$  The fractional interstitialcy of boron was assumed to be constant and equal to the value reported by Packan and Plummer. $^{13}$  Figure 4 compares the measured and simulated junction depths, and the fit is good over the entire range.

These fits were obtained by assuming that the fractional interstitialcy of both boron and phosphorus was constant as a function of doping and temperature. There are three indications that this assumption is justified; First, the phosphorus enhancement is a decreasing function of both

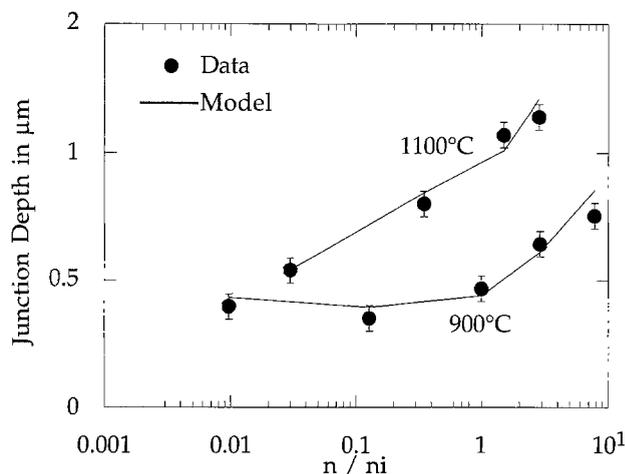


Fig. 3. Measured junction depth compared to predicted junction depth at 900 and 1100°C for dry oxygen ambient plotted vs.  $n/n_i$ .

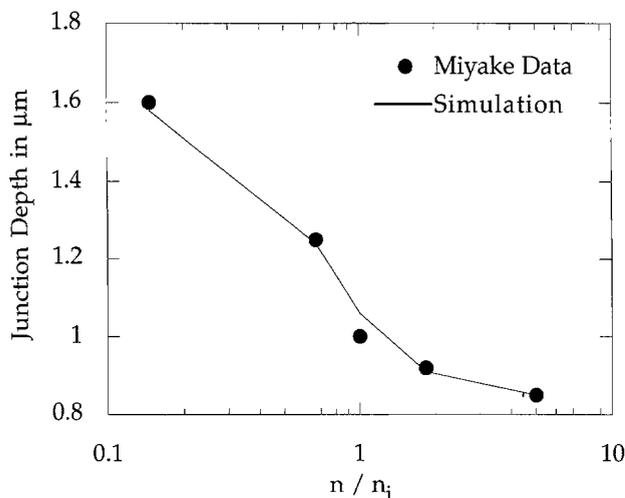


Fig. 4. Miyake's measured junction depth and SUPREM-IV junction depth at 1000°C as a function of  $n/n_i$ .

p- and n-type doping. The full expression for the phosphorus  $f_i$  is

$$f_i = \frac{D_{IP}^0 + D_{IP}^- \left(\frac{n}{n_i}\right) + D_{IP}^{\bar{\bar{}}}\left(\frac{n}{n_i}\right)^2}{D_{IP}^0 + D_{IP}^- \left(\frac{n}{n_i}\right) + D_{IP}^{\bar{\bar{}}}\left(\frac{n}{n_i}\right)^2 + D_{VP}^0 + D_{VP}^- \left(\frac{n}{n_i}\right) + D_{VP}^{\bar{\bar{}}}\left(\frac{n}{n_i}\right)^2} \quad [7]$$

In intrinsic conditions the  $f_i$  of phosphorus is equal to 1<sup>4</sup> and the neutral terms dominate the diffusion.<sup>3,5</sup> As the p-type doping increases, the fractional interstitialcy remains equal to one. Therefore, the  $f_i$  alone cannot account for the decrease in the enhancement.

Second, if the  $f_i$  dependence on doping was the controlling factor, then the experimental results show that both the boron and phosphorus must have the same dependence on doping. This is unlikely, since boron diffuses with neutral and positive terms and phosphorus with neutral, negative, and doubly negative terms unless the terms are constants. Therefore either the  $f_i$  dependence is a secondary effect or the  $f_i$  dependence is constant.

Finally, the temperature dependence of the enhancement is accounted for by the charge states. Equation 1 indicates the temperature dependence of interstitial equilibrium concentration in extrinsic conditions is fixed by the temperature dependence of the bandgap, the charge state levels, and the temperature dependence of the equilibrium

concentration in intrinsic conditions. The free parameters in fitting the temperature dependence included only the charge state levels, which are independent of temperature. If the  $f_i$  dependence on doping was the controlling factor, both the boron and phosphorus  $f_i$  must have the same dependence on temperature. This is unlikely, because the diffusion constants of boron and phosphorus have different activation energies. Again, either the  $f_i$  dependence is a secondary effect or the  $f_i$  dependence is constant.

### Conclusion

An experiment was performed to investigate the dependence of the phosphorus OED on background doping at both 900 and 1100°C. To minimize electric field effects, the experiments were performed in a constant concentration wafer. The amount of enhancement decreased as a function of background doping. The dependence of the OED was modeled using interstitial charge states and the negative level extracted is 0.11 eV below the conduction band and the positive level is 0.17 above the valence band. These same levels also were used to model the OED of boron in extrinsic material. Modeling both dopants indicates that charge states of the interstitials is more likely to control the enhancement than the fractional interstitialcy. Additionally, since the enhancement is a decreasing function of doping for phosphorus, the phosphorus  $f_i$  cannot account for the entire dependence.

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