Diffusion of single quantum well $Si_{1-x}Ge_x$/Si layers under vacancy supersaturation

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The interdiffusion of a $Si/Si_{0.85}Ge_{0.15}$/Si single quantum well heterostructure subjected to thermal annealing in a nitriding ambient was investigated as a function of anneal temperature and time. Nitridation of the silicon surface alters equilibrium vacancy point defect populations throughout the structure, which allows the determination of the point defect species important in interdiffusion. Diffusion coefficients of Ge after nitridation of $\sim 1 \times 10^{-14}$ cm^2/s for 1100 °C and $\sim 1 \times 10^{-13}$ cm^2/s for 1200 °C were extracted. The extent of diffusion in a nitriding ambient was much less than in an inert ambient, which indicates minimal vacancy contribution to interdiffusion. This is in contrast to results from previously published studies performed in an oxidizing ambient. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1341208]

INTRODUCTION

Recent progress in heterojunction bipolar transistor technology using epitaxial SiGe base layers has generated a need to control interface and dopant diffusion within the layers.[1–3] High-temperature device processing steps can create imprecise emitter–base and collector–base junctions, which can severely degrade device performance. In this article the interdiffusion of a $Si/Si_{0.85}Ge_{0.15}$/Si single quantum well (SQW) heterostructure in a nitriding ambient is investigated at temperatures of 1100 and 1200 °C. It is generally accepted that thermal nitridation of the silicon surface injects excess vacancies into the bulk material.[4,5] The extent of enhancement or retardation of Ge diffusion upon vacancy injection allows the determination of the interstitial and vacancy-mediated diffusion components for this material structure.[4] The diffusion profiles, coefficients, and enhancements from these nitridation experiments are compared to results from similar experiments in an oxidizing ambient.[6]
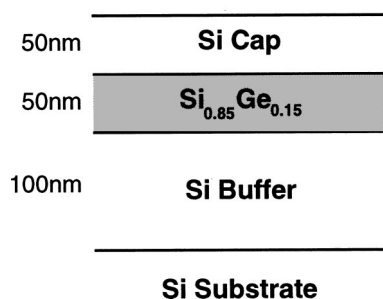
EXPERIMENT

A SQW test structure, shown in Fig. 1, was grown using an ASM Epsilon 1 vapor phase epitaxy reactor at a temperature of 700 °C, with growth details described previously.[6] The Ge concentration of the $Si_{0.85}Ge_{0.15}$ layer was verified by Rutherford backscattering spectroscopy (RBS) and layer thicknesses were verified by cross-sectional transmission electron microscopy. The Ge depth versus concentration profiles for as-grown and annealed samples were determined by secondary ion mass spectrometry (SIMS) using a Perkin Elmer PHI 6600 quadrapole analyzer with 6 keV O_2^+ ions, at a typical sputter rate of 24 nm/min, and a 60° incident angle. The profile depth scales were determined from Tencor Alpha-Step 500 surface profiler measurements of the SIMS sputtered craters. The variation of the sputter rate in the SIMS analysis was accounted for by a linearization technique, which relates the secondary ion signal of the Ge to the secondary ion signal of the Si based on the counts from a sample of known Ge concentration using RBS.[7,8] The depth scale of the SIMS profiles of the annealed samples was laterally shifted no more than 20 nm (within 1 s.d., estimated at 0.05, in relative depth scale error of SIMS)[9] so that the peaks aligned with that of the as-grown profile. The Ge concentration scale of the SIMS profiles was standardized by equalizing the total dosage in each peak. Samples were rapid thermal processed (RTP) in an AG Associates Heatpulse 2101 with NH_3 gas flowing at 1.5 slm.

RESULTS AND DISCUSSION

The Ge diffusion coefficients have been extracted by comparing SIMS profiles of annealed samples with those predicted by simulation using the Florida Object Oriented Process Simulator (FLOOPS).[10] Details of the diffusion model and extraction of diffusion coefficients have been previously presented in Griglione *et al.*[6] In that investigation, the same SQW structure used in the present study was ther-

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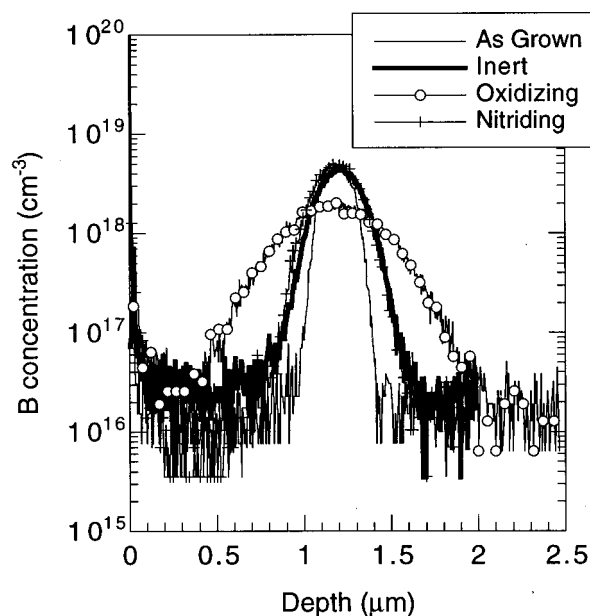FIG. 1. Schematic representation of the Si/Si$_{1-x}$Ge$_x$ test structure.

FIG. 2. Diffusion of the B marker layer in all ambients. The sample was annealed at 1100 °C for 2 min. Diffusion of B in oxidizing ambient is noticeably greater than in inert and nitriding ambients.

mally processed in both inert and oxidizing ambients, and diffusion coefficients were calculated. No enhancement of diffusion was observed in an oxidizing ambient (interstitial injection) as compared to an inert ambient. A value of f_I of ~0.02 at both 1100 and 1200 °C was estimated, indicating a diffusion mechanism dominated by vacancies. From these results, it is expected that thermal processing in a nitriding ambient during vacancy injection will result in significantly enhanced diffusion compared to that in an inert ambient.

The thickness of the Si$_{0.85}$Ge$_{0.15}$ layer in the SQW structure is greater than the critical thickness for this composition,[11] therefore relaxation through dislocation formation is expected. This was verified through transmission electron microscopy and reported in earlier work.[6] Cowern *et al.* have reported in previous studies a large enhancement of Ge diffusion in Si$_{1-x}$Ge$_x$/Si structures due to compressive strain.[12,13] However, they investigated structures that were free of dislocations. Cowern *et al.* specifically stated that diffusivity enhancement in samples that relax by dislocation growth is much weaker.[13] Due to the presence of relaxation via dislocations in the samples used in this investigation, strain effects on diffusivity values will be considered negligible. These dislocations, however, might later affect the vacancy injection and concentration in the bulk normally expected from surface nitridation. A boron marker layer structure (reported in detail, along with the analytical technique, in Griglione *et al.*[6]) was used to qualitatively determine that vacancies were indeed injected into the Si$_{1-x}$Ge$_x$ layer region in adequate concentrations to participate in the diffusion process. Movement of the B marker layer cannot quantitatively determine the vacancy supersaturation as a result of surface nitridation because B is primarily an interstitial diffuser. Any evidence of retardation of B diffusion can, however, qualitatively show that vacancies are being injected to the extent that they are depleting the interstitial concentration. The marker layer structure used in previously reported oxidation experiments[6] underwent RTP at 1100 °C for 2 min and at 1200 °C for 1 min in NH$_3$. Qualitatively, B diffusion in NH$_3$ ambient was comparable to diffusion in Ar ambient and much less than in O$_2$ ambient for both temperatures as determined by SIMS (Fig. 2). The extent of B diffusion determined experimentally for 1100 °C was less than that predicted by simulation, indicating a slight retardation of the diffusion of the B marker layer compared to default values used in FLOOPS. This result indicates that the interstitial concentration is slightly depleted from its equilibrium value,

and that vacancies are indeed being injected into the bulk and are traveling to some extent through the Si$_{1-x}$Ge$_x$ layer.

After confirming point defect injection conditions, analysis was then directed toward the interdiffusion of the Si$_{1-x}$Ge/Si$_x$ layers. At processing temperatures of 1100 and 1200 °C, the Ge diffusion profiles in a nitriding ambient show significant retardation compared to diffusion profiles in inert and oxidizing ambients at all processing times. This is apparent in Fig. 3, which shows, as an example, the SIMS profiles of the structure after processing at 1200 °C for 2 min in all three ambients. The extracted diffusivity values after processing in a nitriding ambient are given in Table I along with our previously published values for the diffusivities in
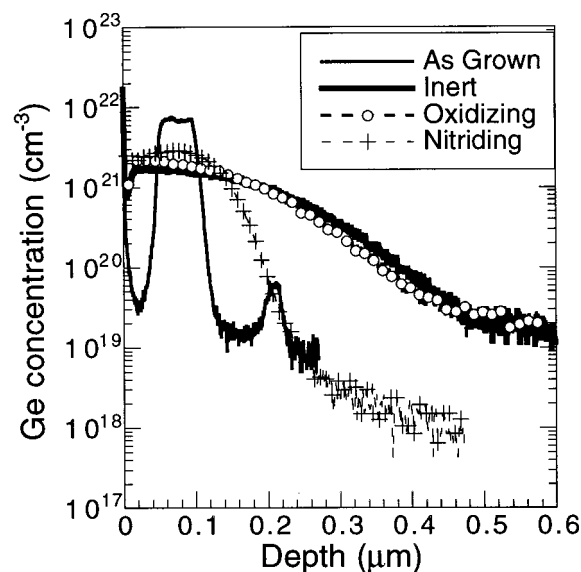

FIG. 3. Comparison of Ge SIMS profiles in inert, oxidizing, and nitriding ambients for the SQW test structure after processing at 1200 °C for 2 min.

TABLE I. Extracted diffusivity values for the test structure in inert and nitriding ambients.

T (°C)	Time (min)	D_{Ge}^{Inert} (cm²/s)	D_{Ge}^{Nit} (cm²/s)
1100	1	5.20×10^{-14}	1.13×10^{-14}
	2	7.93×10^{-14}	4.88×10^{-15}
	3	6.69×10^{-14}	1.13×10^{-14}
	4	8.60×10^{-14}	1.04×10^{-14}
1200	1	2.38×10^{-12}	1.10×10^{-13}
	1.5	8.55×10^{-13}	3.39×10^{-14}
	2	1.08×10^{-12}	1.02×10^{-13}
	3	1.08×10^{-12}	5.02×10^{-14}

an inert ambient.[6] The values of the diffusivities as a function of reciprocal temperature in inert, oxidizing, and nitriding ambients are shown in Fig. 4. The error in the determined diffusion coefficients was estimated using a Monte Carlo approach detailed in Gossmann *et al.*,[9] and the results are given as the error bars in Fig. 4. Diffusivities extracted are much lower and not within the error of those determined for inert and oxidizing ambients. This indicates that interstitials are the dominant diffusing point defect species and that injected vacancies recombine with intrinsic interstitials to lower the interstitial concentration and retard diffusion. These results contradict the behavior predicted from our oxidizing experiments, as well as a study by Cowern *et al.*,[12] which indicated that *vacancies* are the dominant point defect diffusion species. Diffusion dominated by vacancies, as predicted by the oxidation experiments, would be expected to show large enhancements under vacancy supersaturation. A possible explanation for this contradictory behavior is that stress effects at the nitride/silicon interface near the $Si_{1-x}Ge_x$ layer, which are not present at the depths of the B marker layer, contribute to this anomalous behavior of the diffusion Ge. Chaudhry[14] observed that stress values change with depth into the sample under regions of nitride mask. Additionally, several previous
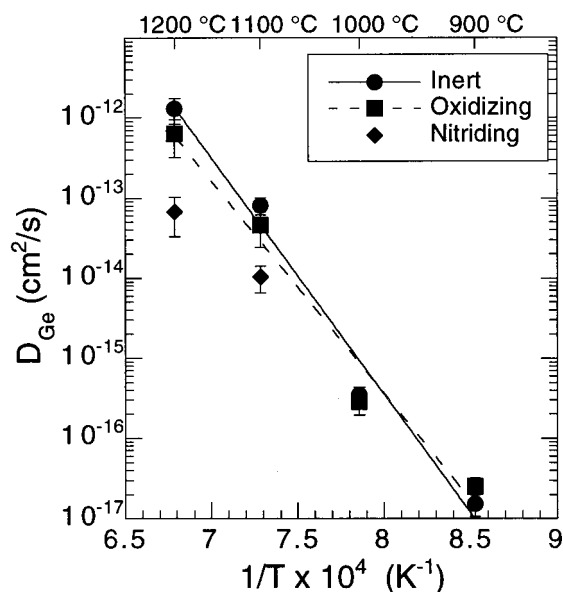
studies have reported a close relation between the stress level in the nitride film and the deviation of point defect concentrations from their equilibrium values in the region near the nitride/silicon interface.[15–17] Future work addressing this stress effect, along with use of Sb marker layers (Sb is known to diffuse almost entirely via a vacancy mechanism) would allow a more accurate quantitative estimate of the vacancy supersaturation under nitriding ambient.

SUMMARY

The diffusion of Ge in a $Si/Si_{0.85}Ge_{0.15}/Si$ SQW structure during surface nitridation has been investigated at 1100 and 1200 °C. The results reported are specific to the particular structure and processing conditions used. Diffusivities of $\sim 1 \times 10^{-14}$ cm²/s for 1100 °C and $\sim 1 \times 10^{-13}$ cm²/s for 1200 °C in nitriding ambient were estimated. Significant retardation of diffusion occurred in nitriding ambient compared to inert ambient, which indicates a diffusion mechanism controlled by interstitials. This contradicts the low f_I ~ 0.02 estimated from previous oxidation experiments. Stress effects at the nitride/silicon interface could possibly explain this unexpected behavior.

ACKNOWLEDGMENTS

[1] U. König, IEEE Colloquium Adv. Semiconductor Devices **1999/025**, 48 (1999).
[2] S. Subbana, D. Ahigren, D. Hatame, and B. Meyerson, *1999 IEEE International Solid-State Circuits Conference Digest of Technical Papers* (IEEE, Piscataway, NJ, 1999), p. 508.
[3] G. Freeman *et al.*, Mater. Res. Soc. Symp. Proc. **533**, 19 (1998).
[4] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).
[5] S. M. Hu, J. Electrochem. Soc. **139**, 2066 (1992).
[6] M. Griglione, T. J. Anderson, Y. Haddara, M. E. Law, K. S. Jones, and A. van de Bogaard, J. Appl. Phys. (to be published).
[7] G. Prudon, B. Gautier, S. Berthelemy, J. C. Dupuy, C. Dubois, J. Schmitt, J. Delmas, and J. P. Vallard, Proceedings of the 11th International Conference on Secondary Ion Mass Spectrometry (SIMS XI) 1997, Vol. 11, p. 339.
[8] J. P. Newey, D. J. Robbins, and D. Wallis, Proceedings of the 11th International Conference on Secondary Ion Mass Spectrometry (SIMS XI) 1997, Vol. 11, p. 979.
[9] H.-J. Gossmann, A. M. Vredenberg, C. S. Rafferty, H. S. Luftman, F. C. Unterwald, D. C. Jacobson, T. Boone, and J. M. Poate, J. Appl. Phys. **74**, 3150 (1993).
[10] M. E. Law, *FLOOPS User's Manual* (University of Florida Press, Gainesville, FL, 1996).
[11] S. C. Jain, *Germanium-Silicon Strained Layers and Heterostructures* (Academic, New York, 1994).
[12] N. E. B. Cowern, W. J. Kersten, R. C. M. de Kruif, J. G. M. van Berkum, W. B. de Boer, D. J. Gravesteijn, and C. W. T. Bulle-Liewma, Proc.-Electrochem. Soc. **96-4**, 195 (1996).
[13] N. E. B. Cowern, P. C. Zalm, P. van der Sluis, D. J. Gravesteijn, and W. B. de Boer, Phys. Rev. Lett. **72**, 2585 (1994).
[14] S. Chaudhry, Ph.D. thesis, University of Florida, 1996.
[15] S. T. Ahn, H. W. Kennel, J. D. Plummer, and W. A. Tiller, J. Appl. Phys. **64**, 4914 (1988).
[16] K. Osada, Y. Zaitsu, S. Matsumoto, M. Yoshida, E. Arai, and T. Abe, J. Electrochem. Soc. **142**, 202 (1995).
[17] F. Gracin, J. Lopez, and M. Mijares, Rev. Mex. Fis. **45**, 156 (1999).

FIG. 4. Effective Ge diffusivity of the test structure as a function of processing temperature in inert, oxidizing, and nitriding ambients.