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Quantitative Measurement of Reduction of Phosphorus Diffusion by Substitutional Carbon Incorporation

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Abstract

Complete suppression of transient enhanced boron diffusion (TED) and oxidation enhanced boron diffusion (OED) in silicon have been achieved using substitutional carbon to reduce the excess point defect concentration in the dopant region [1]. Recent efforts have focused on removing the carbon from the active regions of the device [2,3] to avoid device degradation due to electrically active carbon defects [4] and exploring remote carbon's effect on boron TED and OED, while using the boron diffusion to probe point defect concentrations.

In this paper we measure quantitatively the effect of remotely located carbon on phosphorus and boron diffusion above a buried SiGeC layer at 850°C in oxygen or nitrogen ambients. Remote carbon, located 1250 Å below the phosphorus edge, is found to reduce the phosphorus diffusion enhancement factor due to OED from 8 to 2. The effect of the remotely located SiGeC buried layer on the excess interstitial concentration profile, which is responsible for the enhanced dopant diffusion, is probed by measuring boron and phosphorus diffusivites of in-situ doped boron and phosphorus layers above a buried SiGe(C) layer after oxidation or nitrogen anneals at 850°C. The enhanced boron diffusivity during oxidation is found to have a near linear dependence on depth ranging from 5-1.25. Finally, using x-ray diffraction and photoluminescence measurements of as-grown, buried, strained SiGe(C) structures and annealed SiGe(C) structures in oxygen or nitrogen ambient at 850°C the number of substitutional carbon atoms effectively consumed by oxidation is unambiguously correlated to the absolute number of injected interstitials using published values for the interstitial injection rate during oxidation [5].

Introduction

As silicon devices are continuously scaled to smaller sizes, there is an ever greater demand to reduce the diffusion of dopants. However, the enhancement of boron diffusion due to ion implant damage and oxidation, transient enhanced diffusion (TED) and oxidation enhanced diffusion (OED), poses severe challenges to this goal. It is generally accepted that boron and phosphorus diffuse primarily via an interstitial mechanism and the two dopant diffusivites are, therefore, dependent on the silicon interstitial concentration. Ion implant damage and oxidation are sources of excess interstitials which enhance the diffusivity. Therefore the reduction of TED and OED depend on the effective ability to trap or annihilate any excess interstitials that are produced during processing. Interest in the relationship between carbon and enhanced boron diffusion was recently spurred after TED was observed to strongly depend on the concentration of substitutional carbon in silicon [6], and in SiGe alloys [4,7]. Interstitial carbon can, however, introduce undesirable stable electrical defects which can degrade device quality [4,8], and therefore, the effects of remotely located substititutional carbon on boron OED and TED are being examined [2,3]. This work quantifies the dependence of phosphorus and boron diffusion above a SiGeC layer where point defects, interstitials, are injected during oxidation. Introduction of a remote, buried, SiGeC layer located below a doped surface region is found to reduce OED of both boron and phosphorus markers in the overlying region. A non-uniform interstitial profile is observed during oxidation in samples with buried SiGeC, determined using dopant diffusivities as a probe to monitor the excess interstitial concentrations in the surface region. Dopant diffusivities are found to depend on the substitutional carbon concentrations in the buried SiGeC layer, and lower carbon concentrations are observed to be saturated by the dose of injected point defects. A deeper understanding of the point defect relationship with the substitutional carbon in the SiGeC layer is, therefore, desirable in order to determine the necessary carbon concentrations to optimize the reduction of boron and phosphorus OED and TED both above and below the remote SiGeC layer. The substitutional carbon dependence on point defect injection is, therefore, examined using x-ray diffraction and photoluminescence measurements of the SiGeC layer. The deduced substitutional carbon concentration is found to linearly depend on time of oxidation and the dependence on oxidation time is compared with the expected net interstitial dose injected during oxidation [8] to determine a relationship betweeen injected interstitials and substitutional carbon consumed. A ratio of one injected interstitial to 1.85 ± 0.7 substitutional carbons effectively removed from their substitutional sites is found.

Experiment

All test structures were grown using rapid thermal chemical vapor deposition (RTCVD) [7], between 600 and 750°C using methylsilane as the carbon source. In test structure A, see figure 1 (a), two boron doped silicon layers and one phosphorus layer at the surface with and without a $Si_{1-x-y}Ge_xC_y$ or $Si_{1-x}Ge_x$ layer placed between the boron layers were used to test the effect of the alloy layers on dopant diffusivities at different locations (above and below) with respect to the SiGe(C) layer. The phosphorus layer was grown 650Å thick and doped to $1x10^{19}/cm^{-3}$, immediately below the surface. Both boron peaks were approximately 250Å thick and were grown to have a peak boron concentration of $5x10^{19}/cm^3$ centered 2000Å and 3000Å away from the surface respectively, while the 250Å thick SiGe(C) layer was centered 2300Å from the surface.

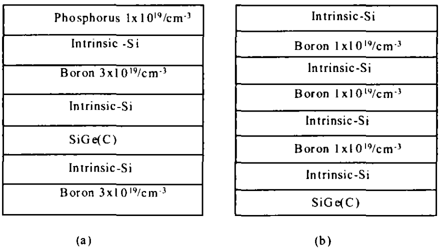
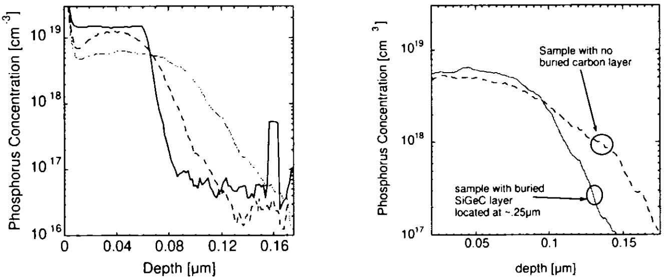


Figure 1 (a) Test structure to study boron and phosphorus oxidation enhanced diffusion. This paper discusses only the top phosphorus edge and deepest boron marker. (b) Test structure to examine the resulting non-uniform interstitial profile during oxidation resulting from introduction of the buried SiGeC layer 6000 Å below the surface

To quantify dopant OED dependence on substitutional carbon level as-grown samples were cleaved and annealed in nitrogen and oxygen ambient atmospheres at 850°C for 30 minutes. The phosphorus and boron profiles were characterized using secondary ion mass spectroscopy (SIMS) with 2 KeV Cs^+ ions and an estimated 1-5% error in depth scales. The effect of the substitutional carbon incorporation on the boron diffusion below the SiGe(C) layer has previously been reported [2]. Boron diffusion above the SiGeC layer is complicated by diffusion across the alloy interface and segregation effects, so the discussion and quantification of its diffusion is neglected in this paper. Figure 2a shows profiles of the



(a) (b)

Figure 2 (a) Phosphorus concentration profiles (measured using SIMS) of as-grown all-silicon sample and all-silicon samples annealed at 850°C for 30 minutes in nitrogen and oxygen ambient. Phosphorus OED indicated by deeper phosphorus profile after anneal in oxygen ambient. (b) Phosphorus profiles of all-silicon sample overlaid on phosphorus profile of sample with buried 200 Å thick $Si_{0.795}Ge_{0.20}C_{0.005}$ layer both annealed at 850°C for 30 minutes in an oxygen ambient. Note phosphorus OED is reduced in case with buried SiGeC sample.

overlying phosphorus edge in an all-silicon control sample, with a background carbon concentration below SIMS detection limits. Broadening of the phosphorus edge is observed after the nitrogen anneal, and in the oxidation case clear enhancement of the phosphorus diffusion is observed by the deeper location of the phosphorus. In order to quantify the observed reduction in diffusivity the profiles were modeled using a numerical simulator PROPHET, obtained from Lucent technologies, to quantitatively compare numerically simulated dopant profiles and those obtained by SIMS profiling.

In this case, the phosphorus diffusivity during oxidation is found to be 8 times that of the average phosphorus diffusivity during the nitrogen anneal. In figure 2b, the phosphorus profiles after oxidation in the all-silicon case and that with a buried $Si_{0.795}Ge_{0.20}C_{0.005}$ are overlain. A 4x reduction of phosphorus diffusion in the sample containing the buried SiGeC under the same oxidizing conditions is observed, even when the SiGeC layer is buried 1500Å below the phosphorus edge. A summary of the measured diffusivities after oxidation relative to the measured diffusivities after the nitrogen anneal are shown in figure 3 for the silicon case and two carbon concentrations of 0.05% and 0.5%.

OED of boron in the marker located below the SiGeC region was observed to be completely supressed in the 0.5% carbon case but not in the 0.05% carbon case [2], this indicates that in the 0.05% case some interstitials injected at the surface, during oxidation, passed through the SiGeC blocking layer, whereas in the 0.5% case approximately all excess interstitials injected during oxidation were reacted before penetrating to the underlying silicon region. The interstitial concentration above and below the SiGeC layer is seen to depend on the reaction efficiency of the SiGeC layer with the injected interstitials.

A second test structure was epitaxially grown to examine the depth dependence of the diffusivity between the surface and the SiGeC layer during oxidation, (fig. 1b). Three boron markers are located above a buried $Si_{0.795}Ge_{0.20}C_{0.005}$ layer to probe the interstitial

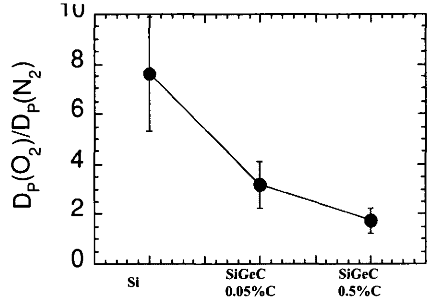


Figure 3 Relative phosphorus diffusivity dependence on carbon levels in buried SiGe(C) layer. Average diffusivity during anneal at 850°C for 30 min in oxygen ambient is compared to that measured in nitrogen ambient.

concentration in the surface region. As-grown samples were cleaved and annealed for 120 minutes at 850°C in oxygen and nitrogen ambients, see figure 4. Broadening of the as-grown peak is observed in both the nitrogen and the oxygen cases, however the boron profiles in the oxidation case are clearly broader than those in the nitrogen anneal. After oxidation, the width of the three diffused boron markers is clearly not uniform over the depth from surface to the SiGeC alloy layer. The boron profile closer to the surface is clearly broader and its peak concentration is lower than those markers located closer to the SiGeC layer. Boron diffusivities are extracted from the boron profiles and the diffusivity is observed to have a near linear dependence on depth, see figure 4.

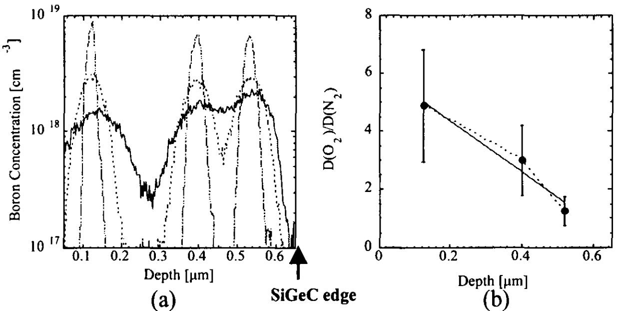
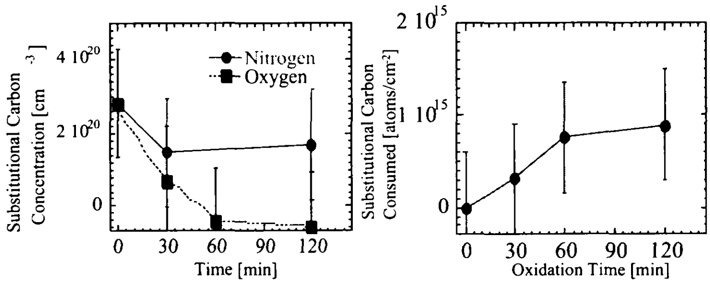


Figure 4 (a) Boron concentration profiles of as-grown samples with a 200 Å buried $Si_{0.795}Ge_{0.20}C_{0.005}$ layer centered at 0.7 microns below the surface (centered at the edge of figure 4a), and those of the same as-grown samples annealed at 850°C for 120 minutes in nitrogen or oxygen ambient. Note the non-uniform broadening of the boron markers after oxidation. The extracted average relative diffusivites from the same samples are shown in figure 4 (b). Note the near linear dependence of boron diffusivity on depth. Note the boron diffusivity, which is a measure of the excess interstitial concentration, extrapolates to approximately zero at the location of the buried SiGeC layer.

The ability to pin the interstitial profile to near zero at the SiGeC layer depends on the SiGeC layer containing enough substitutional carbon to react with the interstitials injected during oxidation. To determine how much carbon is required a third set of test structures were grown. Two completely undoped samples with either 400Å thick buried $Si_{0.8}Ge_{0.2}$ or $Si_{0.795}Ge_{0.2}C_{0.005}$ layers centered 800 Å below the surface were epitaxially grown to examine the substitutional carbon dependence on anneal times in nitrogen and oxygen ambients. As-



(a) (b)

Figure 5 (a) substitutional carbon concentration measured in the as-grown sample of an undoped, buried, 400 Å thick $Si_{0.795}Ge_{0.20}C_{0.005}$ layer and in the same as-grown samples annealed in nitrogen and oxygen ambients at 850°C in oxygen or nitrogen ambient for 30,60 or 120 total minutes. The substitutional carbon is deduced from the lattice constant of the 400 Å SiGeC layer measured by x-ray diffraction. Note that all the substitutional carbon is consumed after 60 minutes of annealing in an oxygen ambient, but not after annealing in nitrogen ambient. Figure 5 (b) describes the difference of consumed substitutional carbon atoms after oxidation deduced from fig 5 (a) and the as-grown substitutional carbon concentration

grown samples containing either the SiGe or SiGeC layer were cleaved and annealed and the band-gap and lattice constant of the alloy layers was measured using standard photoluminescence and x-ray diffraction methods respectively. Using either the lattice constant or band-gap measurements the total substitutional carbon was deduced for each of the anneal conditions and found to agree well with one another, within 5% for all anneal conditions. The effective substitutional carbon concentration determined by x-ray diffraction is found to depend on annealing conditions and to decrease with increasing oxidation time, see figure 5.

Discussion

The total consumed carbon rate may be calculated from the measured substitutional carbon concentration's dependence on time. The net injected interstitials during oxidation

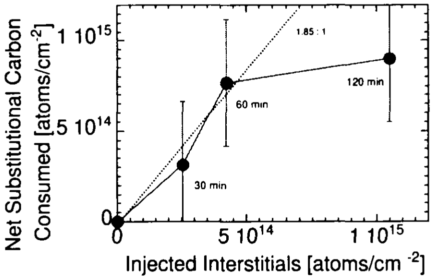


Figure 6 The injected interstitial concentration as determined by type II loop defect growth [Meng et al.] is correlated to the consumed substitutional carbon measured by x-ray diffraction for oxidation times of 30, 60, and 120 minutes at 850°C.

was determined by measuring the growth of loop defects during oxidation at 900°C by Meng et al. [8]. Assuming that the point defect injection during oxidation scales with oxidation rate, the injection rate of interstitials may be calculated for oxidation at 850°C from the measured interstitial injection at 900°C. In figure 6 the consumed carbon rate is shown correlated to the calculated interstitial injection rate by a ratio of 1.85 ± 0.7 to 1 consumed subtitutional carbons to interstitials. This indicates that for high substitutional carbon concentrations the carbon-interstitial interaction in the SiGeC alloy is more complex than just a simple relationship of one interstitial required to knock-out one carbon from its substitutional site. For times greater than 60 minutes the total consumed substitutional carbon saturates because by this time most of the as-grown substitutional carbon has been completely consumed by the reaction.

Conclusion

The introduction of substitutional carbon in buried SiGeC layers is found to reduce the oxidation enhanced diffusion of both boron and phosphorus located above the SiGeC layer. A near linear depth dependent diffusivity is observed during oxidation when there is a buried SiGeC layer, and the diffusivity is greatest near the surface. The rate of substitutional carbon consumed by oxidation was measured by x-ray diffraction and photoluminescence versus annealing times and ambients. Using published values of interstitial injection versus oxidation rate, the ratio of substitutional carbon atoms effectively driven from their substitutional sites to injected interstitial is correlated to be 1.85 ± 0.7 :1 respectively.

Acknowledgements

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References

[1] P. A. Stolk, H-J Gossman, D. J. Eaglesham, D. C Jacobson, C. S. Rafferty, G. H. Gilmer, M. Jaraiz, J. M. Poate, H. S. Luftman, T. E. Haynes, J. Appl. Phys 81, (9), 1997
[2] M. S. Carroll, C-L. Chang, J. C. Sturm, T. Büyüklimanli, APL 73, (25) p 3695, 1998
[3] H-J. Gossmann, C. S. Rafferty, G. Hobler, H-H. Vuong, D. C. Jacobson, IEDM 98 (to be published)
[4] L. D. Lanzerotti, J. C. Sturm, E. Stach, R. Hull, T. Buyuklimanli, C. Magee, App. Phys. Let, 70, (23), 1997
[5] H. L. Meng, S. Prussin, M. E. Law, K. S. Jones, J. Appl. Phys. 73 (2), 1992, 955
[6] P. A. Stolk, H-J Gossman, D. J. Eaglesham, J. M. Poate, Sci. Eng. B 36, 275 (1996)
[7] H. J. Osten et al, IEDM 1997 p 803
[8] G. Davies and R. C. Newman, in *Handbook on Semiconductors*, edited by T. S. Moss (Elsevier, New York, 1994), vol. 3b, p 1558-1629