Determination of Silicon Point Defect Properties from Oxidation Enhanced Diffusion of Buried Layers

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Accurate knowledge of point defect properties is essential to successful modeling of integrated circuit fabrication processes; however, there is substantial disagreement among reported values for some of the most fundamental properties. For example, at temperatures of interest for integrated circuit fabrication, the published calculations of silicon interstitial diffusivity vary over several orders of magnitude [1-7]. These reported values appear to be correlated with the type of experiment performed. Calculations from lateral [1] and backside [2-4] oxidation experiments yield diffusivities on the order of $10^{-9}\,\mathrm{cm}^2/\mathrm{s}$ at 1100°C, while those from metal diffusion and gettering experiments [6, 7] yield diffusivities greater than $10^{-7}\,\mathrm{cm}^2/\mathrm{s}$. These huge discrepancies can at least partially be attributed to the fact that what is most often calculated is the *effective* diffusivity, using models which ignore important effects such as bulk reactions and surface film interactions beyond a constant recombination rate [8]. For example, recombination with vacancies can be expected to slow down the interstitial diffusion front, leading to a lower calculated effective interstitial diffusivity when Frenkel pair recombination is ignored in the calculation.

A particularly attractive experiment for quantifying bulk point defect properties is to measure the dependence of oxidation-induced interstitial supersaturation on depth into the wafer (distance from the oxidizing wafer surface). Such an experiment markedly reduces the effects of interactions at nonoxidizing interfaces and can be performed by using buried dopant marker layers whose measurable diffusion enhancement can be directly related to interstitial supersaturation. A previous experiment using phosphorus and antimony buried layers [5], found no significant difference between diffusion at depths of 10 and 40μm and led to an estimated lower bound of 2.7×10^{-8} cm^2/s for interstitial diffusivity. In this work, we use a shorter oxidation time (60 min versus 200 min) and a slightly larger range of buried layer depths, and are able to measure a decrease in enhanced phosphorus diffusion with depth. We analyze the results both in terms of a simple model (without recombination, as in most previous work) to calculate an effective interstitial diffusivity, as well as with a model including bulk recombination of interstitials and vacancies, which leads to a calculation of the ratio of the concentration of vacancies to that of interstitials in equilibrium.

For our experiments, the starting substrates were high resistivity (>500 Ω-cm) phosphorus-doped <100> float-zone silicon. The wafers were implanted with phosphorus at 150keV with a dose of 2×10^{13}cm^{-2} (small enough so that the material remained intrinsic at processing temperatures). After implant annealing, epitaxial silicon was grown on the implanted substrates at 1040°C for 80 minutes to yield 45μm of epi. Following epi-growth, a 1500Å thermal oxide was grown and a final 1500Å nitride film was then deposited using low pressure chemical vapor deposition. The oxide/nitride multilayer serves as an oxidation barrier. The wafers were patterned to yield 1 cm^2 openings in this SiO_2/Si_3N_4 multilayer, with each wafer cleaved such that every sample piece had one window. The exposed silicon in these windows was etched anisotropically in KOH to varying depths to obtain the final test structures, for which the distance of the buried layer from the exposed silicon surface (L) ranged from 6 to 45μm. A schematic of the resulting test structure is shown in Figure 1. As a final step, the buried layer samples were diffused in dry O_2 at 1100°C for 1 hour.

Spreading resistance measurements were used to measure the doping profiles for each membrane, both before and after the final oxidation. The buried layer membrane thickness was determined by measuring the distance of the peak of the phosphorus doping profile from the oxidizing Si-SiO_2 interface. SERAPES, a spreading resistance analysis program which includes the effects of carrier spilling [9], was used to calculate the pre-oxidation doping profile from the measured spreading resistance profile. This calculated pre-oxidation doping profile was subsequently used as a starting profile for diffusion simulation via the process simulator SUPREM IV [10]. From the resulting doping profiles, simulated resistance profiles were calculated (again using SERAPES) and compared to the measured post-oxidation spreading resistance profiles. For each membrane thickness, the values of phosphorus diffusivity which resulted in the best match to the measured profiles were calculated using PROFILE, a nonlinear optimization program [11].

Our experimental results show a decrease in phosphorus diffusivity with increasing buried layer depth, in contrast with a previous measurement of buried layer diffusion by Griffin *et al.* [5], which found no dependence on epi thickness beyond the estimated error in their experiment of $\pm 5\%$. In this work, we found a difference of about 20% in the phosphorus diffusivity between depths of 6 and 45μm.

Dopant diffusivity can be written in terms of interstitial and vacancy components:

$$\frac{D_P}{D_P^*} = f_I^P \frac{C_{\rm I}}{C_{\rm I}^*} + (1 - f_I^P)\frac{C_{\rm V}}{C_{\rm V}^*}, \tag{1}$$

where $C_{\rm I}$ and $C_{\rm V}$ are the interstitial and vacancy concentrations, respectively, and the * represents the equilibrium value in intrinsic material. Since phosphorus diffuses predominantly via interstitials ($\mathrm{f}_I^P \cong 1$) [12], the phosphorus diffusivity enhancements are approximately equivalent to the interstitial supersaturation, or in terms of time-averaged values (represented by brackets),

$$\frac{\langle D_P \rangle}{D_P^*} \cong \frac{\langle C_{\rm I} \rangle}{C_{\rm I}^*}. \tag{2}$$

We compare our experimental results to two models, simple interstitial diffusion, with no recombination, and the coupled diffusion of interstitials and vacancies, including bulk generation/recombination processes. For all simulations, the boundary condition at the oxidizing interface is modeled by interstitial generation and fast interface recombination, leading to interstitial supersaturation as a function of oxidation rate. The magnitude of the interstitial generation used in the simulations is determined from matching the enhanced diffusion data and is primarily dependent on the diffusion of the shallowest buried layer. At non-oxidizing SiO_2 film interfaces, we use a constant interface regrowth velocity for both interstitials and vacancies. However, for these experiments, interactions at non-oxidizing interfaces have a negligible effect on the results since the backside is a full wafer thickness ($\sim 500\mu$m) from the buried layers and the lateral non-oxidizing regions are several thousand microns away.

In order to compare our results to other work, our first model includes only simple interstitial diffusion (ignoring bulk recombination):

$$\frac{\partial C_{\mathrm{I}}}{\partial t} = D_{\mathrm{I}} \frac{\partial^2 C_{\mathrm{I}}}{\partial x^2}. \tag{3}$$

We use SUPREM IV to simulate the diffusion of interstitials during the oxidation process. The time-averaged interstitial supersaturation as a function of distance from the oxidizing interface is calculated from the simulations and compared to the experimental values of interstitial supersaturation calculated from buried layer diffusion. The PROFILE [11] optimizer is used to extract an effective interstitial diffusivity from the best fit. The resulting calculated effective interstitial diffusivity was $D_{\mathrm{I}}^{\mathrm{eff}} = 4.1 \times 10^{-8}$ cm^2/s, slightly larger than the lower bound of 2.7×10^{-8} cm^2/s at 1100°C reported by Griffin *et al.* [5].

The second model includes recombination of interstitials with vacancies, in addition to the diffusion of interstitials and vacancies. We solve the continuity equations for interstitials and vacancies in the bulk, with the same boundary conditions as for the first model, again using SUPREM IV:

$$\frac{\partial C_{\mathrm{I}}}{\partial t} = D_{\mathrm{I}} \frac{\partial^2 C_{\mathrm{I}}}{\partial x^2} - k_r (C_{\mathrm{I}} C_{\mathrm{V}} - C_{\mathrm{I}}^* C_{\mathrm{V}}^*) \tag{4}$$

$$\frac{\partial C_{\mathrm{V}}}{\partial t} = D_V \frac{\partial^2 C_{\mathrm{V}}}{\partial x^2} - k_r (C_{\mathrm{I}} C_{\mathrm{V}} - C_{\mathrm{I}}^* C_{\mathrm{V}}^*). \tag{5}$$

The solution to this coupled system of equations, together with the boundary conditions, yields the interstitial supersaturation, which we then compare to our data.

In the simulations using the bulk recombination model, we assume that the interstitial diffusivity is the fast value of $D_{\mathrm{I}} = 6.7 \times 10^{-7}$cm^2/s at 1100°C obtained from metal gettering experiments [7], and we use a rapid recombination rate ensuring $C_{\mathrm{I}} C_{\mathrm{V}} \cong C_{\mathrm{I}}^* C_{\mathrm{V}}^*$ as observed experimentally [13]. The values of C_{I}^* and D_{V} were chosen so that the $C_{\mathrm{V}}^* D_{\mathrm{V}}$ and $C_{\mathrm{I}}^* D_{\mathrm{I}}$ products are consistent with silicon self-diffusion data [6], although for the conditions simulated, the results were nearly independent of D_{V}.

The equilibrium ratio of vacancies to interstitials, $C_{\mathrm{V}}^*/C_{\mathrm{I}}^*$, determines the decrease in effective interstitial diffusivity due to recombination with vacancies. For small values of this parameter, recombination has little effect. As $C_{\mathrm{V}}^*/C_{\mathrm{I}}^*$ increases, more and more interstitials must go to annihilating the vacancies before the interstitial concentration can rise. The result is a stronger dependence of interstitial concentration on depth, which can be interpreted as a smaller effective interstitial diffusivity.

Figure 2 shows simulation results from solving Equations (4) and (5) for a series of times at 1100°C. The surface concentration drops as a function of time because the oxidation rate slows as the oxide grows. From such simulations, the time-averaged interstitial supersaturation as a function of the distance from the injecting interface can be determined and compared to the measurements of enhanced buried layer dopant diffusion. It is clear from these simulations that for shorter times a much larger variation of enhanced dopant diffusion with depth can be expected.

Figure 3 is a comparison of experiment and simulation for the diffusion of buried phosphorus marker layers during oxidation. The normalized time-averaged interstitial supersaturation for a 60 min oxidation at 1100°C in a dry oxygen ambient is plotted as a function of the distance of the buried layer from the oxidizing interface, where the normalized supersaturation is defined as the ratio of the interstitial concentration at the buried layer depth to the concentration at the wafer surface ($\langle C_{\mathrm{I}}(L)\rangle / \langle C_{\mathrm{I}}(0)\rangle$). The error bars represent estimated error bounds on the calculated phosphorus diffusivity based on the accuracy of bevel angle measurements ($\pm 1\%$) and variations between multiple profiles on the same bevel. The best fit of the two models to the data give results which are indistinguishable, so only the model utilizing fast interstitial diffusion and including bulk recombination is included in Figure 3, as represented by the solid line. The fact that simulation results using the two models are equivalent demonstrates that rapid diffusion in conjunction with bulk recombination can indeed lead to experimental results which appear to be the result of a much smaller effective diffusivity. Table 1 provides the data used in this graph.

We found that a value of $C_V^*/C_I^* = 27$ gave the best fit to the experimental data. This ratio is somewhat smaller than the value of 84 calculated by Tan *et al.* [6] at 1100°C based on silicon self-diffusion and metal diffusion, but appears reasonable given the approximations and experimental errors involved in both calculations. When the same parameters as obtained from our bulk-recombination model were used to simulate the experimental conditions of Griffin *et al.*, the predicted differences in average diffusivity calculated were significantly reduced, as expected for longer times (see Figure 2), and fell within the $\pm 5\%$ estimated error reported in that work.

In summary, we have measured the diffusion of phosphorus buried layers at depths of 6 to 45μm during oxidation of silicon at 1100°C. From the dependence of the diffusivity enhancement on the distance of the buried layer from the oxidizing interface, we have calculated an effective diffusion coefficient for silicon interstitials in epitaxial material of 4.1×10^{-8}cm^2/s, which is consistent with the lower bound calculated in previous work.

These results, along with other reported calculations of effective interstitial diffusivity, can be explained consistently by considering the recombination of interstitials with vacancies. This reaction slows the movement of the interstitial diffusion front, since initially excess interstitials are annihilated by vacancies and only when the vacancy concentration is reduced can the silicon interstitial concentration rise. Thus, under conditions where bulk recombination is important, the value that would be calculated for effective interstitial diffusivity can be greatly reduced. We have successfully modeled our results using an interstitial diffusivity derived from metal gettering experiments and considering Frenkel pair recombination. We find that we get good agreement with our measurements for $C_V^*/C_I^* = 27$ at 1100°C.

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Figure 1: Test structure prior to final oxidation.

Figure 2: Interstitial supersaturation as a function of distance into the wafer from the solution to Equations (4) and (5) for $C_{\mathrm{V}}^{*}/C_{\mathrm{I}}^{*} = 84$ after 30, 60, 120 and 200 minutes at 1100°C.

Figure 3: Measured values of normalized diffusivity enhancement for phosphorus buried layers during a 60 min oxidation at 1100°C in a dry oxygen ambient compared to simulation of time-averaged interstitial supersaturation as a function of distance of buried layer from the oxidizing interface using a model including bulk recombination with $D_{\mathrm{I}} = 6.7 \times 10^{-7}$ and $C_{\mathrm{V}}^{*}/C_{\mathrm{I}}^{*} = 27$. The normalization is given by the value at each buried layer depth divided by the value at the oxidizing interface.

Table 1: Interstitial supersaturation as a function of buried layer depth.

Buried Layer Depth (μm)	6	14	24	45
$\langle C_{\mathrm{I}} \rangle / C_{\mathrm{I}}^{*}$	2.15	1.85	2.01	1.74
$\langle C_{\mathrm{I}} \rangle / \langle C_{\mathrm{I}}(0) \rangle$	1.0	0.86	0.93	0.81

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