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Suppression of boron diffusion due to carbon during rapid thermal annealing of SiGe based device materials—some comments

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The development of silicon-germanium alloys to extend the range of silicon high-frequency circuits has highlighted the need to understand diffusion mechanisms in this important material. To optimise performance, it is necessary to minimise the diffusion of dopants such as boron, in these very narrow width devices. This paper discusses recent progress in understanding the role of carbon doping in retarding boron diffusion. Much progress in understanding the diffusion mechanisms in silicon has been gained using selective defect injection, building on the discovery in 1972 that broadening of marker layers could monitor the injection of defects. The technique has now been used successfully in silicon-germanium alloys, and has shown that interstitial type defects are responsible for boron diffusion both in SiGe and in SiGe:C. The effects of carbon in retarding boron diffusion in as-grown structures, as well as ion-implanted structures, are discussed. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

It is a great honour to be invited to submit a paper for the 40th Anniversary Special Edition of Journal of Materials Science, particularly as one of us co-authored a paper [1] in the first issue of the journal in 1966, and was honoured to have a micrograph selected for the front cover of the third issue [2]. In the third volume [3], a review of diffusion effects in silicon was published in the journal, recognising the rising importance of silicon, and the crucial role of diffusion in its applications as a semiconductor. Germanium was still a significant semiconductor in those days, and, while it is now only used on its own for special applications, this paper recognises the increasing use of silicon–germanium alloys in silicon technology, which has risen to its present dominance in the semiconductor field. Understanding the mechanisms of diffusion in this alloy system is just as vital in maximising the effectiveness of this alloy in extending the range of silicon performance.

The growing importance of germanium in modern semiconductor technology is best illustrated in the Silicon-Germanium based heterojunction-bipolar transistor (HBT) designed for high (radio) frequency applications [4, 5]. These devices benefit from the increased carrier mobility in germanium which is incorporated in to the base of the transistor in the form of a SiGe alloy, commonly doped with boron. Further improvements in the high-frequency performance can be achieved by increasing the boron concentration in the base and also narrowing its width. However, various thermal processing steps that required following the introduction of the dopant cause the boron to diffuse into adjacent emitter

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and collector regions of the transistor. This results in reduced performance levels and diffused profile boundaries. Hence, reducing boron diffusion in SiGe is quite important from the performance point of view.

2. Effect of carbon on diffusion in epitaxial structures

One of the ways in which boron diffusion can be reduced is by introducing in the SiGe, a small ($<0.1\%$) concentration of carbon. Carbon at these low concentrations is known to retard boron diffusion without degrading the electrical properties too much. Use of increasingly popular rapid thermal processing (RTP) techniques also enables diffusion to be minimised because of the use of rapid heating-ramps and short thermal cycles under feedback control [6]. By combining carbon-alloying with rapid thermal processing, diffusion of boron can be minimised and thus the performance of SiGe HBTs can be further enhanced.

In Fig. 1, the retardation capability of carbon on boron diffusion in SiGe is illustrated [7]. The structures shown have been grown epitaxially and have a SiGe layer with approximately 11% Ge sandwiched between two silicon layers. In Fig. 1(b), the SiGe layer additionally has ~0.1% carbon. After subjecting to a rapid thermal anneal at 1000°C for 60 s, the boron distribution in Fig. 1(a) has shown considerable diffusion even to adjacent silicon layers whereas in Fig. 1(b), where carbon is present, diffusion is almost completely suppressed. Therefore, the effectiveness of carbon as a boron diffusion retardant is fairly clear in this case.

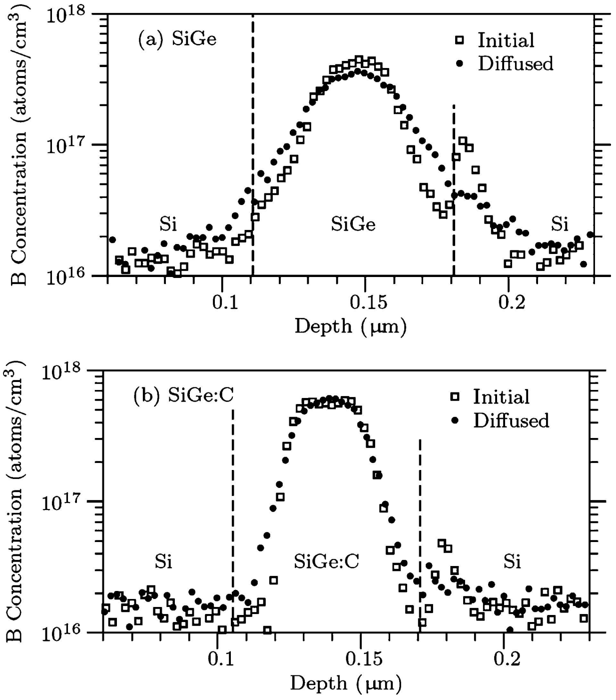

Figure 1 Comparison of the extent of diffusion of boron in (a) silicon-germanium and (b) silicon-germanium with 0.1 % carbon (SiGe:C) after rapid thermal annealing at 1000°C for 60 s. In the epitaxial structure the SiGe (~11%Ge) layer in both is sandwiched between two Si layers. In (a), the initial boron distribution has diffused considerably after the annealing whereas in (b) the presence of carbon has prevented diffusion almost completely [7].

3. Retardation of transient enhanced diffusion (TED)

The retardation effect of carbon is observed not only in epitaxial material. In fact, it was first observed in ion-implanted materials [8]. Transient enhanced diffusion or TED is a well documented phenomenon which occurs during the subsequent annealing step after ion-implantation when an increased diffusion is observed in the tail of dopant concentration profiles for a transient (finite) period of time. It is believed that the increase in diffusion is due to the dissolution of small clusters of interstitials which are emitted during the annealing. Since boron diffusion is aided by interstitials, a significant increase in the diffusion is observed while the clusters are dissolved (see [9] and references therein). The diffusion retardation effect of C was first observed in preamorphised Si when it was shown that implantation of C^+ at sufficient doses reduced transient enhanced diffusion. Using the findings it was concluded that implanted C perhaps acted as a sink for excess interstitials.

One of the problems with using C implantations for suppressing TED is that carbon itself creates its own interstitial damage which needs gettering in addition to the damage caused by the dopant implantation. Incorporation of carbon substitutionally by epitaxy was therefore attempted and shown to be equally effective in suppressing TED [10]. The suppression effects of carbon due to epitaxial SiGe [11, 12] and polycrystalline SiGe [13] have also been observed.

4. Investigation of atomistic mechanisms by selective defect injection

Although diffusion mechanisms without defects, such as direct exchange processes, have been discussed in the past, it is generally agreed that self-diffusion and most dopant diffusion in silicon and germanium is mediated by point defects. In the case of silicon, the point defects responsible for diffusion can be broadly categorised as vacancies (an absence of an atom from a lattice site) or interstitials (an extra atom in the lattice). The type of defect involved is dependent on the type of crystal and the diffusing dopant. Defect injection is a powerful method to study the involvement of point defects in diffusion mechanisms in semiconductor materials. For example, silicon interstitials can be injected during high temperature oxidation of a Si surface [14, 15] as can be inferred from the growth of extrinsic stacking faults under oxidation conditions [16]. Since boron diffusion is enhanced during the oxidation it is now broadly accepted that diffusion of

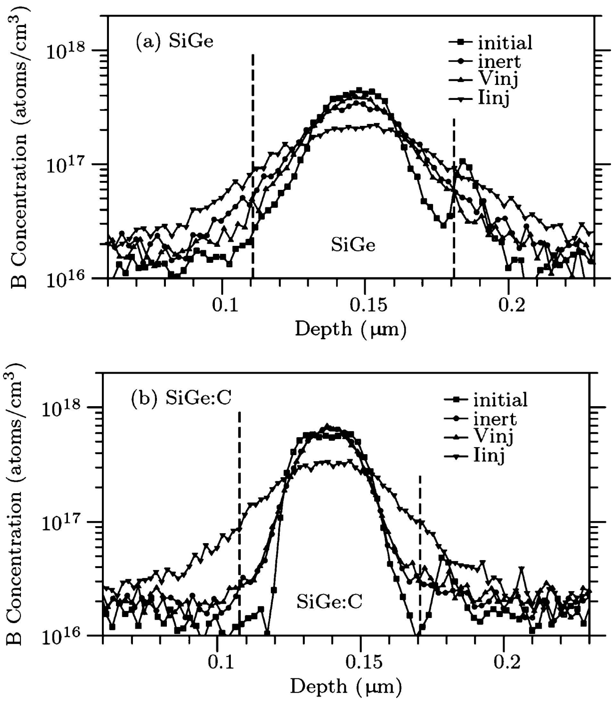

Figure 2 Concentration distributions of B in (a) SiGe and (b) SiGe with 0.1% C peak after annealing at 1050°C for 15 s under inert, vacancy injected (Vinj), and interstitial injected (Iinj) conditions. The initial profile in each case is also shown for comparison [7]. The diffusion enhancement during interstitial injection in both cases is substantial.

boron in silicon is mediated primarily by interstitial type point defects. Vacancy type point defect injection is less commonly encountered during fabrication, but for example is seen when Si is annealed with a silicon nitride film on the surface [14,17–20]. The creation of excess vacancies under these conditions is evident from the shrinking of extrinsic stacking faults under the silicon-nitride films [17].

Fig. 2 shows, boron concentration profiles measured in the sample structures described earlier (a) SiGe and (b) SiGe with ∼0.1%C, after rapid thermal annealing at 1050ºC for 15 s under inert (non-injection) interstitial injected and vacancy injected conditions. Interstitial injection was achieved by annealing the bare Si surface in dry oxygen while a silicon-nitride layer was annealed in oxygen for vacancy injection (further details of the experiment is given in [7]). Initial profiles present prior to annealing are also shown for comparison. During annealing, all three profiles have broadened significantly, but the broadening observed under interstitial injection is quite significant in both (a) & (b). The profiles obtained from vacancy injected samples are only slightly narrower than those from inert samples, although this difference is indistinguishable in the SiGe:C sample. These results show that it is mainly the interstitial type defects which are responsible for boron diffusion in both SiGe and SiGe:C.

Although there is much agreement on the diffusion mechanism of boron in SiGe the exact mechanism by which carbon suppresses boron in both Si and SiGe is not fully understood. There is speculation that carbon act as a sink or trap for interstitials on which boron diffusion depends [e.g. 8, 21]. It has been shown that carbon has a very low bulk solubility in Si [22] and similarly low solubility is predicted for SiGe alloys with low concentrations of Ge. However, for device structure applications such as HBTs carbon can be incorporated substitutionally at supersaturated levels over equilibrium [23, 24] by means of slow growth techniques such as low temperature gas-source molecular beam epitaxy (GSMBE). According to a model proposed to explain the retardation effect of carbon on boron diffusion in these structures [25, 26], the suppression of B diffusion is attributed to an undersaturation of interstitials caused by the out-diffusion of supersaturated C from C-rich regions. This model could be extended to explain the observed retardation effects in SiGe.

5. Conclusions

Much progress in understanding the diffusion mechanisms in silicon has been gained using selective defect injection, building on the discovery in 1972 [27] that broadening of marker layers could monitor the injection of defects. The technique has now been used successfully in silicon-germanium alloys [28], and has shown that interstitial type defects are responsible for boron diffusion both in SiGe and in SiGe:C. The effects of carbon in retarding boron diffusion in as-grown structures, as well as ion-implanted structures, are discussed.

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References

1. R. L. BELL, R. LATKOWSKI and A. F. W. WILLOUGHBY, *J. Mater. Sci.* **1** (1966) 66.
2. R. L. BELL and A. F. W. WILLOUGHBY, *J. Mater. Sci.* **1** (1966) 219.
3. A. F. W. WILLOUGHBY, *J. Mater. Sci.* **3** (1968) 89.
4. D. J. MEYER, D. A. WEBB, M. G. WARD, J. D. SELLAR, P. Y. ZENG and J. ROBINSON, *Mater. Sci. Semicond. Process.* **4** (2001) 529.
5. P. ASHBURN, *Mater. Sci. Semicond. Process.* **4** (2001) 521.
6. P. J. TIMANS, *Mater. Sci. Semicond. Process.* **1** (1998) 169.
7. M. S. A. KARUNARATNE, A. F. W. WILLOUGHBY, J. M. BONAR, J. ZHANG and P. ASHBURN. *J. Appl. Phys.* **97** (2005) 113531.
8. S. NISHIKAWA, A. TANAKA and T. YAMAJI, *Appl. Phys. Lett*, **60** (1992) 2270.
9. S. C. JAIN, W. SCHOENMAKER, R. LINDSAY, P. A. STOLK, S. DECOUTERE, M. WILLANDER and H. E. MAES, *Appl. Phys. Rev.* **91** (2002) 8919.

10. P. A. STOLK, D. J. EAGLESHAM, H. J. GOSSMANN and J.M. POATE, *Appl. Phys. Lett.* **66** (1995) 1370.
11. M. S. CARROLL, C.-L. CHANG, J. C. STURM and T. BÜYÜKLIMANLI, *Appl. Phys. Lett.* **73** (1998) 3695.
12. H. RÜCKER and B. HEINEMANN, *Solid-State Electron.* **44** (2000) 783.
13. C. L. CHANG and J. C. STURM, *Appl. Phys. Lett.* **74** (1999) 2501.
14. P. M. FAHEY, P. B. GRIFFIN and J. D. PLUMMER, *Rev. Mod. Phys.* **61** (1989) 289.
15. S. M. HU, *Mater. Sci. Eng. R* **13**(1994) 105.
16. S. M. HU, *J. Appl. Phys.* **45** (1974) 1567.
17. S. T. AHN, H. W. KENNEL, J. D. PLUMMER and W. A. TILLER, *J. Appl. Phys.* **64** (1988) 4914.
18. K. OSADA, Y. ZAITSU, S. MATSUMOTO, M. YOSHIDA, E. ARAI and T. ABE, *J. Electrochem. Soc* **142** (1995) 202.
19. R. F. LEVER, J. M. BONAR and A. F. W. WILLOUGHBY, *J. Appl. Phys.* **83** (1998) 1988.
20. J. M. BONAR, A. F. W. WILLOUGHBY, A. H. DAN, B. M. MCGREGOR, W. LERCH, D. LOEFFELMACHER, G. A. COOKE and M. G. DOWSETT, *J. Mater. Sci. - Mater. Electron.* **12** (2001) 219.
21. P. A. STOLK, H. J. GOSSMANN, D. J. EAGLESHAM and J. M. POATE, *Mat. Sci. Eng.* **B36** (1996) 275.
22. A. R. BEAN and R. C. NEWMAN, *J. Phys. Chem. Solids* **32** (1971) 1211.
23. K. EBERL, S. S. IYER, J. C. TSANG, M. S. GOORSKY and F. K. LEGOUES, *J. Vac. Sci. Technol.* **B 10** (1992) 934.
24. A. R. POWELL, K. EBERL, B. A. EK and S. S. IYER, *J. Cryst. Growth* **127** (1993) 425.
25. R. SCHOLZ, U. GÖSELE, J. Y. L HUH and T. Y. TAN, *Appl. Phys. Lett.* **72** (1998) 200.
26. R. F. SCHOLZ, P. WERNER, U. GÖSELE and T. Y. TAN, *Appl. Phys. Lett.* **74** (1999) 392.
27. D. B. LEE and A. F. W. WILLOUGHBY, *J. Appl. Phys.* **43** (1972) 245.
28. A.F.W. WILLOUGHBY, J.M. BONAR and A.N. PAINE, *Mat. Res Soc. Symp. Proc Vol* **568** (1999) 253.