# A comparison of boron and phosphorus diffusion and dislocation loop growth from silicon implants into silicon

Jingwei Xu
*Computer Peripheral and Control Products, Semiconductor Group, Texas Instruments Incorporated, Dallas, Texas 75243*

V. Krishnamoorthy and Kevin S. Jones
*Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611*

Mark E. Law
*Department of Electrical and Computer Engineering, University of Florida, Gainesville, Florida 32611*

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Transient enhanced diffusion (TED) results from implantation damage creating enhanced diffusion of dopants in silicon. This phenomenon has mostly been studied using boron marker layers. We have performed an experiment using boron, phosphorus, and dislocation markers to compare TED effects. This experiment shows that phosphorus is enhanced significantly more than boron during damage annealing. Dislocation growth indicates that a number of interstitials greater than the damage dose is captured during these anneals. The time to saturate the dislocation growth agrees well with phosphorus diffusion saturation, and is greater than the boron saturation. © *1997 American Institute of Physics*. [S0021-8979(97)04402-2]

## INTRODUCTION

In oxidizing conditions, boron has been shown to have a fractional interstitialcy equal to about 80% of the value of phosphorus.[1] Phosphorus at low concentrations is known to be a pure interstitial diffuser.[2] This is certainly valid for the kinds of supersaturation found during oxidation, which is where the value was extracted. For an interstitial supersaturation, phosphorus would be expected to be enhanced about 25% more than boron, based on this result. Boron has been used to study interstitial phenomena as a doping marker since it responds proportionally to the interstitial supersaturation and because it is easier to grow marker layers with boron.

Transient enhanced diffusion (TED), has supersaturations that are very much larger than those found in oxidation experiments. TED results from the Frenkel pair generation and damage generated during implantation. This damage causes large enhancements that last until annealing of the damage occurs. This regime of diffusion enhancement is very different than that found during oxidation. No verification of whether boron is an appropriate marker of interstitial phenomena in this supersaturation regime has been done.

Dislocation loops have been used to capture interstitials injected from oxidation[3] and implantation processes.[4] These studies have determined the integrated flux of interstitials captured during the process of interest. This technique can be used to capture and count an interstitial population.

This study was designed to investigate whether boron and phosphorus continue to show interstitial dominated behavior at high supersaturations found in TED conditions. Additionally, we use loops to capture interstitials on separate wafers that are processed together. This allows us to compare the diffusion results with those from loop capture.

## EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental flow chart. The starting wafers were Czochralski high resistivity wafers with a thickness of about 0.6 mm. The wafers had an initial thin oxide grown of 400 Å at 1000 °C in dry oxygen. Splits were made for boron, phosphorus, and dislocation loops.

The boron implants were performed at 26 keV at a dose of $2\times10^{14}$ cm$^{-2}$. The phosphorus implants were done at $10^{14}$ cm$^{-2}$ at 60 keV. Both sets of samples were then given a 900 °C anneal for 10 min in an inert ambient to anneal the damage from the implant. Wafers were pulled from the split at this point to measure the initial conditions.

The loop samples had two implants of germanium, $10^{15}$ cm$^{-2}$ at 75 keV and then $10^{15}$ cm$^{-2}$ at 170 keV. Previous studies have shown that this creates a continuous amorphous layer at a depth of approximately 1800 Å. The loop samples were annealed at 550 °C for 16 h and then 800 °C for 30 min. This cycle regrows the amorphous material and forms end-of-range dislocation loops at a depth of the original amorphous/crystalline interface.

Half of the boron, phosphorus, and loop samples were separated to serve as controls and the remainder received a $5\times10^{13}$ cm$^{-2}$ 80 keV silicon implant to create damage. Final anneals were done at a variety of temperatures and times on both the controls and the damaged samples to compare the effect of the damage on diffusion and loop growth.

Doping profiles of the boron and phosphorus were measured with secondary ion mass spectroscopy (SIMS) performed at Evans East. Diffusivities were extracted using the Florida object oriented process simulator (FLOOPS) by reading in the initial implant condition and then diffusing that profile with a constant diffusivity until it fit the final, annealed measured profile. The enhancements are determined by using the fitted diffusivity ratio to the default value of the diffusivity. Default intrinsic diffusivities in FLOOPS for boron and phosphorus are $1.51\times e^{-3.52/kT}$ and $0.5\times e^{-3.40/kT}$ cm$^{-2}$/s, respectively. These values are within 50% of the measured value of diffusivity from the longest time anneals in the control samples. Dislocation loop atomic density was

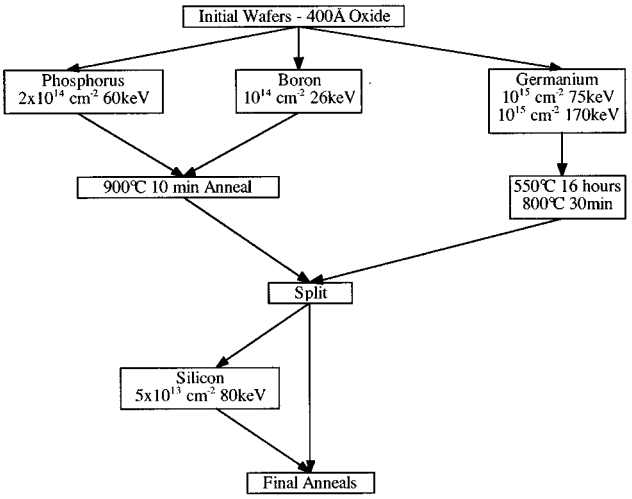


FIG. 1. Experimental flow chart.

measured using plan-view transmission electron microscopy (TEM).

## BORON AND PHOSPHORUS DIFFUSION RESULTS

Figure 2 shows the boron and phosphorus diffusion enhancements for 800 °C annealing as a function of time. The slopes of the two curves are for longer anneals approximately the same, but the magnitude of the phosphorus enhancement is larger. At short times the difference is roughly an order of magnitude and drops to a little less than that at longer times. It appears that the first three data points have similar enhancements for the boron at short times, compared to the phosphorus results. At this temperature, there was some evidence of inactive, immobile boron concentration at values above $10^{18}$ cm$^{-3}$. This could be due to the formation

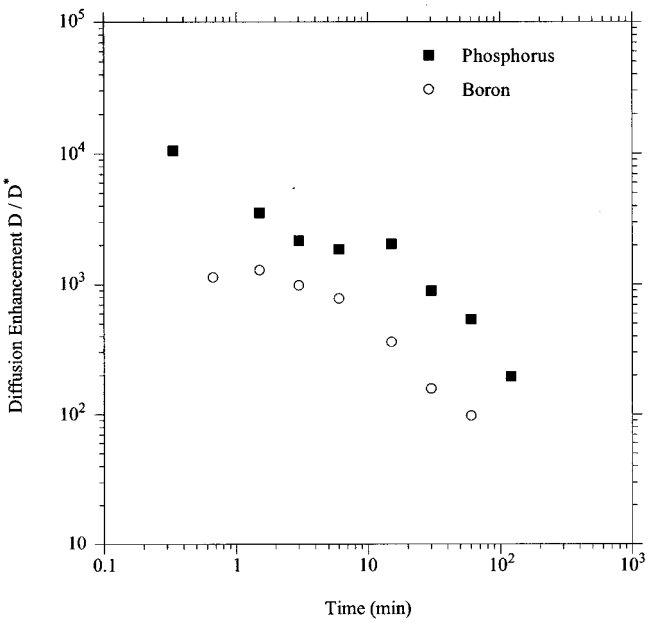


FIG. 2. Comparison of diffusion enhancements of boron and phosphorus for a 800 °C anneal as a function of time.

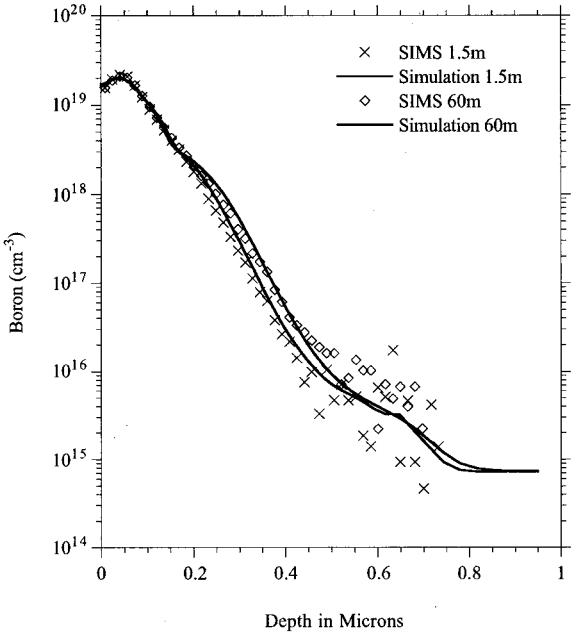


FIG. 3. Boron SIMS results at 800 °C showing the inactive portion of the profile and the results from FLOOPS used in extracting the best fit constant diffusivity.

of boron interstitial clusters (BICs) which have been reported previously[5] in doping superlattices during silicon implant damage annealing. The immobile, inactive portion of the profile was subtracted from the fitting by artificially setting solid-state solubility to the observed immobile concentration break point. Figure 3 shows the results of the boron SIMS and extracted fits.

The ratio of the phosphorus enhancement to the boron enhancement is larger than expected due to a simple analysis based on the fractional interstitialcy. As discussed in the introduction, the simple analysis would produce a difference in the enhancement of only 25%. The phosphorus is about an order of magnitude larger. There are two possible explanations. The first would be that the damage created is different due to the differing background species. The second is that boron and phosphorus interact with the interstitials differently. This data does not allow us to draw a conclusion about the mechanism.

The standard assumption is that the boron enhancement is proportional to the interstitial supersaturation (interstitial concentration divided by the equilibrium interstitial concentration, $C_I/C_I^*$). We can conclude that this assumption is dangerous. It is possible to conjecture mechanisms that can account for a diffusion enhancement less than the interstitial supersaturation, but it is difficult to suggest something that accounts for the enhancement to be greater than the defect supersaturation. This means that it is incorrect to assume that the boron diffusion enhancement is a correct measure of the excess interstitial supersaturation. Previous work has shown that boron clusters after silicon implants.[5] In extracting the data from these studies, the boron did not seem to move above a concentration of $2\times10^{18}$ cm$^{-3}$ at 800 °C. This indicates that boron may be clustered at this temperature, which can influence the annealing kinetics.

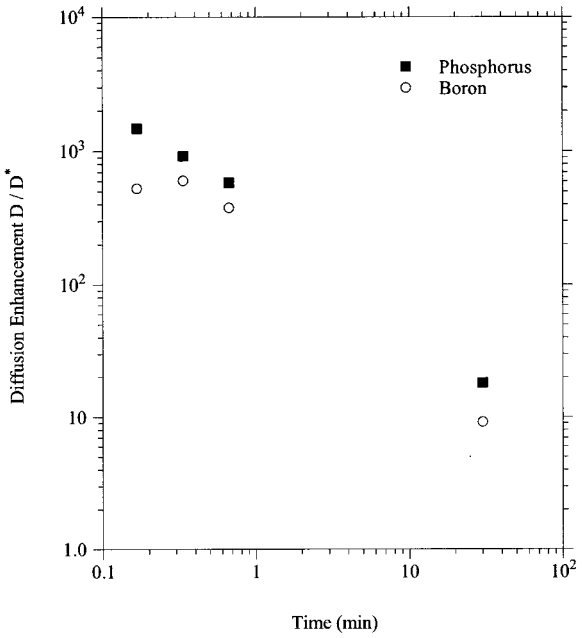


FIG. 4. Comparison of diffusion enhancements of boron and phosphorus for a 900 °C anneal as a function of time.

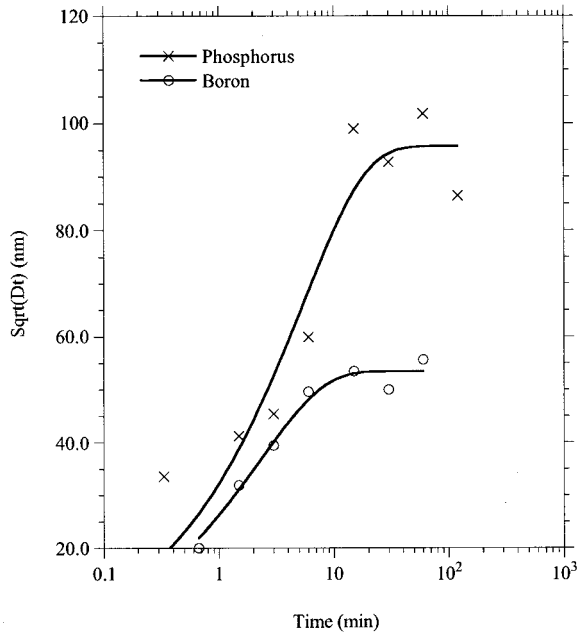


FIG. 6. Junction motion ($\sqrt{Dt}$) for boron and phosphorus at 800 °C. The fit is obtained assuming an exponential decay of the interstitial supersaturation.

Figure 4 shows diffusion enhancements for boron and phosphorus for the 900 °C anneals as a function of time. As at 800 °C, the boron enhancement is less than that for phosphorus. The boron tends again to look like it has a constant enhancement at short times, while the phosphorus enhancement drops linearly with time. Figure 5 shows the results for 1000 °C anneals as a function of time. At short times, the phosphorus enhancement is larger, although at long times the enhancement factor is the same. At these higher temperatures, it was not necessary to use an immobile fraction of the boron in performing fits. The boron appears to be declustered at these times and temperatures. No immobile fraction was observed, and the profiles were fit well by Gaussians.

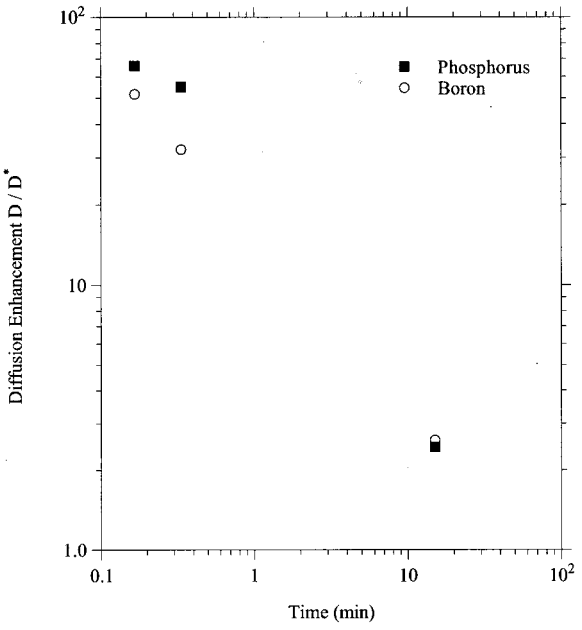


FIG. 5. Comparison of diffusion enhancements of boron and phosphorus for a 1000 °C anneal as a function of time.

Figure 6 shows $\sqrt{Dt}$ for the 800 °C anneal as a function of time. This plot is essentially a measure of the total junction shift during the annealing process. Analytic fits based on exponentially decaying diffusivity are also shown. The supersaturation time can be extracted from these plots by extracting the time decay of the diffusivity from the analytic best fit. Twice the decay time accounts for 90% of the junction motion, and is defined to be the saturation time of the damage enhancement. It is a rough measure of the time it takes to anneal the damage from the wafer. Similar plots and extraction were performed at all temperatures.

Figure 7 plots the extracted saturation time as a function of temperature for Arrhenius plot. Phosphorus requires a longer time to saturate than boron. Over temperature, this difference is about a factor of 5. The slope of the two curves is very similar, suggesting that the damage annealing in these samples is controlled by the same physical mechanism independent of the dopant species. This tends to suggest that the damage and its annealing is independent of the species, and that the main reason for the difference in the enhancement is differences in the species—defect interactions. The activation energy of the two curves is approximately 3.25 eV, which is similar to previously reported values of 3.6 eV.[6,7]

## DISLOCATION GROWTH RESULTS

Figure 8 shows the difference between the damaged and undamaged samples in the number of interstitials contained in the dislocation loop samples as a function of time and temperature. Error bars are estimates of the counting accuracy for the observed dislocation loop densities and sizes. A negative value indicates that the undamaged sample has a

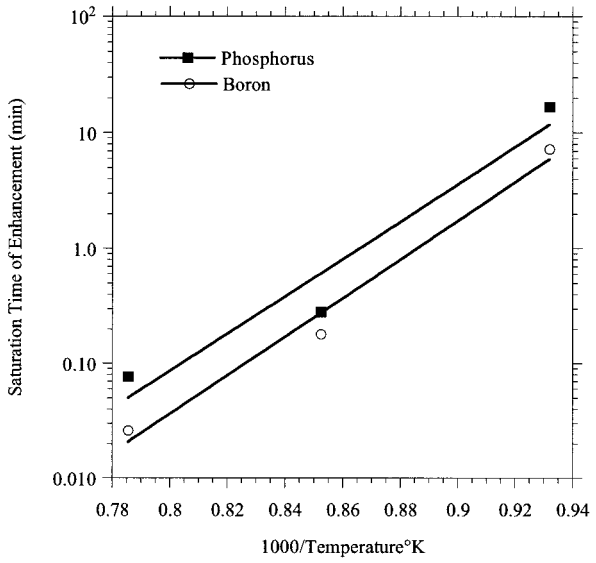


FIG. 7. Saturation time for diffusion for phosphorus and boron in Arrhenius plot.

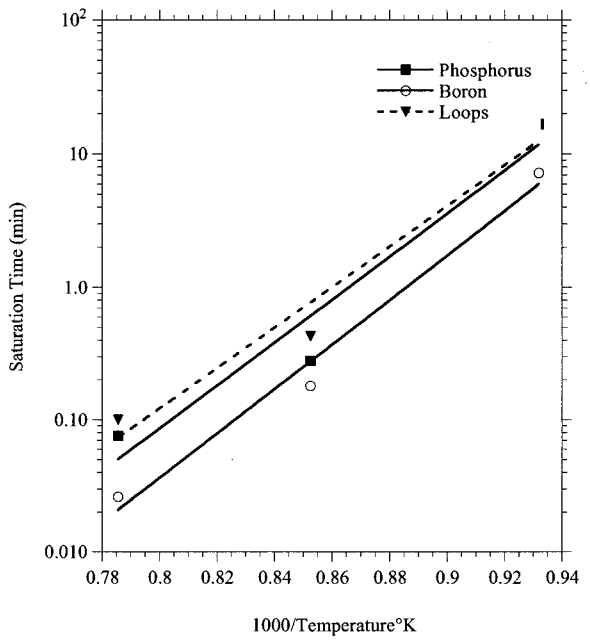


FIG. 9. Comparison of saturation times for dislocations, boron, and phosphorus.

greater atomic density than the damage sample. This could be caused by the capture of vacancies from the Frenkel pairs generated during the silicon damage implant. The damage generates an interstitial excess, which is captured by the dislocations in time. At longer times, as the interstitials release from the damaged region they are captured by the dislocation loops, resulting in a greater number of atoms contained in the dislocation loop layer in the damaged samples.

Figure 8 also shows the fits to this data assuming the interstitial concentration decays exponentially in time, and that the dislocation loops capture defects proportional to the supersaturation. These fits allow an extraction of the saturation time of dislocation loop growth. This saturation time is a measure of the damage annealing process. The extracted saturation times decrease with increasing temperature.

The number of atoms contained in the defects at long times increases with increasing temperature. At 1000 °C, the number of atoms contained is about 2.5 times the silicon implant dose. This value decreases with temperature to about 1.4 at 800 °C. At long times, the number of captured interstitials is greater than the simple ''plus 1'' rule of thumb often used.

The difference tends to saturate in time and become constant. Since the damage is annealing out, past the saturation time there will be few available interstitials to capture. At this point, the loop distribution stabilizes and no further change in the difference is observed. The saturation time seems to decrease with increasing temperature, which is consistent with the diffusion saturation times extracted in the previous section. Figure 4 also allows extraction of the saturation time of dislocation loop growth. This saturation time is a measure of the damage annealing process. The extracted saturation times decrease with increasing temperature.

Figure 9 shows a comparison of the dislocation loop saturation time with that obtained from diffusion of boron and phosphorus as a function of temperature. The loop saturation time is very similar to that obtained from the phosphorus diffusion data. At 800 °C, the times are within 10% of each other. The activation energy of the loop saturation time is 3.0 eV, which is slightly smaller than that for diffusion. Since the phosphorus and loop saturation times are very similar, this indicates that the controlling mechanism is damage annealing and not an interaction between species. It also indicates that boron, since it smaller, is influencing the annealing kinetics in some way. Again, it appears to be dan-

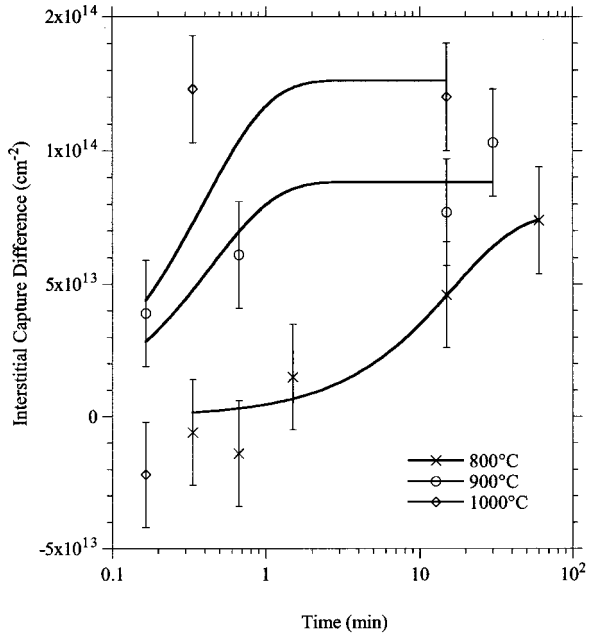


FIG. 8. Number of atoms contained in damaged samples minus the number in undamaged samples as a function of time and temperature. Saturation time fits for the dislocation capture assuming an exponential decay of the interstitial supersaturation are also shown.

gerous to use boron to investigate the interstitial excess during TED.

## CONCLUSIONS

TED has mostly been studied using boron marker layers. We have performed an experiment using boron, phosphorus, and dislocation markers to compare TED effects. This experiment shows that phosphorus is enhanced significantly more than boron during damage annealing. Dislocation growth indicates that a number of interstitials greater than the damage dose is captured during these anneals. The time to saturate the dislocation growth agrees well with phosphorus diffusion saturation, and is greater than the boron saturation.


## ACKNOWLEDGMENT

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[1] P. A. Packan and J. D. Plummer, J. Appl. Phys. **68**, 4327 (1990).
[2] P. Fahey, G. Barbuscia, M. Moslehi, and R. W. Dutton, Appl. Phys. Lett. **46**, 784 (1985).
[3] H. L. Meng, S. Prussin, and K. S. Jones, in *Point Defect Detector Studies of $Ge^+$ Implanted Silicon Upon Oxidation*, 1992 (unpublished).
[4] J. K. Listebarger, K. S. Jones, and J. A. Slinkman, J. Appl. Phys. **73**, 4815 (1993).
[5] P. A. Stolk, H. J. Gossmann, D. J. Eaglesham, D. C. Jacobson, and J. M. Poate, Appl. Phys. Lett. **66**, 568 (1995).
[6] D. J. Eaglesham, P. A. Stolk, H. J. Gossmann, and J. M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).
[7] P. A. Packan and J. D. Plummer, Appl. Phys. Lett. **56**, 1787 (1990).