Quantitative Measurement of Interstitial Flux and Surface Super-saturation during Oxidation of Silicon

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Abstract

During the oxidation of silicon, interstitials are generated at the oxidizing surface and diffuse into the silicon. Boron diffusion was used to map the local interstitial super-saturation, the ratio of interstitial concentration to the equilibrium concentration of interstitials I/I^*, versus depth above buried $Si_{0.795}Ge_{0.2}C_{0.005}$ layers during oxidation. The average interstitial super-saturation at the silicon surface, extrapolated from the depth profiles, is measured as, ~24 and ~11.5 for 750°C and 850°C respectively. Using the measured interstitial concentration at the surface, the silicon interstitial injection into the silicon is calculated for oxidation at 750°C and 850°C. Finally, it is found that the surface boundary condition remains fixed over an interstitial injection rate ranging over 4 orders of magnitude.

Introduction

Recent reports indicate that the introduction of carbon in silicon can suppress the local interstitial concentration and effectively sink interstitials generated either by ion implantation or oxidation [1,2]. In this paper, we describe the use of this property of substitutional carbon in $Si_{0.795}Ge_{0.2}C_{0.005}$ layers to experimentally determine the profile of interstitial atoms during oxidation of silicon. Combining this with previous measurements of the interstitial transport product allows us to determine the number of interstitials injected into the silicon during oxidation at 750°C and 850°C.

Experiment & Discussion

Test structures were grown to measure the local boron diffusivity throughout the surface region of samples containing zero (sample A), one (sample B), or two (sample C) buried $Si_{0.795}Ge_{0.2}C_{0.005}$. The test structures were grown epitaxially using rapid thermal chemical vapor deposition (RTCVD) at temperatures between 600°C and 750°C using dichlorosilane, germane, and methylsilane as the silicon, germanium and carbon sources respectively [3]. Each of the three test structures were grown on top of p-type Czochralski (CZ) (100) silicon wafers. The three different test structures were grown with four 25 nm thick boron marker layers that had peak concentrations of $4\text{-}9 \times 10^{18}$ cm^{-3} centered below the surface at 150, 450, 600, and 900 nm depths. Sample B was grown with one 20 nm thick $Si_{0.795}Ge_{0.2}C_{0.005}$ layer between the boron layers centered at 675 nm below the surface; and sample C was grown with two 20 nm thick $Si_{0.795}Ge_{0.2}C_{0.005}$ layers centered at 300, and 675 nm below the surface. All as-grown boron concentration profiles are shown in figures 1a, b, and c, and the location of the $Si_{0.795}Ge_{0.2}C_{0.005}$ layers are indicated by the carbon concentration profiles. Depths of the boron layers differed from the nominal values, unintentionally, as much as 15% sample to sample.

All test structures were cleaved and annealed in oxygen or nitrogen ambient for various times between 30 and 960 minutes at 750°C or 850°C and the resulting boron, carbon, germanium and oxygen profiles were obtained using secondary ion mass spectrometry (SIMS) done at Evans East in East Windsor, NJ. Samples were sputtered using 2 keV Cs^+ ions, and depths were determined using standard profilometry of the sputtered craters leading to a 5% uncertainty in depths and a 20% uncertainty in boron concentrations. The oxide growth rates measured by ellipsometry were 0.33 Å/min and 0.91 Å/min at 750°C and 850°C respectively, in agreement with previous reports of thin silicon oxide films [4,5].

Boron profiles of the pure silicon structure (sample A) after annealing at 850°C for 30 minutes in oxygen or nitrogen ambient are noticeably broader than the as-grown case (fig 1a). Moreover, the boron profiles in sample A after annealing in oxygen ambient are clearly broader, at all depths, than those after nitrogen anneal for the same time and temperature, indicative of the well documented oxygen enhanced diffusion effect [6]. Boron profiles in the two samples containing $Si_{0.795}Ge_{0.2}C_{0.005}$ layers before and after annealing in the identical conditions as in sample A (Fig. 1(a)) show different behavior above and below the buried $Si_{0.795}Ge_{0.2}C_{0.005}$ layers (Fig. 1(b), (c)).

(a)   (b)   (c)
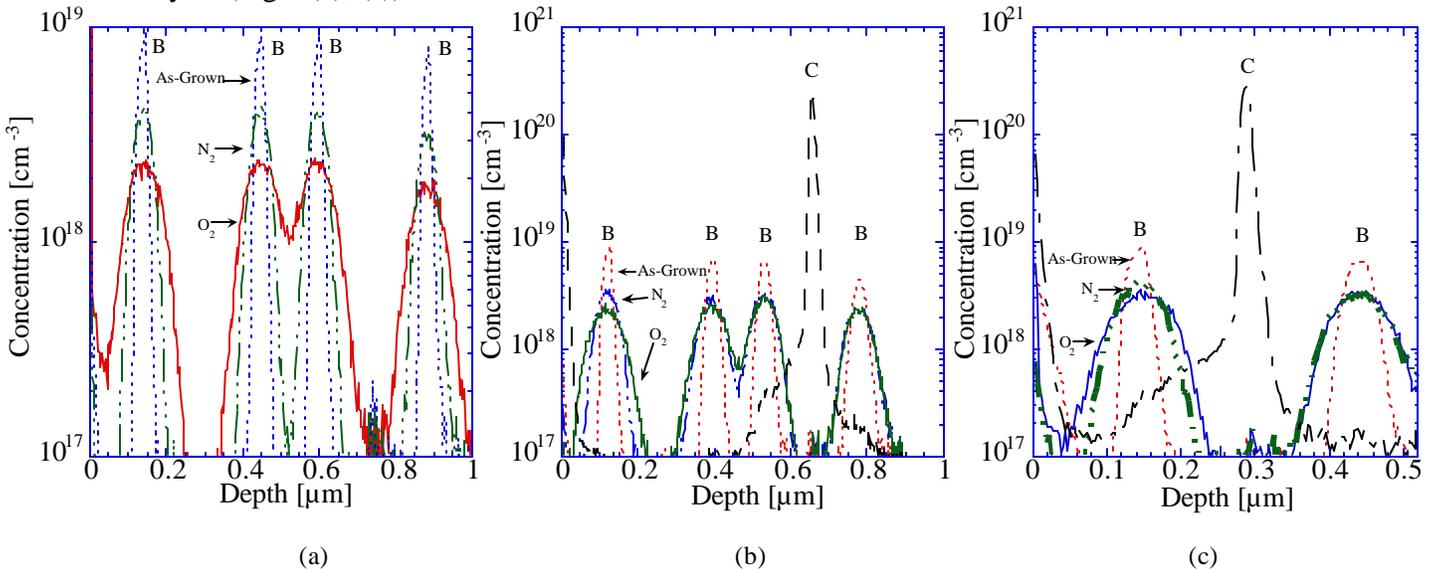
Figure 1: Boron profiles, by SIMS, of as-grown samples and samples annealed in either nitrogen or oxygen ambients at 850°C for 30 minutes with as-grown carbon profiles to indicate where the SiGeC layers were located. Samples A, B, and C containing 0, 1, and 2 SiGeC layers between the boron diffusion markers are shown (a, b, and c respectively). The solid lines correspond to annealing in oxygen ambient.

Boron profiles below the $Si_{0.795}Ge_{0.2}C_{0.005}$ layers after 30 minutes of oxidation are identical to those after nitrogen anneal. As reported previously, the carbon layer prohibits interaction between the injected interstitials from the surface region and the boron below the carbon layer for this oxidation condition [2]. Boron profiles after oxidation above the $Si_{0.795}Ge_{0.2}C_{0.005}$ layers are, however, broader than their respective counterparts annealed in nitrogen ambient. The differences in boron profile widths after oxidation versus nitrogen anneals, from marker to marker, are not however uniform. The profiles are clearly broader the nearer the boron marker is to the surface (Fig. 1(b)).

Average local boron diffusivities during annealing for each individual boron marker were estimated by fitting each experimental boron concentration profile to boron concentration

profiles simulated using the process simulator PROPHET [7]. Annealed profiles were simulated using the as-grown boron concentration profiles, determined by SIMS, as the boron concentration initial conditions. All diffusivity estimates were done using a single diffusion enhancement variable as the fitting parameter, and average boron diffusivities during nitrogen anneals (sample A), extracted this way, agreed within the uncertainty of the measurement with those previously reported [8].

For boron in silicon at temperatures near 800°C, boron diffusion is nearly entirely through an interstitial mechanism [9], therefore, the observed average boron diffusivity enhancement can be used as a measure of the local interstitial super-saturation:

$$\frac{D_B^{meas}}{D_B^*} \cong \frac{I}{I^*} \qquad\qquad (1)$$

where $\dfrac{D_B^{meas}}{D_B^*}$ is average boron diffusivity enhancement during oxidation with respect to intrinsic diffusion (* indicates intrinsic value taken from literature), $\dfrac{I}{I^*}$ is the interstitial super-saturation.

Linear fits of the relative interstitial concentration above the $Si_{0.795}Ge_{0.2}C_{0.005}$, as deduced from the local boron diffusivities, are extrapolated to the surface of the silicon/oxide interface and show that the interstitial concentration at the surface, $n_{surf} = \dfrac{I_{surf}}{I^*}$, is nearly the same as that of the sample without buried $Si_{0.795}Ge_{0.2}C_{0.005}$ layers (sample A) for oxidation times of 240 and 30 minutes at 750°C and 850°C, respectively, (Fig. 2).
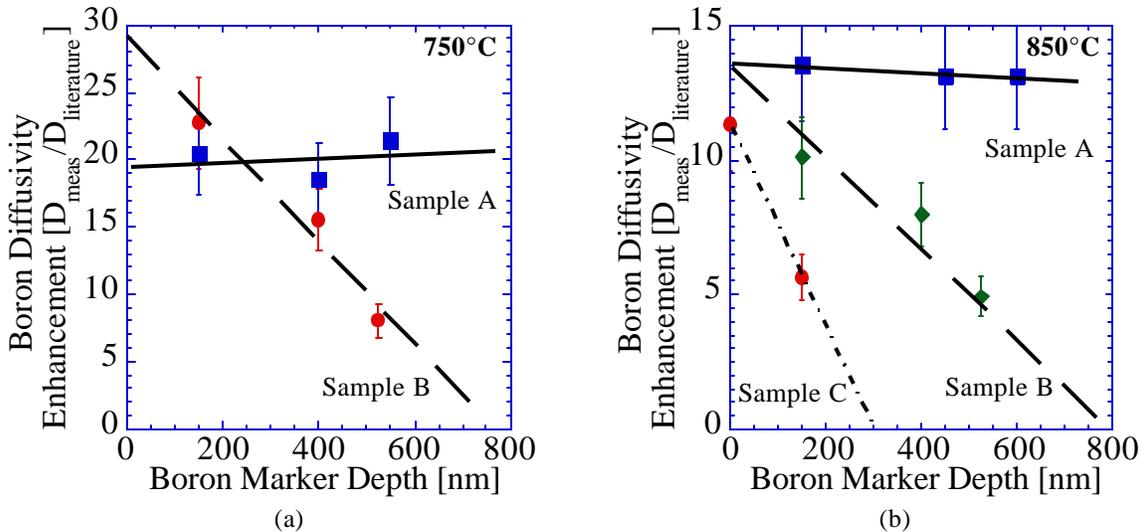
Figure 2: Fitted boron diffusivity enhancements for all the samples and their marker depths are shown for oxidations at (a) 750°C and (b) 850°C for 240 and 30 minutes, respectively. Diffusivities varied by less than 10% over all oxidation times examined.

For all times examined, 240-960 minutes at 750°C and 30-120 minutes at 850°C, the measured diffusivities at their respective locations varied no more than 10%. The interstitial saturation at the surface, extrapolated from the diffusivity profiles like that shown in figure 2a and b, are shown in figure 3a. The uncertainty of the extrapolated interstitial surface

concentrations, resulting from the uncertainty in the best linear fits, is indicated by the error bars in figure 3a. For all oxidation times all the interstitial concentration at the surface are measured within 20% of the average values, ~24 and ~11.5 for 750°C and 850°C, respectively, within the uncertainty of the measurement. The interstitial surface concentration remains, therefore, relatively constant regardless of the proximity of the SiGeC layer and no further conclusions are made about the observed surface concentration variations from the observed average concentrations.

The interstitial concentration profiles may, moreover, be used to deduce an interstitial flux in combination with the interstitial transport product $D_I^* I^*$ that has been measured using metal tracer diffusion [10]. The silicon interstitial flux injected into the silicon may be described by,

$$J_I = -D_I^* \frac{dI}{dx} = n_{surf} \times \frac{D_I^* I^*}{\Delta x} \tag{2}$$

where Δx is the depth of the $Si_{0.795}Ge_{0.2}C_{0.005}$ layer, and n_{surf} is the experimentally obtained relative interstitial super-saturation at the surface (fig 3a). Assuming that the interstitial concentration at the SiGeC layer is near zero [1,11], the total number of injected interstitials for samples B and C may be calculated by integrating the interstitial flux injected during oxidation (eq'n. 2) over the oxidation time of 120 minutes (fig. 3(b)). For comparison the injected number of interstitials for the pure silicon sample (A) is estimated assuming a constant surface boundary condition. The resulting interstitial concentration in the silicon can therefore be described by an erfc(x) function, which is integrated to find the total number of injected interstitials for the pure silicon case, sample A (fig. 3b). Literature values for the silicon interstitial diffusivity and equilibrium interstitial concentration were used [10].
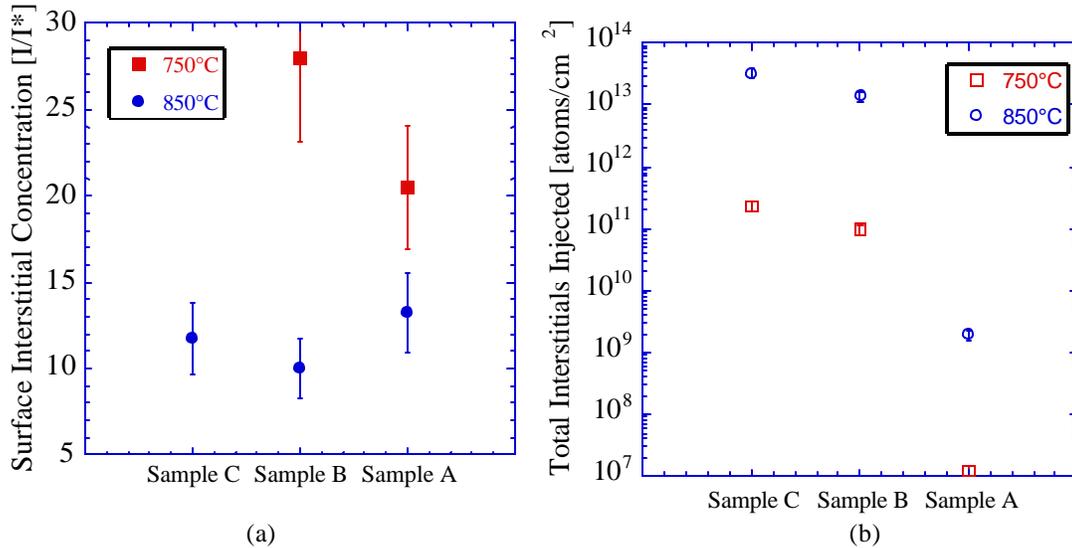
Figure 3: (a) relative interstitial super-saturation at the surface of the silicon during oxidation estimated from the boron diffusivity enhancement profiles, and (b) the total injected interstitial atoms into the silicon after 120 minutes of oxidation for both temperatures calculated using the measured surface super-saturation.

Samples B and C (those with buried SiGeC layers) show a significant increase in interstitial flux into the silicon bulk compared to sample A (pure silicon) in figure 3b. The

interstitial flux into the silicon bulk is assumed governed by simple diffusion and is therefore determined entirely by the difference of interstitial concentrations at the surface (observed to be constant) and in the region directly below the surface. The calculated increase of interstitial injection (fig. 3b) due to the proximity of the SiGeC layer is, therefore, because the SiGeC layer acts as a local sink for injected interstitials reducing the interstitial concentration in the region directly below the surface, which in turn draws more interstitials from the surface into the bulk. When there is no interstitial sink present, the interstitial concentration in the surface region increases to a concentration near the surface concentration, which then reduces the overall interstitial flux into the silicon from the surface (sample A, pure silicon).

Recently, the interstitial flux due to oxidation was also measured by monitoring the growth of type II loop defects that strongly interact with nearby silicon interstitials under different annealing conditions [12]. The interstitial flux was, therefore, measured by the growth of defect loops formed approximately 110 nm below the oxide/silicon surface, which consumed 84% of the injected interstitials [5]. To compare the two works, the expected number of interstitials injected into the bulk for the loop defect experiment is estimated assuming that the measured interstitial super-saturation is fixed at the surface (~9.5 and 11.5, B and C respectively) and the interstitial concentration is near zero at the reported loop depth. The comparison is made for the measured super-saturations for two samples B and C for times of 30, 60 and 120 minutes (fig 4). The estimated interstitial injection is slightly less than that reported, however, the disagreement is well within the error of either measurement.
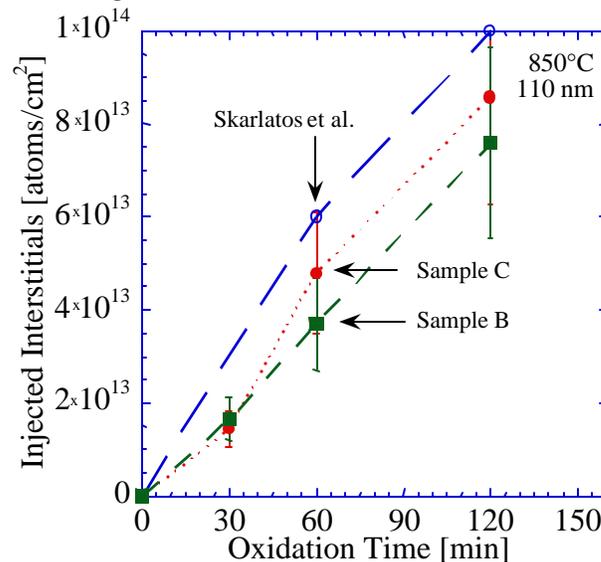
Figure 4: The total number of injected silicon interstitials after oxidation measured using the boron marker method (this work) is compared to that measured using type II loop defects at a depth of 110nm in the work by Skarlatos et al [5].

No comparison was available for 750°C, which may be because the number of injected interstitials is far below the currently reported resolution of the loop defect method of 2-3x10^{13} atoms/cm^2. No comparison for sample A (pure silicon) is made because the loop defects perturb the interstitial concentration below the surface and therefore are not representative of case A (pure silicon, no interstitial sink).

The observation that the surface super-saturation of interstitials remains unchanged despite an increase of the total number of injected silicon interstitials of more than 4 orders of magnitude is in agreement with the proposed oxidation model by Dunham [13] that predicts that the interstitial concentration at the silicon surface is pinned by a large reservoir of silicon interstitials that form and reside at the oxide/silicon interface above the silicon surface. This demonstrates the stiffness of the surface boundary condition during oxidation and shows that the surface concentration of interstitials in the silicon is, therefore, determined solely by the segregation of interstitials between the surface and the interstitial reservoir at the silicon/oxide interface created by the oxidation.

Conclusion

In conclusion, the average boron diffusivity during oxidation above carbon rich $Si_{0.795}Ge_{0.2}C_{0.005}$ layers has been used to quantify the total number of interstitials injected into the silicon substrate by determining the interstitial super-saturation concentration at the surface for 750°C and 850°C. The average interstitial super-saturation concentration is found not to depend on the rate of interstitials injection in the bulk silicon, despite increasing the total number of injected interstitials by 4 orders of magnitude.

Acknowledgements

References

[1] R. F. Scholz, P. Werner, U. Gosele, T. Y. Tan, Appl. Phys. Lett. 74, 392 (1999)
[2] M. S. Carroll, C-L. Chang, J. C. Sturm, T. Buyuklimanli, Appl. Phys. Lett. 73, (3695)
[3] J. C. Sturm, P. V. Schwartz, E. J. Prinz, H. Manoharan, J. Vac. Sci. Tech. B9, 2011 (1991)
[4] E. A. Irene, J. Electrochem. Soc. 125, 1708 (1978)
[5] D. Skarlatos, M. Omri, A. Claverie, D. Tsoukalas, J. Electrochem. Soc. 146, 1999 (2276-2283)
[6] D. A. Antoniadis, I. Moskowitz, J. Appl. Phys. 53, 6788 (1982)
[7] M. R. Pinto, D. M. Boulin, C. S. Rafferty, R. K. Smith, W. M. Coughran Jr., I. C. Kizilyalli, and M. J. Thoma, in Tech. Digest IEDM, 1992, p923.
[8] Fair R. B., 1981a, in Processing Technologies, edited by D. Khang, Applied Solid State Science, Supplement 2B, (Academic, NY). Pg. 1.
[9] H-J. Gossmann, T. E. Haynes, P. A. Stolk, D. C. Jacobson, G. H. Gilmer, J. M Poate, H. S. Luftman, T. K. Mogi, M. O. Thompson, Appl. Phys. Lett. 71, 3862 (1997)
[10] H. Bracht, N. A. Stolwijk, H. Mehrer, Phys. Rev. B 52, 16542 (1995)
[11] P. Werner, H-J. Gossmann, D. C. Jacobson, U. Gosele, Appl. Phys. Lett. 73, 2465 (1998)
[12] D. Tsoukalas, private communication.
[13] S. T. Dunham, J. Appl. Phys. 71, 685 (1992)