

Diffusion of implanted nitrogen in silicon

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Growth of thinner gate oxides and their thickness control is one of many challenges in scaling technologies today. Nitrogen implantation can be used to control gate oxide thicknesses. This article reports a study on the fundamental behavior of nitrogen diffusion in silicon. Nitrogen was implanted as N_2^+ at a dose of 5×10^{13} ions/cm² at 40 and 200 keV through a 50 Å screen oxide into Czochralski silicon wafers. Furnace anneals at a range of temperatures from 650 to 1050 °C have revealed anomalous diffusion behavior. For the 40 keV implants, nitrogen diffuses very rapidly and segregates at the silicon/silicon-oxide interface. Qualitative modeling of this behavior is also discussed in terms of the time taken to create a mobile nitrogen interstitial through the kick-out, Frenkel pair, and the dissociative mechanisms. © 2000 American Institute of Physics. [S0021-8979(00)09205-7]

I. INTRODUCTION

Recently, it was shown that nitrogen implantation retards gate oxidation kinetics and thus can be used to grow thinner gate oxides.^{1,2} The nitrogen implantation process is especially useful if the process requires different gate oxide thicknesses across different parts of the wafer. While nitrogen has been used to grow ultrathin gate oxides, the physics of how this occurs is not yet well understood. Since the reduction in gate oxide thickness is due to the diffusion of nitrogen in silicon and its incorporation close to the Si/SiO₂ interface, it is important to understand the diffusion behavior of nitrogen in silicon.

II. EXPERIMENTAL ANALYSIS

In this study, we report the results and analysis of a study that was done on 40 and 200 keV N_2^+ implants into silicon. Nitrogen was implanted as N_2^+ at 40 keV into Czochralski silicon wafers at a dose of 5×10^{13} ions/cm² through a 50 Å screen oxide. The wafers were then furnace annealed under an inert ambient at 900 and 1050 °C for 15, 30, and 45 min. Secondary ion mass spectroscopy (SIMS) performed at Evans East, Inc., on these samples showed that there was no detectable nitrogen in the 900 °C samples even for the shortest anneal time of 15 min. This indicated that either the nitrogen had segregated to the silicon/silicon-oxide interface or had redistributed in the bulk. We then extracted a lower bound on the diffusivity value (1×10^{-3} cm²/s at 900 °C) and thus designed the second set of experiments to study nitrogen diffusion. The matrix chosen on this basis was 650 and 750 °C at 12, 30, and 120 min, respectively. Figures 1 and 2 show the SIMS plots for these cases. There are two interesting observations:

(1) The motion of the profile is anomalous and cannot be explained by conventional Fickian diffusion. While the peaks of the profiles decrease with increasing time, there is no spreading of the profile in the bulk with increasing time as one might expect. This behavior is much more rapid at 750 °C than at 650 °C. This shows that there is a large energy-dependent barrier to this anomalous diffusion.

(2) There is also a shift in the peak of the profile towards the surface with increasing time. This is interesting because this indicates that the nitrogen is being released (i.e., made mobile) deeper rather than closer to the surface. Figure 3 shows the plot of the extracted projected range of the profiles with time. Correlating Fig. 3 with Figs. 1 and 2, shows that the extent of shrinkage of the profile is more in the region that is deeper in the bulk rather than that closer to the surface.

It can be argued that the observed motion of nitrogen could be because of a high surface electrostatic attraction on the nitrogen atoms. In order to investigate this, a 200 keV N_2^+ implant was performed through a 50 Å screen oxide. These samples were then annealed at 750 °C for 12, 30, and 120 min under an inert ambient. Figure 4 shows the profiles. The same type of anomalous diffusion behavior is observed. In this case, any surface attraction force would have to operate at lengths much larger than the projected range of the 200 keV implant.

To investigate where the nitrogen goes to, a time-of-flight SIMS (TOF-SIMS) was performed on the 40 keV samples. It was observed that nearly 75% of the total number of as-implanted nitrogen counts was within 20 Å of the interface upon annealing at 750 °C, 120 min. This is consistent with the observation that nitrogen implantation leads to a retardation of the gate oxidation kinetics because one would expect that the nitrogen atoms have to be close to the SiO₂/Si interface to influence gate oxidation kinetics. Of course, a better quantification would be in terms of the inter-

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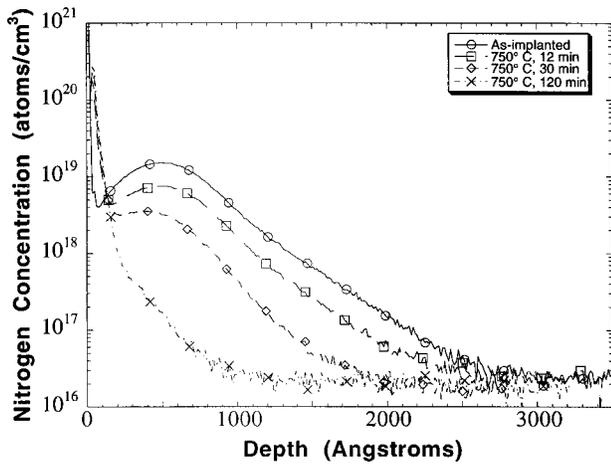


FIG. 1. SIMS profiles of 5E13, 40 keV, N_2^+ , 750 °C anneal samples.

facial nitrogen concentration itself. However, to do this a calibration of the TOF-SIMS equipment is necessary as nitrogen has few standards. This work is currently under progress.

Transmission electron microscopy (TEM) was performed on both the as-implanted samples and the samples annealed at 650 °C for 12 and 120 min and the samples annealed at 750 °C for 12 and 120 min. The TEM performed on the as-implanted samples did not show an amorphous layer. So, the dose used in this study was below amorphization. The TEMs performed on the annealed samples did not reveal any extended defects for any of the cases. Hence, there is no observable extended defect-assisted mechanism that could explain this diffusion behavior. This indicates that nitrogen does not conform to a “+1” type of model.³ Based on a “+1” model, we might expect to see some type of extended defect as these have been observed for boron and silicon implants into silicon.³ However, this is not the case for nitrogen.

III. MODELING

In order to explain the anomalous diffusion behavior of nitrogen in silicon, we propose that the diffusion of nitrogen in silicon is limited by the time taken to create a mobile

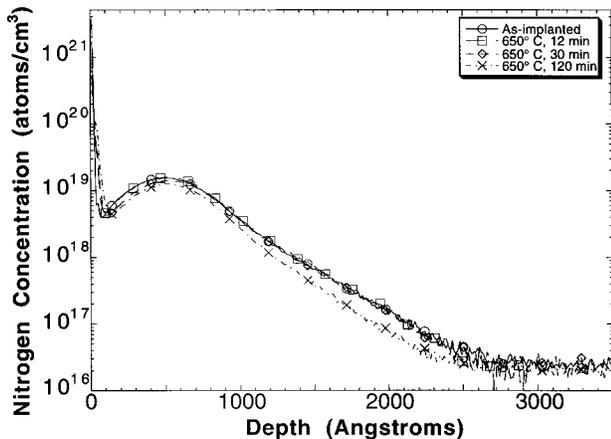


FIG. 2. SIMS profiles of 5E13, 40 keV, N_2^+ , 650 °C anneal samples.

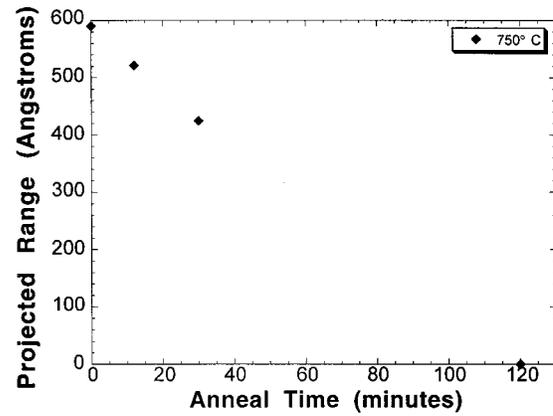


FIG. 3. Projected range for the profiles annealed at 750 °C. “0” on the time scale refers to the as-implanted profile.

nitrogen interstitial. Once the nitrogen goes mobile, it diffuses very rapidly and can be trapped at the surface. This proposition has similarities with metallic diffusion behavior.⁴⁻⁶ The proposed nitrogen diffusion model is based on the following reactions:

Reaction (1): $N_{\text{immobile}} + I = N_{\text{interstitial}}$,

Reaction (2): $I + V = 0$,

Reaction (3): $N_{\text{interstitial}} + V = N_{\text{immobile}}$.

Reactions (1), (2), and (3) were solved simultaneously for N_{immobile} , $N_{\text{interstitial}}$, I , V using very simple boundary conditions. The boundary condition is as shown below:

$$J_s = -k_r * C_{x=0} \tag{1}$$

In the above reactions, N_{immobile} refers to immobile nitrogen, I refers to a silicon self-interstitial, $N_{\text{interstitial}}$ refers to a nitrogen interstitial, J_s refers to the surface flux, k_r refers to the surface recombination velocity, and $C_{x=0}$ refers to the surface concentration of the species considered. The effect of a sink at the SiO_2/Si interface is modeled by the boundary condition Eq. (1), as any nitrogen atom that reaches the Si surface is removed from the system. The self-interstitial and vacancy profiles were obtained from the damage profile of a

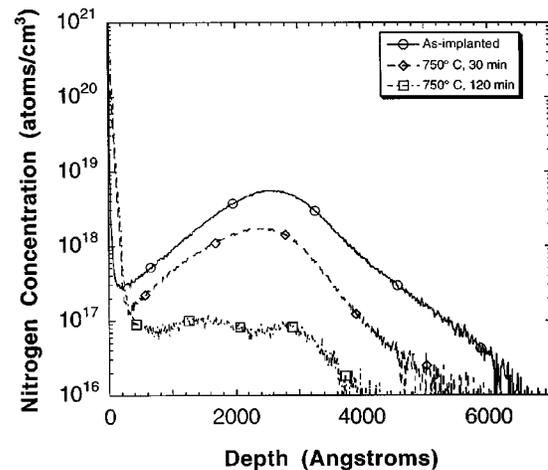


FIG. 4. SIMS for 200 keV profiles.

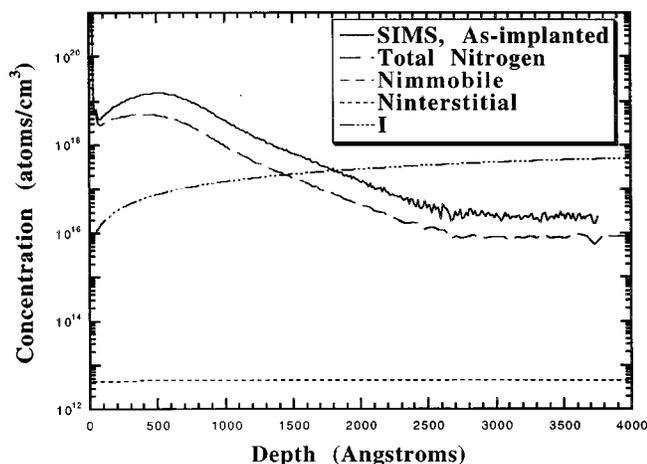


FIG. 5. Simulation results.

UT-MARLOWE (Ref. 7) simulation that was tuned according to the boron-to-nitrogen mass ratio with a correction factor that was less than 20%. It has to be mentioned here that we feel we could have reasonable confidence in the damage profiles as predicted by UT-MARLOWE because we were able to get good agreement with SIMS over a range of doses and energies (not reported here) using the same boron-to-nitrogen ratio as mentioned above.

By varying the reaction rates of reactions (1) and (3) and solving the appropriate equations numerically using the process simulator, the Florida Object Oriented Process Simulator (FLOOPS),⁸ we were able to get qualitative agreement with the observed anomalous behavior as shown in Fig. 5. This was because the reaction rates were such that it produced a self-interstitial gradient towards the surface over the depth range of the total nitrogen profile. This in turn produced a nitrogen interstitial gradient towards the surface through the knockout reaction, reaction (1). Since the diffusivity of the nitrogen interstitial is very high, the gradient of the nitrogen interstitial towards the surface is not observable on the scale of the plots in Fig. 5. Furthermore, since the nitrogen interstitial concentration is much less than the immobile nitrogen concentration, the concentration of total nitrogen is almost the same as that of the immobile nitrogen. Hence, the profiles for the N_{immobile} and total nitrogen are on top of each other in Fig. 5. However, the nitrogen interstitial is the only nitrogen-related mobile species in the system of reactions considered. Therefore, a nitrogen interstitial gradient towards the surface implies the total nitrogen profile has to shift towards the surface with time. Since the vacancy diffusivity is faster than the self-interstitial diffusivity,⁸ the vacancy profile is below the concentration range of Fig. 5 and, hence, not observable in Fig. 5. As can be seen from Fig. 5, the simulations were able to capture the following effects:

(a) the peaks decreasing in concentration with increasing anneal time;

(b) the profile shrinking with increasing anneal time; and
 (c) the peaks shifting towards the surface with increasing anneal time.

However, the simulations did not predict the time dependence correctly. The profiles in Fig. 5 were obtained after a simulation anneal of 10 s at 750 °C. Since the self-interstitial profile is not large enough to sustain the knockout reaction, reaction (1), in the forward direction, there was no change in the immobile nitrogen profile and, consequently, no change in the total nitrogen profile beyond 10 s. This implies the reactions were proceeding too fast although the gradients were consistent with what we would expect if the total nitrogen profile were to move towards the surface with anneal time. This model needs to be improved and its development is under progress. It is possible that a more complex model might be required to predict the behavior of nitrogen diffusion.

IV. CONCLUSION

In summary, the annealing of 40 keV samples shows that the diffusion behavior is anomalous and cannot be explained by conventional Fickian theory. On a comparison between the 650 °C and the 750 °C samples, we observe that the peaks shift towards the surface and simultaneously the whole profile shrinks. Similar diffusion behavior exists for 200 keV implants. Preliminary diffusion modeling is based on the proposition that the diffusion of nitrogen is limited by the time taken to create a mobile nitrogen interstitial. Qualitative agreement with the observed anomalous diffusion behavior was obtained on the basis of this idea. TEM performed on the samples did not reveal any observable extended defects indicating that there is no obvious extended defect-assisted mechanism to explain this anomalous diffusion behavior. Time-of-flight SIMS indicated that 75% of the total number of as-implanted nitrogen counts is at the interface after a 750 °C, 120 min anneal.

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¹C. T. Liu, Y. Ma, J. Becerro, S. Nakahara, D. J. Eaglesham, and S. J. Hillenius, *IEEE Electron Device Lett.* **18**, 105 (1997).

²C. T. Liu, E. J. Lloyd, Y. Ma, M. Du, R. L. Opila, and S. J. Hillenius, *Tech. Dig. Int. Electron Devices Meet.*, 499 (1996).

³D. J. Eaglesham, P. A. Stolk, H.-J. Gossmann, and J. M. Poate, *Appl. Phys. Lett.* **65**, 2305 (1994).

⁴H. Zimmermann and H. Ryssel, *Appl. Phys. A: Solids Surf.* **55**, 121 (1992).

⁵U. Gösele, W. Frank, and A. Seeger, *Appl. Phys.* **23**, 361 (1980).

⁶G. B. Bronner and J. D. Plummer, *J. Appl. Phys.* **61**, 5286 (1987).

⁷UT-MARLOWE, version 4.1, manual, University of Texas, Austin, Texas, January 30, 1998.

⁸M. E. Law and S. M. Cea, *Comput. Mater. Sci.* **12**, 289 (1998).