

Effect of the silicon/oxide interface on interstitials: Di-interstitial recombination

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Interstitials can recombine at an oxide/silicon interface. Previous experimental work produces contradictory results. Transient enhanced diffusion experiments suggest a nearly infinite surface recombination rate, while oxidation enhanced diffusion suggests a much weaker recombination rate. A di-interstitial mechanism is investigated, and analytic solutions are developed. This is compared to the more commonly used interstitial mechanism. The di-interstitial mechanism can account for most of the discrepancy in the data. © 1998 American Institute of Physics.
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I. INTRODUCTION

Diffusion of dopants in silicon is controlled by the interaction of the dopants with point defects, interstitials, and vacancies. Therefore, to predict with any certainty what happens to the dopants during thermal cycling, an understanding of how the point defects behave is required. The point defect populations can be perturbed by many of the processes in use in integrated circuit processing, that lead to nonequilibrium diffusion phenomena. Two of the major perturbations to the defect populations are oxidation of the silicon surface and implantation damage.

Implantation of dopants creates large numbers of Frenkel pairs in the lattice. This large excess of point defects gives rise to transient enhancement of the dopant diffusion (TED). TED is qualitatively explained through the following steps. The large number of Frenkel pairs recombine fairly quickly and self annihilate. However, since an extra number of atoms equal to the dose were added to the crystal, there is an interstitial surplus equal to the dose. This is known as the “plus one” model of damage.¹ These extra interstitials precipitate into {311} rod-like defects. Interstitials are released from the {311} defects slowly as the {311}'s dissolve, with a time constant approximately the same as the TED.² These released interstitials contribute to the enhanced diffusion of the dopant present. The interstitials cannot be annihilated by vacancies, since there are not enough of them, but they can be annihilated by the surface. Diffusion to and annihilation at the silicon surface (which is typically covered with silicon dioxide) control the time length of the transient diffusion.

When the surface is oxidized, a volume expansion is required. Part of this volume expansion can be accommodated by injecting silicon interstitials into the bulk. Some of these injected interstitials can recombine at the oxidizing interface and the rest diffuse into the silicon.^{3,4} These excess interstitials also give rise to enhanced diffusion, oxidation enhanced diffusion (OED). Experimental observations indicate that this enhancement is proportional to the square root of the oxide growth rate.³⁻⁶ This enhancement lasts as long

as the oxide is growing, and the enhancement depends on the oxidation rate. The injected interstitials can diffuse laterally and recombine at surfaces and with vacancies.

For both processes, the silicon/oxide interface is crucial to understanding the behavior of the interstitials. Unfortunately, published data from these differing conditions give different predictions of the magnitude of the surface recombination. It would be very helpful to have a unified picture of the surface behavior. In the next section, simplified analytic solutions are developed to help understand different models of the surface behavior.

II. ANALYTIC SOLUTIONS ALONG AN INTERFACE

In general, the point defect concentrations are given by the set of coupled differential equations:

$$\begin{aligned}\frac{\partial C_I}{\partial t} &= \nabla D_I \nabla C_I - K_R (C_I C_V - C_I^* C_V^*), \\ \frac{\partial C_V}{\partial t} &= \nabla D_V \nabla C_V - K_R (C_I C_V - C_I^* C_V^*).\end{aligned}\quad (1)$$

In these equations, C is the concentration, D is the diffusivity, K_R is the bulk recombination, the subscript I is for interstitials, the subscript V is for vacancies, and the superscript* is for equilibrium concentration. These equations represent continuity of interstitials and vacancies. Additional terms may be necessary to account for other sources of bulk annihilation, e.g., on dislocations. The following equations represent the boundary conditions:

$$\begin{aligned}g_I &= D_I \nabla C_I \cdot \mathbf{n} + K_{\text{surf}I}, \\ g_V &= D_V \nabla C_V \cdot \mathbf{n} + K_{\text{surf}V},\end{aligned}\quad (2)$$

where g is the surface injection and K_{surf} is a function representing surface annihilation. These equations balance the flux at the surface of the wafer. These can account for any surface mechanism, depending on the functional form of K_{surf} and g .

These equations do not have analytic solutions except under very specific cases. However, we can make some simplifying assumptions that can still provide significant insight

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into the behavior of point defects. First, we can neglect bulk recombination which effectively decouples the differential equations from one another. At low temperatures (800–900 °C), the bulk lifetime is on the order of several weeks.⁷ At higher temperatures, the lifetime is shorter and this becomes a more questionable assumption.^{8,9} However, if the vacancies are not replenished by the surface, then $C_I C_V$ becomes approximately $C_I^* C_V^*$, and the bulk recombination term becomes zero.

Once the equations are decoupled, it becomes easier to treat the cases of TED and OED which are dominated by interstitial behavior. The vacancies can now be neglected. To compute the interstitial concentration under a surface injection condition, we can neglect the diffusion term in the boundary condition of Eq. (2). This corresponds to a very strong surface source, that effectively pins the surface concentration. Griffin and Plummer⁵ have observed that there is no reduction in OED for small oxidizing stripe widths, which indicates that oxidation is a very strong surface source. In this case, the injection must equal the surface recombination.

If we ignore two-dimensional diffusion and consider lateral diffusion in a thin boundary layer under the surface, we may recast Eq. (2) as

$$-g = hD_I \frac{\partial^2 C_I}{\partial x^2} - K_{\text{surf}I}, \quad (3)$$

where x is the distance along the interface and h is the thickness of the boundary layer. This effectively assumes that the defects diffuse in a laminar fashion—primarily laterally under the mask edge. Diffusion into the bulk and back to the surface is neglected. The appropriateness of this approximation will be discussed later. With this simple formula, it is now possible to derive solutions to the interstitial concentration laterally and at an injecting surface for different forms of $K_{\text{surf}I}$.

A. Interstitial case

If the surface recombination is dominated by recombination of single interstitials, then $K_{\text{surf}I}$ can be written as

$$K_{\text{surf}I} = K_{se}(C_I - C_I^*), \quad (4)$$

where K_{se} is the effective surface recombination rate.^{3,4} Approximating the surface injection by a step function (g_0 under the oxide and 0 under the nitride), Eq. (3) becomes

$$-g_0 \mathcal{H}(-x) = hD_I \frac{\partial^2 C_I}{\partial x^2} - K_{se}(C_I - C_I^*), \quad (5)$$

where $\mathcal{H}(-x)$ is the Heavyside function having a value of 1 for $x < 0$ (oxidizing region) and 0 for $x > 0$ (inert region).

If we limit the discussion to intrinsically doped material, we can assume that C_I^* is a fixed value in space and time. Equation (5) can be solved analytically. Under the oxidizing surface ($x < 0$), we have

$$c = \frac{C_I}{C_I^*} = 1 + \frac{g_0}{K_{se}C_I^*} - \frac{g_0}{2K_{se}C_I^*} \exp\left(\frac{x}{L_D}\right), \quad (6)$$

where c is the scaled interstitial concentration. Away from the mask edge ($x \ll 0$), the diffusion term in Eq. (5) is negligible and the injection and recombination terms must balance. This pins c at $(1 + g_0/K_{se}C_I^*)$. As the injection drops to zero, the surface concentration returns to the equilibrium value. L_D is the lateral diffusion length of the interstitials and is given by

$$L_D = \sqrt{\frac{hD_I}{K_{se}}}. \quad (7)$$

Recall that h is the thickness of the boundary layer through which the lateral flow was assumed to take place. If the thickness of that layer is taken to be the same as the diffusion length, we obtain

$$L_D = \frac{D_I}{K_{se}}. \quad (8)$$

Under the inert surface ($x > 0$), the excess interstitials decay exponentially with the same diffusion length:

$$c = \frac{C_I}{C_I^*} = 1 + \frac{g_0}{2K_{se}C_I^*} \exp\left(-\frac{x}{L_D}\right). \quad (9)$$

B. Di-interstitial case

If we assume that the surface recombination is dominated by a di-interstitial process,¹⁰ and we also assume that the number of di-interstitials is at equilibrium with the interstitial concentration, then the surface recombination can be written as

$$K_{\text{surf}I} = K_{s2}(C_I^2 - C_I^{*2}), \quad (10)$$

where K_{s2} contains both the surface recombination rate and the temperature-dependent factor for the number of di-interstitials as a function of interstitials. Under an injecting surface away from the mask edge, the scaled excess interstitial concentration can be written as

$$c = \frac{C_I}{C_I^*} = \sqrt{\frac{g_I}{K_{s2}C_I^{*2}} + 1}. \quad (11)$$

Again, the limiting case is correct. As the injection drops to zero, the scaled excess interstitial concentration drops to one.

Away from the mask edge, we can apply Eq. (3). If we limit the discussion to intrinsically doped material, we can assume that C_I^* is a fixed value in space and time. For the surface recombination in Eq. (10), the differential Eq. (3) can be solved analytically. Under the mask ($x > 0$), we obtain

$$z = \frac{(z_0 + 1) + (z_0 - 1)\exp(-x/L_{D2})}{(z_0 + 1) - (z_0 - 1)\exp(-x/L_{D2})}, \quad (12)$$

$$L_{D2} = \sqrt{\frac{hD_I}{2K_{s2}C_I^*}},$$

where z is a modified variable related to the scaled interstitial concentration, c , according to

$$z = \sqrt{\frac{c+2}{3}} \quad (13)$$

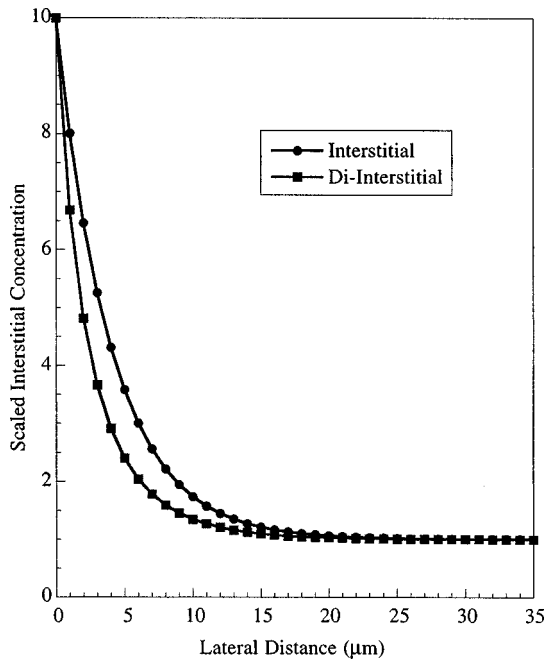


FIG. 1. Comparison of a di-interstitial and interstitial dominated surface recombination process under a mask with the scaled interstitial concentration held at 10 at the mask edge.

and z_0 is the value of z at the edge of the mask. L_{D2} is the lateral diffusion length of the interstitials.

While the solution given by Eqs. (12) and (13) seems complex, we can gain significant physical insight into the problem by examining the important features of the solution. Since the surface recombination is bimolecular, this solution tends to fall off faster than for a single interstitial near the mask edge. Both solutions limit to an exponential decay at distances farther from the edge. Figure 1 compares the two solutions for a value of the scaled interstitial concentration at the mask edge of 10, and the same final decay length ($L_D = L_{D2}$). Both have the same limiting value of the decay length, $4 \mu\text{m}$. The di-interstitial model falls off much more rapidly as the distance from the mask edge increases. We will now apply this solution to data reported in the literature on OED and TED to resolve the apparent contradictions in reported decay lengths.

III. OXIDATION ENHANCED DIFFUSION DATA

A. 1D OED enhancement

Under the mask edge, Griffin and Plummer⁵ have reported that the surface is a very strong source, so the limiting cases discussed above can be used. Figure 2 shows the time dependence of OED as reported by several researchers^{5,6,11} at 1100°C . The best-fit power dependence is also plotted, and as can be seen the time decay of the scaled interstitial concentration goes as roughly $t^{-0.25}$.

The oxide growth velocity at high temperatures and longer times depends on $t^{-0.5}$. In the case of the di-interstitial recombination, a $t^{-0.25}$ dependence occurs naturally if the injection rate, g_I , is assumed to be proportional to the growth rate. Equation (11) shows that the excess intersti-

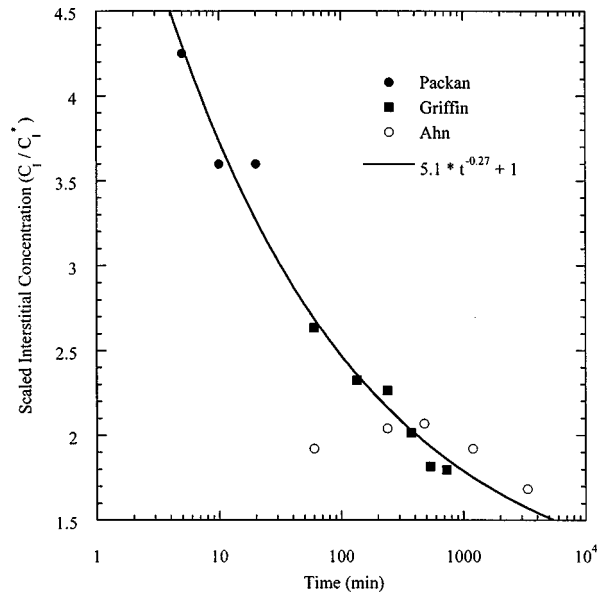


FIG. 2. One-dimensional OED diffusion enhancements as a function of time (see Refs. 5, 6, and 11) at 1100°C . The best-fit line is also shown.

tial concentration will go as the square root of the injection. This fact is one of the reasons that the di-interstitial mechanism was proposed.¹⁰

For the case of interstitial recombination, however, it is not so easy. If the injection rate is proportional to growth velocity, then the surface recombination rate, K_{se} , must be made proportional to the square root of the velocity to obtain the desired time dependence. One common assumption is to make the effective surface recombination rate proportional to the oxide growth velocity.¹² K_{se} can then be written as

$$K_{se} = K_{s1} \left[K_{rat} \left(\frac{\nu_{ox}}{\nu_{ref}} \right)^{1/2} + 1 \right], \quad (14)$$

where K_{s1} is the surface recombination rate, K_{rat} is the ratio between the surface recombination at a growing and inert oxide interface, ν_{ox} is the growth velocity, and ν_{ref} is the reference velocity. This accounts for the time decay appropriately, but at a considerable increase in model complexity. However, it quite nicely accounts for the surface strength. By increasing K_{rat} and g_I , the diffusion term in Eq. (2) can be made arbitrarily small. The other alternative is to make the injection go as the square root of the velocity, but this leads to a weak source that does not duplicate Griffin's observed result.⁵

B. 2D lateral enhancement

Two-dimensional studies of the lateral extent of the OED can be made by using differing width stripes of masked pad oxide between oxide regions. By measuring the junction depth at the center of the masked regions, a decay length can be extracted. Figure 3 plots the extracted decay lengths for $900, 1000,$ and 1100°C as a function of time along with the best-fit power dependence from Griffin and Plummer.⁵ Over the times measured, the decay length continues to increase.

For the interstitial surface recombination model, the decay length should be constant once the interstitials reach

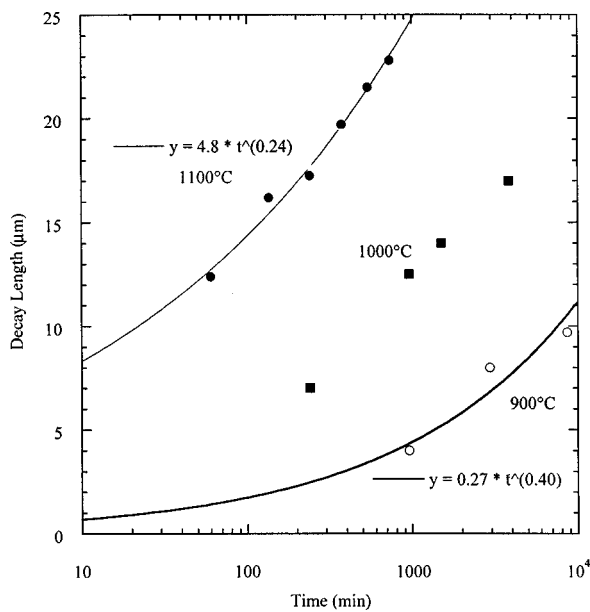


FIG. 3. Lateral decay length measured by extraction from stripes as a function of time and temperature. Best-fit power dependencies are also shown for 1100 and 900 °C.

steady state. The data do not indicate this type of behavior, and therefore Griffin suggested that the interstitials diffuse very slowly due to interaction with substrate traps. The traps also explained prior observations of differences in the apparent diffusivity in differing substrate materials.^{13,14} However, Ahn showed that, in float-zone silicon, interstitials diffused entirely across a 20 μm membrane in 6 h at 1100 °C. In the stripe experiments, steady state is not achieved at 12 h at 1100 °C, and the decay length is approximately 20 μm . These two facts are very difficult to fit simultaneously.^{15,16}

For di-interstitial recombination, however, the case is different. The lateral decay depends on the magnitude of the scaled interstitial concentration near the mask edge. The di-interstitial recombination can be factored and then written as

$$K_{\text{surf}l} = K_{s2}(C_I + C_I^*)(C_I - C_I^*). \quad (15)$$

For small values of the interstitial excess, we can treat $C_I + C_I^*$ as approximately constant and equal to $C_I^* \times c_0$. For this simplification, Eq. (5) would hold with K_{se} being replaced by $K_{s2} \times C_I^* \times (c_0 + 1)$. Effectively, the recombination length would become time dependent, with the time dependence of the decay length equal to one over the time dependence of the surface concentration as in Eq. (8). Figure 3 shows that the 1100 °C time dependence best fit is close to 1/4 power, which is very close to one over the surface concentration time dependence of $-1/4$.

van Dort also measured the lateral decay length using a different technique. Alternating stripes were used on top of uniform doping superlattices, and then deconvoluted with large area secondary ion mass spectroscopy (SIMS).¹⁷ van Dort's results showed a smaller decay length for 900 °C than those Griffin reported, although the time was also shorter. van Dort found a value of 1.5 μm in the deep spikes (comparable to the junction depths that Griffin looked at) at this time. Another key difference was that van Dort looked at

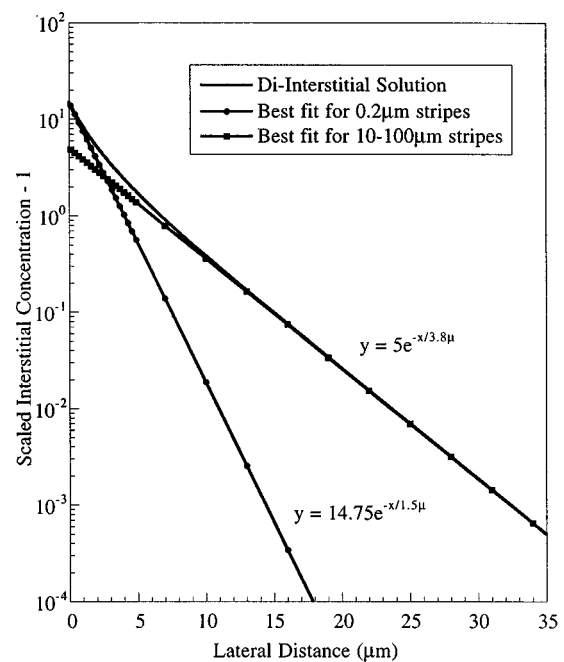


FIG. 4. Comparison of analytic di-interstitial solutions for OED for Griffin's and Van Dort's experiments. Shorter decay lengths would be measured over shorter distances.

smaller structures than Griffin. van Dort also reported a strong depth dependence to the decay length, which would be attributable to two-dimensional diffusion, e.g., flow from the bulk back to the surface. In Sec. II, we assumed that this effect was not strong, so the analytic solutions can be used only for insight and not for predictive numerical modeling.

Figure 4 shows a sample solution to the lateral decay using di-interstitial surface recombination and an edge scaled interstitial concentration of 16. The decay length factor used for the di-interstitial recombination is 3.8 μm . Fitting an exponential decay solution over the shorter stripe widths used by van Dort, leads to a best fit decay length of 1.5 μm . Because the di-interstitial solution falls off faster than a single interstitial solution, as shown in Fig. 3, over short widths a faster fall in the interstitial concentration is observed. Over the stripe widths used by Griffin, the best-fit decay length works out to 3.8 μm close to the value of decay length specified. Since the experiment looked at wide stripes, a value close to the limiting value is found. The design of an experiment becomes a critical factor. Experiments, like Griffin's, that are set to investigate a long decay length discover a long decay length. However, an experiment, like van Dort's, that is designed to look over shorter lengths finds a much smaller decay length. This model also successfully explains the fact that Griffin's junction depths did not extrapolate to the 1D value at the mask edge.

For OED cases, the di-interstitial surface recombination model offers two advantages to the single interstitial model. First, the time dependence of the injection is more accurately and easily accounted for. The di-interstitial model predicts the time evolution of the lateral decay length at 1100 °C quite accurately. Second, the difference in decay lengths between van Dort and Griffin is accounted for by the difference in experimental design. Experiments designed to extract a

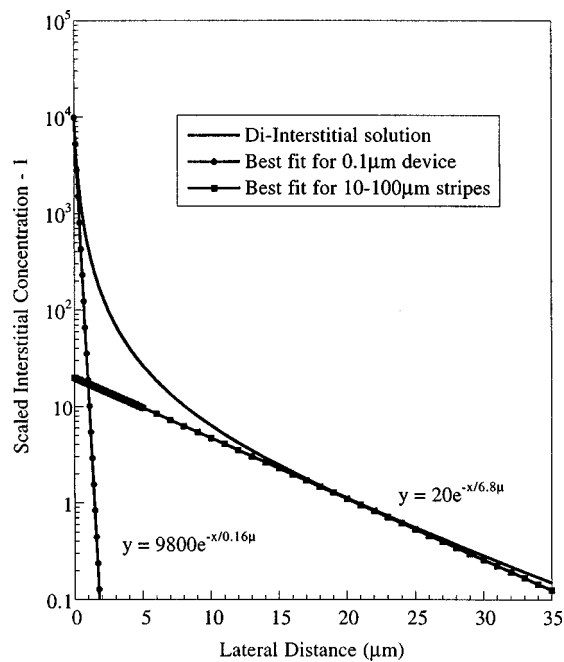


FIG. 5. Comparison of analytic solutions for TED showing best fit exponential decay over two different distances.

short decay length find one, and experiments designed to find a long decay length find a longer value.

IV. TRANSIENT ENHANCED DIFFUSION (TED) DATA

TED is also controlled by surface processes, and there is a large amount of data that confirms that the TED depends on distance to the surface. The work by Packan and Plummer¹⁸ demonstrated that the amount of diffusion observed by a buried marker layer increased with increasing energy of the silicon damage implant. This could be due to the distance of the surface, but could also be have been due to the increased proximity of the damage to the buried layer.

A cleaner experiment was performed by Lim *et al.*¹⁹ This experiment performed surface etching to move the surface closer to a preexisting damage layer. The resulting diffusion enhancement was simulated with a variety of surface decay length factors, and the best fit was found with a decay length of 0.1 μm for two hours at 800 $^{\circ}\text{C}$. This time and temperature should have completed the TED, so the 0.1 μm should be an effective number for the entire time.

van Dort used the same technique of doping superlattices and stripes to investigate TED as he used for OED.²⁰ Instead of oxidizing to create an effective lateral enhancement, he implanted silicon at 40 keV with a dose of 10^{14} cm^{-2} in the stripe openings. The anneals were performed for 30 min at 900 $^{\circ}\text{C}$. The extracted lateral decay length was 0.16 μm .

A similar experimental approach to Griffin's stripes⁵ was also used for TED by Frank and Law.²¹ Masking patterns of wide open areas and varying mask widths were used on the wafer. Long lines were used to eliminate three-dimensional effects and to make a shallow bevel possible. A Si^+ implant was performed into the open areas and variety of times and temperatures of anneals were performed. Junction cleave and stain was used to delineate junction depths under the masked

stripes. Resolution was only attained for patterns that were greater than 2.0 μm . For this experiment, junction depth decay lengths similar to those obtained by Griffin and Plummer⁵ for OED (5–10 μm) were obtained.

Figure 5 shows the lateral decay of the interstitial supersaturation as given by Eqs. (12) and (13). These were calculated assuming that the silicon damage and resulting defect structures maintained a constant supersaturation under the open area. In the current accepted theory of TED,² an atmosphere of interstitials is maintained in the vicinity of {311} defects that form early in the anneal cycle. For this case, the assumption is valid. The supersaturation at the edge of the mask was set to 10^4 . For the interstitial recombination case, the decay is a straight line. For the di-interstitial case, recombination is higher near the mask edge. Best fits are shown over the distances measured by van Dort²⁰ and Frank.²¹ These decay lengths are consistent with the experimental observations. In a way similar to that for OED, experiments designed to extract a short decay length find one, and experiments designed to find a long decay length find a longer value.

V. CONCLUSIONS

A di-interstitial surface recombination mechanism was originally proposed to account for the time dependence of OED. It can also explain many inconsistencies in the reported strength of the surface on interstitials. Over long lateral distances, the interstitial decay approximates an exponential with a limiting decay length on the order of tens of microns long. Over short distances, however, the fall off is much more rapid. A best-fit exponential fit over short lateral distances finds a decay length on the order of tenths of a micron. This is consistent with several reported experimental observations of the interstitial surface recombination behavior.

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