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C/ORNL94-0270

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**CRADA Final Report
for
CRADA Number ORNL 94-0270**

**ION IMPLANTATION PROCESSING TECHNOLOGIES
FOR TELECOMMUNICATIONS ELECTRONICS**

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Industrial Partner-Bell Laboratories, Lucent Technologies

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Lockheed Martin Energy Research
Corporation
for the
U.S. Department of Energy
under contract DE-AC05-96OR22464**

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CRADA Final Report
on
CRADA No. ORNL94-0270

Ion Implantation Processing Technologies for Telecommunications Electronics

ORNL Principal Investigator: T. E. Haynes

Industrial Partner: Bell Laboratories, Lucent Technologies

The subject CRADA was a collaboration between Oak Ridge National Laboratory and Bell Laboratories, Lucent Technologies (formerly AT&T Bell Laboratories) to explore the development of ion implantation technologies for silicon integrated circuit (IC) manufacturing. This CRADA effort resulted in significant scientific contributions that have had, and will continue to have, substantial impact on the design of silicon IC manufacturing processes, both directly and indirectly. The direct impact has resulted from laboratory evaluation of ion implantation-based solutions to three key problems in IC manufacturing: dopant diffusion, metal contamination, and the availability of low-cost silicon-on-insulator (SOI) wafers. Without such solutions, enhanced diffusion of dopants would soon limit the density and speed of ICs while metal contamination would cause device failures and excess power consumption. In addition, the industry will soon require a large supply of low-cost SOI wafers to enable continued advances in speed, power efficiency, and reliability.

During this CRADA, the Laboratory and Partner conducted laboratory evaluations of ion implantation-based schemes for reducing enhanced diffusion of implanted dopants by the introduction of carbon, more effective removal (gettering) of metal contamination within IC chips by high-energy implantation, and a fourfold reduction of the implant dose needed for separation of SOI layers by co-implantation of He with H. All three of these solutions were demonstrated on the laboratory scale during the course of the CRADA. The CRADA partner is evaluating the first two schemes in a full-scale manufacturing environment. These two developments are summarized in the attached publications #1 (Stolk et al.) and #2 (Benton et al.). The SOI development, summarized in the attached publication #3 (Agarwal et al.), has the potential to significantly reduce the cost and increase the production rate of SOI wafers and is the subject of a pending patent application (Invention Disclosure #ERID-0274C). The economic payoff from these three developments is potentially very large and will be realized by the IC industry within two to five years.

In the latter stages of the CRADA, the team also investigated the basic mechanisms controlling enhanced diffusion of boron in silicon following ultralow-energy ion implantation. The industry trend is to use extremely low ion-implantation energies to create shallower doped layers that are necessary as the devices are made smaller. The outcome of these investigations is summarized in the attached publication #4 (Agarwal et

al.). This work resulted in the demonstration that surface annihilation of excess interstitials reduces the diffusion enhancement caused by the interstitials to negligible levels as the implant energy approaches 1 keV and below. The CRADA team also made the initial discovery of an important new effect—boron-enhanced diffusion. This new effect becomes dominant over traditional transient-enhanced diffusion of boron as the implant energy is lowered (see attached publication 4). This discovery has stimulated a significant amount of continuing research by the Partner, as well as by others who are competitive in this field, in order to determine the underlying mechanism for this effect. It has also motivated a redirection of development efforts in the industry away from controlling damage to mitigating chemical reactions at large boron concentrations.

This CRADA will also have a significant indirect impact on IC manufacturing because of the development during the CRADA of sufficient quantitative understanding of enhanced-dopant diffusion and metal gettering to derive accurate physical models suitable for use in manufacturing simulators. As the complexity of IC technology increases, the costs and delays associated with actual manufacturing trials of new processes are becoming prohibitive and chip makers are increasingly relying on these simulators to design, test, and choose winning processes. Specific innovative insights developed during the CRADA include:

- (1) quantitative determination of mechanisms of metal gettering by high-energy implantation;
- (2) quantitative measurements of the amounts and types of implant damage that contribute to enhanced-dopant diffusion as functions of implant dose, energy, and dopant type;
- (3) reduction of damage retention in large boron concentrations;
- (4) experimental demonstration of the reduction of transient-enhanced diffusion with decreasing implant depth; and
- (5) identification of a new mechanism of enhanced diffusion in ultrashallow profiles that arises from a chemical phase transformation instead of implant damage.

The CRADA partner has already incorporated physical models developed in this project into their simulator, and it is anticipated that other chip makers will soon do the same. The new understanding developed in this CRADA will thus enable these chip manufacturers to focus their process-development efforts more efficiently. This work has also refined the process window for 0.1- μm technology, due for production in 2005, thereby providing manufacturers of ion implanters the lead-time they will need to develop the specifications for their future product lines. The payoffs from these indirect contributions to manufacturing technology will be realized in 4–10 years.

This CRADA effort has been recognized by the semiconductor device community as demonstrated by invitations received by team members to give key invited talks (list attached), not only at major international conferences but also at more focused, device-oriented workshops. The presentation at the International Electronic Devices Meeting is particularly noteworthy in that this is a high-profile meeting focusing on leading-edge device technology that rejects approximately 80% of the submitted papers. Acceptance at this meeting is a clear indicator of recognized impact on device technology. In addition,

results of this CRADA were highlighted in two of the leading semiconductor trade journals [A. Agarwal, cited in *Semiconductor International* 20 (4) p. 54 (April 1997); and *Solid State Technology* 40 (7), p. 78 (July 1997)], and the SOI development was recognized with the Best Paper Award at a 1997 SOI conference.

During the course of this CRADA, the ORNL PI (T. E. Haynes) spent approximately 150 days conducting experiments at Bell Laboratories. These intermittent visits provided a valuable opportunity to learn about other related areas of semiconductor processing technology and develop collaborations beyond the scope of this CRADA with other Bell Labs scientists that will continue for at least the next several years.

Documentation of CRADA Accomplishments

CRADA ORNL94-0270

Ion Implantation Processing Technologies for Telecommunications Electronics

Patents

Patent Pending: "Manufacture of Semiconductor Thin Films," application filed June 26, 1997, based on Invention Disclosure No. - Invention Disclosure, ERID-0274C.; Inventors- A. Agarwal (ORNL), T. E. Haynes (ORNL), O. W. Holland (ORNL), V. C. Venezia (ORNL), and D. J. Eaglesham (Lucent Technologies).

Summary Publications (copies attached)

1. P. A. Stolk, H.-J. Gossmann, D. J. Eaglesham, D. C. Jacobson, C. S. Rafferty, G. H. Gilmer, M. Jaraíz, J. M. Poate, and T. E. Haynes, "Physical Mechanisms of Transient Enhanced Dopant Diffusion in Ion-Implanted Silicon," *J. Appl. Phys.* **81**, 6031 (1997).
2. J. L. Benton, P. A. Stolk, D. J. Eaglesham, D. C. Jacobson, J.-Y. Chen, J. M. Poate, N. T. Ha, T. E. Haynes, and S. M. Myers, "Iron Gettering Mechanisms in Silicon," *J. Appl. Phys.* **80**, 3275 (1996).
3. A. Agarwal, T. E. Haynes, V. C. Venezia, O. W. Holland, and D. J. Eaglesham, "Efficient Production of Silicon-on-Insulator Films by Co-Implantation of He⁺ with H⁺," *Appl. Phys. Lett.* **72**, 1086 (1998).
4. A. Agarwal, H.-J. Gossmann, D. J. Eaglesham, L. Pelaz, S. B. Herner, D. C. Jacobson, T. E. Haynes, and R. Simonton, "Damage, Defects, and Diffusion from Ultra-Low-Energy (0-5 keV) Ion Implantation of Silicon," *Mat. Sci. Semicond. Proc.* **1**, 17 (1998).

Additional Publications (reprints available on request)

5. A. Agarwal, H.-J. Gossmann, D. J. Eaglesham, S. B. Herner, A. T. Fiory, and T. E. Haynes, "Boron-Enhanced Diffusion of Boron from Ultra-Low Energy Ion Implantation," *Appl. Phys. Lett.* **74**, 2435 (1999).
6. A. Agarwal, D. J. Eaglesham, H.-J. Gossmann, L. Pelaz, S. B. Herner, D. C. Jacobson, T. E. Haynes, and Yu. E. Erokhin, "Boron-Enhanced Diffusion of Boron from Ultralow-Energy Boron Implantation," p. 1232 in *Semiconductor Silicon 1998 (Electrochem. Soc. Proc. 98-1)*, ed. by H. Huff, U. Gösele, and H. Tsuya (The Electrochemical Society, Pennington, NJ, 1998).
7. A. Agarwal, H.-J. Gossmann, D. J. Eaglesham, L. Pelaz, D. C. Jacobson, J. M. Poate, and T. E. Haynes, "Critical Issues in Ion Implantation of Silicon Below 5 keV: Defects and Diffusion," *Materials Science and Engineering A- Structural Materials* **253** (1-2), 269(1998).

8. A. Agarwal, H.-J. Gossmann, D. C. Jacobson, D. J. Eaglesham, M. Sosnowski, J. M. Poate, I. Yamada, J. Matsuo, and T. E. Haynes, "Enhanced Diffusion From Decaborane Molecular Ion Implantation," *Appl. Phys. Lett.* **73**, 2015 (1998).
9. M. K. Weldon, M. Collot, Y. J. Chabal, V. C. Venezia, A. Agarwal, T. E. Haynes, D. J. Eaglesham, S. B. Christman, and E. E. Chaban, "The Mechanism of Silicon Exfoliation Induced by Hydrogen/Helium Co-Implantation," *Appl. Phys. Lett.* **73**, 3721 (1998).
10. A. Agarwal, D. J. Eaglesham, H.-J. Gossmann, L. Pelaz, S. B. Herner, D. C. Jacobson, T. E. Haynes, Yu. E. Erokhin, and R. Simonton, "Boron-Enhanced Diffusion of Boron: The Limiting Factor for Ultra-Shallow Junctions," *Intl. Electron. Dev. Mtg. Tech. Digest*, 467 (1997).
11. H.-J. Gossmann, T. E. Haynes, P. A. Stolk, C. A. King, R. W. Johnson, D. C. Jacobson, J. M. Poate, H. S. Luftman, T. Mogi, and M. O. Thompson, "The Interstitial Fraction of Diffusivity of Common Dopants in Silicon," *Appl. Phys. Lett.* **71**, 3862 (1997).
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13. Aditya Agarwal, H.-J. Gossmann, D. J. Eaglesham, D. C. Jacobson, T. E. Haynes, Yu. E. Erokhin, R. Simonton, and J. M. Poate, "0.5 to 5 keV Ion Implantation for Ultra-Shallow Junctions," *Proceedings of the Fourth International Workshop on the Measurement, Characterization, and Modeling of Ultra-shallow Doping Profiles in Semiconductors* (April 6-9, 1997, Research Triangle Park, NC).
14. D. J. Eaglesham, T. E. Haynes, H.-J. Gossmann, D. C. Jacobson, P. A. Stolk, and J. M. Poate, "Transient Enhanced Diffusion of Sb and B in Silicon due to MeV Silicon Implants," *Appl. Phys. Lett.* **70**, 3281 (1997).
15. A. Agarwal, T. E. Haynes, D. J. Eaglesham, H.-J. Gossmann, D. C. Jacobson, J. M. Poate, and Yu. E. Erokhin, "Interstitial Defects in Silicon from 1-5 keV Si⁺ Ion Implantation," *Appl. Phys. Lett.* **70**, 3332 (1997).
16. T. E. Haynes, D. J. Eaglesham, P. A. Stolk, H.-J. Gossmann, D. C. Jacobson, and J. M. Poate, "Interactions of Ion Implantation Induced Interstitials with Boron at High Concentrations in Silicon," *Appl. Phys. Lett.* **69**, 1376 (1996).
17. D. J. Eaglesham, A. Agarwal, T. E. Haynes, H.-J. Gossmann, D. C. Jacobson, and J. M. Poate, "Damage and Defects from Low-Energy Implants in Si," *Nucl. Instrum. & Methods Phys. Res. Sect. B* **120**, 1 (1996).
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19. D. J. Eaglesham, P. A. Stolk, J.-Y. Cheng, H.-J. Gossmann, T. E. Haynes, and J. M. Poate, "{311} Defects in Ion-Implanted Silicon: The Cause of Transient Diffusion and a Mechanism for Dislocation Formation," p. 451 in *Microscopy of Semiconducting Materials, 1995*, ed. by A. G. Cullis, A. E. Staton-Bevan, and J. L. Hutchison (Institute of Physics, Bristol, United Kingdom, 1996).
20. P. A. Stolk, J. L. Benton, D. J. Eaglesham, J.-Y. Cheng, J. M. Poate, S. M. Myers, and T. E. Haynes, "The Mechanism of Iron Gettering in Boron-Doped Silicon," *Appl. Phys. Lett.* **68**, 51 (1996).
21. D. J. Eaglesham, P. A. Stolk, H.-J. Gossman, T. E. Haynes, and J. M. Poate, "Implant Damage and Transient-Enhanced Diffusion in Si," *Nucl. Instr. and Methods Phys. Res. Sect. B* **106**, 191 (1995).

Invited Talks by ORNL Members of CRADA

22. A. Agarwal, "Modeling Enhanced Diffusion of Implanted Dopants Based on Physical Understanding of the Phenomena," *International Workshop on Challenges in Predictive Process Simulation* (August 1997, Wandlitz, Germany).
23. A. Agarwal, "New Aspects of Very Low Energy Ion Implantation for Ultrashallow Junctions," *1997 Spring Meeting of the Materials Research Society* (April 1997, San Francisco, CA).
24. A. Agarwal, "Damage, Defects, and Diffusion from Low-Energy Implantation in Silicon," *1997 Annual Meeting of the TMS* (February 1997, Orlando, FL).
25. T. E. Haynes, "Critical Issues in Ion Implantation of Silicon Below 5 keV," *1997 Engineering Foundation Conference on Ion Beam Modification of Ceramics and Semiconductors* (May 1997, Barga, Italy).
26. T. E. Haynes, "Defects and Diffusion in Ultrashallow Ion Implantation of Silicon," *1997 Meeting of the Greater Southwest Implant Users' Group* (October 1997, Denton, TX).

Additional Significant Talks by ORNL Members of CRADA

27. A. Agarwal, "Boron-Enhanced Diffusion of Boron: The Limiting Factor for Ultra-Shallow Junctions," *1997 International Electron Devices Meeting* (December 1997, Washington, DC).
28. A. Agarwal, "0.5 to 5 keV Ion Implantation for Ultrashallow Junctions," *4th Int'l Workshop on Measurement, Characterization, and Modeling of Ultra-Shallow Doping Profiles in Semiconductors* (April 1997, Research Triangle Park, NC).
29. A. Agarwal, "Mechanism of Silicon Exfoliation by Hydrogen Implantation or Hydrogen/Helium Co-Implantation," *1997 IEEE Int'l Silicon-on-Insulator Conference* (October 1997, Fish Camp, CA).

Attachments

Physical mechanisms of transient enhanced dopant diffusion in ion-implanted silicon

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(Received 16 July 1996; accepted for publication 23 September 1996)

Implanted B and P dopants in Si exhibit transient enhanced diffusion (TED) during annealing which arises from the excess interstitials generated by the implant. In order to study the mechanisms of TED, transmission electron microscopy measurements of implantation damage were combined with B diffusion experiments using doping marker structures grown by molecular-beam epitaxy (MBE). Damage from nonamorphizing Si implants at doses ranging from 5×10^{12} to $1 \times 10^{14}/\text{cm}^2$ evolves into a distribution of {311} interstitial agglomerates during the initial annealing stages at 670–815 °C. The excess interstitial concentration contained in these defects roughly equals the implanted ion dose, an observation that is corroborated by atomistic Monte Carlo simulations of implantation and annealing processes. The injection of interstitials from the damage region involves the dissolution of {311} defects during Ostwald ripening with an activation energy of 3.8 ± 0.2 eV. The excess interstitials drive substitutional B into electrically inactive, metastable clusters of presumably two or three B atoms at concentrations below the solid solubility, thus explaining the generally observed immobile B peak during TED of ion-implanted B. Injected interstitials undergo retarded diffusion in the MBE-grown Si with an effective migration energy of ~ 3.5 eV, which arises from trapping at substitutional C. The concept of trap-limited diffusion provides a stepping stone for understanding the enormous disparity among published values for the interstitial diffusivity in Si. The population of excess interstitials is strongly reduced by incorporating substitutional C in Si to levels of $\sim 10^{19}/\text{cm}^3$ prior to ion implantation. This provides a promising method for suppressing TED, thus enabling shallow junction formation in future Si devices through dopant implantation. The present insights have been implemented into a process simulator, allowing for a significant improvement of the predictive modeling of TED. © 1997 American Institute of Physics. [S0021-8979(97)02101-4]

I. INTRODUCTION

The advancing miniaturization of Si integrated circuits continues to expose severe gaps in our understanding of the role of defects and impurities in Si processing. A striking example is the phenomenon of transient enhanced diffusion (TED) which occurs when ion-implanted dopants in crystalline silicon (*c*-Si), such as B and P, are subjected to thermal annealing. The process of enhanced dopant diffusion was first recognized more than 20 years ago by Hofker *et al.*¹ The phenomenon has been extensively investigated in the past decade,^{2–8} and its basic features have been well characterized.^{9–11} As an illustration, Fig. 1 shows enhanced diffusion for a shallow B profile implanted into float-zone (FZ) crystalline silicon. Upon annealing at 800 °C for 35 min, B in the tail of the implanted profile has diffused over ~ 700 Å, whereas the equilibrium diffusion length for these

annealing conditions is only ~ 25 Å.¹² The nonequilibrium diffusion vanishes for longer annealing times,^{6,11} which is the transient signature of TED. An additional feature of TED in Fig. 1 is that the peak portion of the B profile above $10^{18}/\text{cm}^3$ is not electrically activated and has remained immobile during annealing. This is remarkable in view of the fact that the equilibrium solubility of B at 800 °C is higher than $10^{19}/\text{cm}^3$, suggesting that the entire B profile should be soluble and mobile.

It is by now well established that the anomalous diffusion of ion-implanted B and P arises from excess Si self-interstitials that are generated by the implant. The interstitials *I* couple with substitutional dopant atoms *A_s* through the reaction

thereby forming a mobile dopant complex *A_I*.¹² The increased interstitial concentration [*I*] in the ion-implanted region will shift the local equilibrium between substitutional and mobile dopant atoms, and the resulting enhanced dopant diffusivity *D_A^{enh}* is to good approximation given by¹²

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FIG. 1. Secondary-ion-mass spectrometry (lines) and spreading resistance (solid circles) measurements of an implanted B profile ($1.5 \times 10^{14}/\text{cm}^2$, 30 keV B) before and after transient enhanced diffusion at 800 °C for 35 min.

$$D_A^{\text{enh}} = D_A^* \frac{[I]}{[I^*]}, \quad (2)$$

where D_A^* denotes the dopant diffusivity under equilibrium conditions and $[I^*]$ the equilibrium interstitial concentration.

Although TED is minimal under rapid thermal annealing conditions (e.g., 1000 °C, 5 s),⁶ it becomes more and more pronounced and critical with the continuing trend of reducing the thermal budget in device manufacturing. Hence, TED now threatens to impose severe limitations on the minimum device dimensions attainable in next generation devices. In addition, it has been shown that the lateral coupling between excess interstitials and dopants is responsible for the so-called reverse-short-channel effect,^{13,14} which encumbers the scalability of metal-oxide-semiconductor (MOS) transistors. At present, simulation tools designed to predict dopant diffusion during device processing are not capable of dealing with TED in a satisfactory manner. From this perspective, it is crucial to improve our understanding of the physical mechanisms of TED. An additional scientific challenge is the development of processing-compatible methods for suppressing interstitial-enhanced dopant diffusion.

Among the uncertain factors which preclude accurate modeling of TED are the diffusion coefficient D_I and the equilibrium concentration $[I^*]$ of the Si self-interstitial. As shown in a recent article by Bracht, Stolwijk, and Mehrer¹⁵ studies on self-diffusion¹⁶ and metal diffusion^{15,17} in Si have yielded reasonably consistent values for the mass transport properties in Si, which implicitly contains the product $D_I[I^*]$. Separate determinations of D_I and $[I^*]$,¹⁵ on the other hand, have resulted in an enormous spread in these parameters. As suggested by Griffin *et al.*¹⁸ and by Cowern¹⁹ the discrepancies in the values for D_I could be explained on the basis of trap-limited interstitial diffusion; however, no consensus has been reached until now about the nature of these intrinsic traps in silicon.

A more pressing uncertainty in modeling TED is the number of interstitials arising from the implant which contribute to the enhanced diffusion. It was proposed¹⁰ that the implanted atom causes a net imbalance in the ion-generated population of interstitials and vacancies.⁷ Upon annealing, interstitials and vacancies quickly recombine to restore the damaged lattice, leaving one atom per implanted ion which cannot be annealed out immediately. The supersaturation of interstitials during TED is thought to arise from this one excess interstitial per ion, rather than from the entire ion-generated distribution of interstitials; this has become known as the “+1” model. Although this simple model provides an estimate for the level of interstitials injected during TED, it has never been verified experimentally. Furthermore, it is not fully clear whether the excess interstitials emerge instantaneously from the initial distribution, or whether their rate of injection is limited by interstitial clustering.⁹ Finally, modeling the evolution of interstitial damage requires detailed knowledge of the rate at which interstitials recombine, either at the surface or in the bulk, a process which is still poorly understood.

Another ambiguous feature of TED is the fact that the peak portion of implanted B profiles remains static and inactivated upon annealing when an apparent critical dopant concentration is exceeded,^{10,11} as also demonstrated in Fig. 1. It was proposed¹⁰ that this effect arises from the large supersaturation of B atoms in interstitial positions leading to an effective lowering of the equilibrium solubility limit of B in Si. Alternatively, the anomalous B diffusion was ascribed to the trapping of B at extended defects,⁹ or was explained in terms of an enhanced coupling between B and neutral interstitials.²⁰ The latter model was based on the observation that the kink in the dopant profiles after TED appears to be correlated with the intrinsic carrier concentration. In a recent article on process simulations,²¹ the rather unphysical assumption was made that the incomplete B activation results from the formation of immobile, isolated B interstitials through a kick-out reaction with Si interstitials. Each of the above explanations allows for a sufficient number of free parameters to enable fitting of the diffused dopant profiles through process simulations, a situation which calls for decisive experiments.

In the past years, many of the detailed aspects of TED have been investigated by utilizing dopant marker layers in diffusion experiments.^{22–35} These experiments were designed to detect the effect of interstitial injection from a localized source (e.g., implantation damage, oxidizing surface) on well-separated dopant profiles. In the experiments presented in this article, diffusion studies using dopant superlattice structures were linked to damage measurements using transmission electron microscopy (TEM).³⁶ This combination has yielded a wealth of information about the mechanisms of TED, and has significantly improved our insights into the source of interstitials during TED, the diffusion behavior of interstitials in Si, and the mechanism through which B is immobilized during TED.

Several methods have been published through which the interstitial-enhanced dopant diffusion can be suppressed. A significant reduction in TED can be achieved by amorphiz-

ing the *c*-Si substrate prior to dopant implantation and annealing;^{37,38} however, it has proven to be difficult to control the defect band located at the original amorphous Si (*a*-Si)/*c*-Si interface, which can result in increased junction leakage. Furthermore, additional interstitials will be emitted from the defect band during further thermal processing thus causing TED to persist. It has also been demonstrated that the TED of near-surface B implants can be greatly reduced by superimposing a high-energy (MeV) Si implant before annealing.³⁹ Although this reduction was originally ascribed to the trapping of interstitials at the stable dislocation damage formed by the deepest implant,³⁹ it is more likely caused by the excess vacancies in the near-surface region generated by the high-energy implant.⁴⁰ Again, implementation of this recipe for suppressing TED might be precluded by the detrimental effects of the buried damage layers. Recently, it has been reported that C coimplantation can be used to reduce TED of B.^{41,42} This reduction has been attributed⁴³⁻⁴⁵ to the fact that the implanted C provides a sink for excess interstitials during annealing. The efficacy of C coimplantation in suppressing TED is limited by the fact that the C needs to getter its own interstitial damage in addition to the interstitials from the dopant implant.⁴⁴ It could therefore be more efficient to incorporate substitutional C in *c*-Si before implanting the dopant species, which is an additional subject of research in this article.

This article is organized as follows. Section II describes the experimental details of the present work. The complementary TEM and diffusion experiments are presented in Secs. III and IV, respectively. Section V elaborates on an interstitial-driven clustering mechanism of B. It is demonstrated in Sec. VI that incorporating substitutional C in *c*-Si is successful in suppressing TED. Furthermore, Sec. VI discusses in detail how the presence of C in Si is thought to affect the diffusion of interstitials in marker layer experiments and metal diffusion studies. In Sec. VII a Monte Carlo diffusion code is presented which was developed to enrich our understanding of the detailed defect-dopant interactions during annealing. Finally, to illustrate the improvements that have been made, Sec. VII shows how the present results have been implemented into a process simulator.

II. EXPERIMENT

A. Sample preparation

The present experiments were designed to investigate how implantation damage in silicon evolves during annealing, and how it affects the diffusion of dopant atoms. The structure and evolution of implantation damage was identified by means of cross-sectional and plan-view TEM. Dopant diffusion was measured with high sensitivity by using special marker layer structures grown by low-temperature molecular-beam epitaxy (MBE).⁴⁶ These structures consisted of 600-nm-thick films of Si grown on Si (100) substrates (FZ, P-doped to 1000 Ω cm), containing 10-nm-wide spikes of substitutional B. The dopant spikes were separated by ~ 100 nm, with each spike containing 1.5×10^{12} or 1.5×10^{13} B/cm².

Additional diffusion measurements were performed for B marker layers implanted into FZ Si wafers (*p*-type doping, 100 Ω cm, 100 orientation) using a tandem accelerator. The detailed preparation scheme has been given in Ref. 47. In brief, FZ wafers were amorphized at liquid-nitrogen temperature by implanting 0.5, 1, and 2 MeV Si at a dose of 5×10^{15} /cm² each. The amorphized layers were subsequently implanted with 2.3×10^{14} /cm², 60 keV B and 4×10^{14} /cm², 400 keV B. The implanted samples were annealed after implantation leading to regrowth of the amorphized layer through solid-phase epitaxy (SPE) and full activation of the implanted B, as ascertained from spreading resistance profiling (SRP).⁴⁷

Damage and diffusion experiments were also carried out on FZ and MBE samples which were intentionally doped with relatively high levels of C or B. Samples with increased C contents were prepared using two methods. First, the amount of C incorporated in MBE-grown superlattices was enhanced by introducing acetylene gas in the MBE chamber through a leak valve. As measured by secondary-ion-mass spectroscopy (SIMS) at a sputtering rate of 12 $\text{\AA}$ /s using a 3 keV Cs⁺ beam, the background C level increases from 10^{18} /cm³ for the standard growth conditions to 2×10^{19} /cm³ for growth under an acetylene pressure of 10^{-7} Torr. The C incorporation at the B doping spikes is increased by a factor of 3 due to growth interrupts. TEM analysis shows no carbon precipitation upon annealing the C-rich silicon layers at 1000 $^{\circ}\text{C}$ for 1 h, indicating that the incorporated C remains substitutional up to high temperatures.

In a second scheme for achieving C doping, MBE-grown superlattices and FZ Si(100) wafers were amorphized to a depth of 2 μm at ~ 77 K using 0.5, 1, and 2 MeV Si implants to a total fluence of 1.5×10^{16} /cm². Some samples were implanted with C at multiple energies ranging from 10 to 400 keV with doses chosen to approximate a uniform C doping level to a depth of ~ 1 μm . Other samples were implanted at a single energy so as to obtain a buried peak of high C content. After the C implants samples were annealed in vacuum at 500 $^{\circ}\text{C}$ for 1 h, 600 $^{\circ}\text{C}$ for 2 h, and 790 or 900 $^{\circ}\text{C}$ for 15 min to regrow the *a*-Si layer by SPE and dissolve the implanted C in the *c*-Si lattice. It should be noted that C is known to regrow onto substitutional sites during SPE of *a*-Si for C levels as high as ~ 1 at. %.⁴⁸

Heavily boron-doped silicon substrates were prepared by the following procedure. Six FZ (100) silicon wafers (B doped, 1 Ω cm) were first oxidized in dry O₂ at 1000 $^{\circ}\text{C}$ to form a 20-nm-thick screen oxide. Boron was then introduced into five of these wafers by ion implantation of ¹⁰B⁺ at 120 keV to various doses, followed by annealing at 1050 $^{\circ}\text{C}$ for 2 h. This anneal accomplished two objectives: It removed all of the observable implantation damage caused by the B implant, and it diffused the implanted B profile uniformly over a considerable depth. The implantation and annealing conditions had been chosen with the help of the process simulator PROPHET⁴⁹ to produce B profiles that were uniform (within 10%) over a distance of at least 300 nm from the surface. The implanted ¹⁰B doses were 6×10^{13} /cm², and 2, 3, 4, and 6×10^{14} /cm², producing boron concentrations [B] of 1, 3, 5, 7×10^{18} , and 1×10^{19} /cm³, respectively, in the uniform sur-

face region after the diffusion anneal. Spreading resistance measurements were used to verify the quoted B concentrations and depth distributions. The sixth oxidized wafer received no ^{10}B implant and was used as a reference.

B. Implants, annealing, and diffusion

Low-energy implants (<70 keV) were performed by extracting negatively charged ions from a sputter source biased at the desired voltage, without net acceleration inside the tandem accelerator. The standard procedure to introduce near-surface implantation damage in silicon samples consisted of room-temperature implants of 40 keV Si^- at dose rates of $(1.3 \pm 0.6) \times 10^{12}$ ions/cm²/s to total doses ranging from 5×10^{12} to 5×10^{14} ions/cm². A typical B doping implant was done at room temperature using a 60 keV B_2 beam at a dose of 7.5×10^{13} /cm², which corresponds to implanting 30 keV B to a dose of 1.5×10^{14} /cm².

After implantation, samples were chemically cleaned by successive rinsing with trichloroethylene, acetone, and methanol, followed by a standard RCA cleaning step. Prior to being annealed, samples received a 20 s dip in a 1:20 diluted solution of HF. Most anneals were carried out in a conventional tube furnace with a base vacuum pressure well below 10^{-7} mbar. Samples were carried by a support wafer in a quartz boat and annealed in vacuum or under forming gas (85% N_2 , 15% H_2 , flow rate 1.5 l/min). Varying between these two annealing ambients was found not to affect the present nonequilibrium damage and diffusion experiments to a measurable extent, provided that the furnace settings were changed to compensate for temperature shifts.⁵⁰ Other gas flow conditions have occasionally been used and are specified in this article where necessary.

The furnace temperature settings were carefully calibrated in separate runs using a thermocouple mounted at the exact location of the samples. Temperature differences between annealing in vacuum and under gas flow were measured to be as high as, for instance, $\sim 40^\circ\text{C}$ for a furnace setting temperature of 700°C . The temperatures quoted in the remainder of this article are the calibrated values of the actual sample temperature during annealing, which are believed to be accurate to within 10°C . Some samples were subjected to a rapid thermal annealing (RTA) step under forming gas flow. In that case, the temperature was calibrated to within 25°C by measuring the rates of SPE regrowth of ion-beam-amorphized layers on $\text{Si}(100)$ substrates.⁵¹

In order to study interstitial-enhanced diffusion, ion-damaged B superlattices were annealed under various thermal conditions. Boron depth profiles before and after diffusion were obtained by SIMS at a sputtering rate of $4 \text{ \AA}/\text{s}$ using $2 \text{ keV } \text{O}_2^+$. The time-averaged intrinsic B diffusivity (D_B^{int}) was derived from each diffused doping spike using the optimization procedure described elsewhere.^{28,52} The B spike confined to ion-damaged regions has been excluded in the diffusion analysis, as it is unclear *a priori* to what extent the diffusion of this spike is perturbed by the implantation damage.

FIG. 2. Cross-section high-resolution electron micrograph showing {311} habit plane, and typical image contrast of {311} defects.

III. INTERSTITIAL INJECTION

A. Results

This section presents TEM studies of the annealing behavior of ion-implanted FZ samples. Identical implantation and annealing conditions were used to study interstitial-enhanced diffusion in B marker layer structures (Sec. IV), which will enable a direct link between implantation damage and TED.

Figure 2 shows a cross-section electron micrograph of a FZ sample that was implanted with 40 keV Si , $5 \times 10^{13}/\text{cm}^2$ and annealed at 815°C for 15 s using RTA. The high-resolution image of Fig. 2 clearly demonstrates the presence of a defect with a {311} habit plane. A series of cross-section images demonstrates that these defects are confined to the top $0.1 \mu\text{m}$ surface region of the sample. Plan-view analysis shows a high concentration of elongated defects along $\langle 110 \rangle$ directions, see Fig. 3, and this appearance is consistent with the notorious "rodlike" or "{311} defects."⁵³ These defects consist of an agglomeration of excess Si self-interstitials and are known to form in response to the nonequilibrium injection of interstitials resulting from oxidation,⁵⁴ electron bombardment,⁵⁵ or ion implantation.^{54,56} Although {311} have recently been presented as a band of interstitials on a compact disk,^{56,57} it is generally recognized that {311} interstitial clusters have an anisotropic, elongated shape. For a detailed discussion on the structural properties of {311} defects, the reader is referred to a recent review article by Takeda and co-workers.⁵³

Cross-section and plan-view microscopy were combined to follow the evolution of {311} defects during annealing. As is clear from Fig. 3, the areal density of {311} defects drops by several orders of magnitude upon increasing the annealing time at 815°C from 5 to 30 s. Simultaneously, the average length of the defects increases from roughly 5 to 20 nm. No defects were detectable for annealing times in excess of 5 min, suggesting complete damage dissolution. The quantitative measurements of defect density and average defect size, as summarized in Fig. 4, were used to calculate the number of interstitials contained in {311} defects.⁵⁸ Figure 5 shows

FIG. 3. Plan-view (220) dark-field images of FZ silicon implanted with $5 \times 10^{13}/\text{cm}^2$, 40 keV Si after rapid thermal annealing at 815 °C for (a) 5 s, (b) 30 s.

that the areal interstitial density falls off exponentially with characteristic decay times ranging from ~ 40 s at 815 °C to ~ 4 h at 670 °C. It should be noted that the width of {311} defects could not be accurately measured for very short annealing times, while the statistics for the defect density are rather poor in the final stage of the {311} decay. These uncertainties could imply that the decay curves are not purely exponential as in Fig. 5, but are likely to be more convex instead. The decay rates derived from the exponential fits in Fig. 5 are reproduced in the Arrhenius graph of Fig. 6, showing an activation energy of 3.8 ± 0.2 eV for the dissolution of {311} defects.

FIG. 4. Development of the density and the average length of {311} defects during annealing at 815 °C.

FIG. 5. Transmission electron microscopy measurements of the total interstitial areal density in {311} defects as a function of annealing time. Data are shown for float-zone Si samples which were implanted with $5 \times 10^{13}/\text{cm}^2$, 40 keV Si and annealed in forming gas at various temperatures.

It is noteworthy that the interstitial density in {311} defects in the initial annealing stages (Fig. 6) is similar to the implanted Si dose of $5 \times 10^{13}/\text{cm}^2$. Apparently, about one excess interstitial is formed for each implanted ion during annealing, in accordance with the +1 model. This observation is reconfirmed by measurements of the interstitial density as a function of ion dose in Fig. 7, which demonstrate a +1.4 dependence. It should be noted that no {311} defects were observed for implantation doses below $\sim 5 \times 10^{12}/\text{cm}^2$.

Figure 8 shows TEM measurements of the number of interstitials contained in {311} defects for samples which were doped with a high B background (see Sec. II for details). In similar experiments, FZ substrates were controllably doped with a uniform C level by ion-beam amorphization of the substrates followed by a series of C implants and epitaxial regrowth (Sec. II), and the results are shown in Fig. 9. Both types of samples were implanted with 60 keV Si, $1 \times 10^{14}/\text{cm}^2$, and annealed at 740 °C for 15 min. It is clear that the interstitial density in {311} defects decreases strongly with increasing B or C content. It thus appears that substitu-

FIG. 6. Arrhenius graph of the time constant for {311} decay derived from the annealing curves in Fig. 5.

FIG. 7. Dose dependence of the number of interstitials in {311} defects during the early stages of annealing for 60 keV Si implants into float-zone silicon.

tional B and C reduce the formation of {311} defects; the implications of this observation are discussed extensively in Secs. V and VI of this article.

For implantation doses exceeding $\sim 1 \times 10^{14}/\text{cm}^2$, the damage annealing behavior in FZ samples becomes more complex in that dislocation loops are observed in addition to {311} defects.^{59,60} The defects observed⁵⁹ upon annealing a $1.5 \times 10^{14}/\text{cm}^2$, 145 keV Si implant at 900 °C for 15 min are predominantly $\frac{1}{2}[111]$ Frank loops frequently arranged in linear chains, suggesting that the loops may form from the 1- μm -long rodlike defects seen at lower doses and shorter anneals.

B. Discussion

In the dose range from 5×10^{12} to $\sim 1 \times 10^{14}/\text{cm}^2$, {311} defects are the only defect structures visible at the peak of the implant damage during annealing. The observation that the defect density drops while the average defect size increases (Fig. 4) is indicative of Ostwald ripening. This shows

FIG. 8. Areal density of interstitials in {311} defects observed after annealing a $1 \times 10^{14}/\text{cm}^2$, 60 keV Si implant at 740 °C for 15 min, as a function of the B background doping level. The solid and dashed lines are fits to the data assuming interstitial trapping through B clustering.

FIG. 9. Density of interstitials in {311} defects observed after annealing a $1 \times 10^{14}/\text{cm}^2$, 60 keV Si implant at 740 °C for 15 min, as a function of the C background doping level.

that interstitials are emitted from and recaptured by {311} defects, favoring the growth of larger (i.e., more stable) defects at the expense of smaller ones. However, as interstitials are lost from the damage region through diffusion to the surface or into the bulk of the material, the interstitial content held by {311} defects gradually decreases with time.

The presence of {311} defects implies that the interstitial concentration in the interior of the implanted sample is maintained above equilibrium. Hence, the interstitials which are gradually lost from the {311} defect distribution will give rise to enhanced dopant diffusion when they are captured by a dopant atom. Therefore, the evaporation of {311} defects will determine the time scale and the instantaneous strength with which TED takes place. It is shown in the following section that the time scales for enhanced B diffusion in marker layer experiments are indeed consistent with the {311} decay rates in Fig. 5. The presently derived activation energy for interstitial injection of 3.8 ± 0.2 eV is in perfect agreement with the value of 3.7 eV, which was estimated from a collection of measurements of the time needed to saturate the enhanced diffusion of implanted B.¹¹

Figures 6 and 7 show that the interstitial content of {311} defects is in remarkable agreement with the +1 model. Earlier experiments on the formation and growth of dislocation loops in ion-implanted Si have also indicated that the interstitial densities emerging during annealing are close to +1 approximation.^{61,62} Monte Carlo simulations have been used to investigate how this simple rule of thumb can be reconciled with the complex interactions between interstitials and vacancies that govern the generation and annealing of ion damage.⁶³ Parts of these simulations are presented in Sec. VII A.

Figure 10 gives a tentative summary in the form of a "phase diagram" for {311} behavior, based on the observations for Si implants into FZ silicon in the energy range from 20 to ~ 150 keV. For doses below the amorphization threshold, the defect processes are only weakly dependent on the initial damage level, so that the diagram can be mapped in terms of implantation dose versus annealing "strength." At

FIG. 10. Schematic diagram of the annealing behavior of {311} defects in relation to the implanted ion dose and the thermal annealing "budget."

implantation doses below $5 \times 10^{12} \text{ I/cm}^2$, no {311} defects are observed. This could indicate that the interstitial clusters formed from the implantation damage are too small to be detected by TEM. Alternatively, this threshold dose could reflect a nucleation barrier for the formation and growth of {311} defects. For doses in between $5 \times 10^{12} \text{ I/cm}^2$ and $1 \times 10^{14} \text{ I/cm}^2$, {311} defects are the only visible defects and they evaporate for a sufficiently high thermal budget (i.e., annealing time and temperature). The evaporation rate at a given temperature is dependent on implantation dose and energy.^{60,64} Above a threshold dose of $\sim 10^{14} \text{ I/cm}^2$, {311} defects undergo unfaulting, leading to both Frank loops and perfect dislocations. Since these dislocations are more stable than {311} defects, significantly stronger annealing steps are needed to fully dissolve the dislocation damage. Further studies are necessary to identify how the time scales and strength of interstitial injection are affected by the transformation of {311} defects into dislocation loops.

IV. INTERSTITIAL DIFFUSION

A. Results

The injection of interstitials from {311} defects was detected by probing the broadening of B marker layers during annealing. It was verified that the annealing behavior of {311} defects in MBE material is quantitatively similar to the studies on FZ material presented in Sec. III, at least for the implant conditions presently used ($5 \times 10^{13} \text{ I/cm}^2$, 40 keV Si).

Figure 11 shows the as-deposited and diffused B doping profiles in MBE-grown superlattice structures. After implantation and annealing, each of the doping spikes has broadened well beyond the initial width of $\sim 100 \text{ Å}$ as a result of the injection of interstitials. The broadening exceeds thermal diffusion for all markers and is most pronounced near the ion-implanted region. This behavior clearly demonstrates the diffusion mechanism underlying TED: Excess interstitials injected from the ion damage cause enhanced diffusion of the substitutional B markers. It is obvious that portions of the three doping markers closest to the surface remained immobile during annealing. The Gaussian fits in Fig. 11(b) show this particular shape can be reproduced by assuming that the markers consist of a mobile and an immobile component. This diffusion behavior very much reproduces the key fea-

FIG. 11. (a) SIMS measurements of the B doping profile for an as-deposited superlattice and for a superlattice implanted with $5 \times 10^{13} \text{ I/cm}^2$, 40 keV Si and annealed in vacuum at 790 °C for 10 min. (b) Deconvolution of the doping markers into Gaussian diffusion profiles. Portions of the three near-surface markers are assumed to be immobile. The dashed line in (a) indicates the region in which stable {311} clusters are formed during annealing.

tures of TED as shown in Fig. 1. In Sec. V it is demonstrated that the static B peaks result from clustering of B driven by the interstitials.

Figure 12(a) shows the time-averaged intrinsic B-diffusivity (D_B^{int}) as a function of depth derived from the diffusion profiles in Fig. 11(a) together with data obtained for 790 °C, 30 min annealing. The enhanced B diffusivity (i.e., the ratio of D_B^{int} to the equilibrium diffusivity D_B^*) is proportional to the amount by which the time-averaged local concentration of self-interstitials $\langle I \rangle$ exceeds the equilibrium level $[I^*]$, as indicated on the right-hand-side axis of Fig. 12. The average interstitial concentration near the ion-implanted region drops from about $200 \times [I^*]$ to about $60 \times [I^*]$ upon increasing the annealing time from 10 to 30 min, indicating that the injection of interstitials has diminished after ~ 10 min. The time-averaged interstitial diffusion profiles in Fig. 12(a) were modeled by calculating the time-average of a Gaussian peak broadening with a fixed effective interstitial diffusivity. Reasonable agreement was obtained by assuming $\sim 1.3 \times 10^{-12} \text{ cm}^2/\text{s}$ for the diffusivity independent of annealing time.

The diffusion studies of Fig. 11 were repeated for B marker layers implanted in FZ Si wafers (see Sec. II and Ref. 47). Figure 13 shows SIMS profiles of the marker layer after preparation and after implantation with $5 \times 10^{13} \text{ I/cm}^2$, 40 keV Si followed by annealing at 790 °C for 10 min. The B peak near the damage region broadens considerably upon annealing, whereas the deepest peak remains unaffected. The broadening of the near-surface peak is remarkably asymmetric, which is presumably due to the fact that the clustering of

FIG. 12. Time-averaged intrinsic B diffusivity as a function of depth derived from the broadened portion of each doping marker after annealing at (a) 790 °C and (b) 670 °C for various times. The depth dependence of the diffusivity reflects the time-averaged interstitial diffusion profile (right-hand axis). Solid lines are (a) fits of the interstitial profile assuming an interstitial diffusivity of $1.3 \times 10^{-12} \text{ cm}^2/\text{s}$ and (b) fits of exponential decays according to Eq. (3).

B suppresses diffusion near the damage source. By analyzing the broadening of the B peaks as a function of depth,⁴⁷ the interstitial diffusivity was estimated to be $\leq 4 \times 10^{-12} \text{ cm}^2/\text{s}$.

Figure 12(b) shows interstitial diffusion profiles obtained by measurements on MBE-grown superlattices at 670 °C. In contrast to the diffusion behavior at 790 °C, the interstitial supersaturation near the damage source and the decay length of the diffusion profiles remain unchanged during annealing for $t \leq 1 \text{ h}$. It thus appears that the interstitial diffusion profiles are initially stationary at 670 °C. Stationary profiles

FIG. 13. SIMS measured B concentration profiles of FZ marker layers after preparation (Ref. 47) and after implantation with $5 \times 10^{13}/\text{cm}^2$, 40 keV Si followed by annealing in vacuum at 790 °C for 10 min.

with similar decay lengths were also observed for thermal annealing 550 °C up to $\sim 150 \text{ h}$.⁶⁵ The diffusion profile after annealing at 670 °C for 5 h deviates from this steady-state situation [see Fig. 12(b)], indicating that interstitials have diffused beyond the initial decay length.

B. Discussion

The diffusion data in Figs. 11 and 12 indicate that the injection of interstitials lasts for $\sim 10 \text{ min}$ at 790 °C and $\sim 5 \text{ h}$ at 670 °C, and these time scales are consistent with the measured evaporation rate of $\{311\}$ defects in Fig. 6. Therefore, it appears that the duration of interstitial injection is correlated with the evaporation of $\{311\}$ defects, reconfirming the notion of Sec. III that $\{311\}$ defects act as the source of interstitials during TED.

The profile of excess interstitials exhibits regular, diffusional broadening at 790 °C, and the diffusion constant D_I^{eff} was estimated to be $\approx 1.3 \times 10^{-12} \text{ cm}^2/\text{s}$ for MBE material. Similar diffusion studies at 720 °C yield $D_I^{\text{eff}} \approx 1.1 \times 10^{-13} \text{ cm}^2/\text{s}$. The stationary interstitial profiles observed at 550 and 670 °C, on the other hand, indicate that the penetration depth of injected self-interstitials is limited by the capture at trapping centers in the material. Under these conditions, the time-averaged interstitial profile is given by the steady-state profile $[I^{\text{ss}}(x)]$,¹⁹

$$[I^{\text{ss}}(x)] = [I^*] + ([I^0] - [I^*])\exp(-x/L_I), \quad (3)$$

where $[I^0]$ is the interstitial concentration at the source (assumed to be constant), x the distance from the source, and L_I a characteristic decay length related to the trap density $[T]$ and the trapping radius a_T according to $L_I = (4\pi a_T [T])^{-1/2}$.

The solid line in Fig. 12(b) is a least-squares fit of Eq. (3) to the diffusion profiles for 15 min and 1 h, yielding $L_I = 480 \pm 50 \text{ Å}$ and $[I^0]/[I^*] = (7.7 \pm 3.8) \times 10^3$.⁶⁶ The density of traps in the MBE-grown superlattice can be estimated from the value for L_I by taking a_T equal to the interatomic distance ($a_T = 2.35 \text{ Å}$), yielding $[T] = (1.5 \pm 0.2) \times 10^{17}/\text{cm}^3$. The vacancy level in our MBE-grown samples is below the detection limit of positron annihilation spectroscopy ($5 \times 10^{15}/\text{cm}^3$),⁶⁷ suggesting that the dominant traps are associated with impurities. Indeed, the background C level $[C_{\text{MBE}}]$ in the MBE superlattices is $\sim 10^{18}/\text{cm}^3$, and it is shown below (Sec. VI) that substitutional C is a strong trap for self-interstitials. The fact that the above estimate for $[T]$ is slightly lower than $[C_{\text{MBE}}]$ could indicate that not all carbon is active as a trap, or that a_T is smaller than 2.35 Å due to a small activation barrier to trapping ($\sim 0.15 \text{ eV}$).

For diffusion times exceeding $t_c = 1 \text{ h}$, the interstitials migrate beyond the trapping length at 670 °C. This effect either arises from the saturation of centers available for interstitial trapping,¹⁹ or from the reemission of interstitials initially bound to traps. The effective interstitial diffusivity D_I^{eff} in this regime can be estimated from the criterion that $\sqrt{D_I^{\text{eff}} t_c} \geq L_I$, yielding $D_I^{\text{eff}} \approx 6.4 \times 10^{-15} \text{ cm}^2/\text{s}$. The present values for D_I^{eff} are in good agreement with our previous studies on oxidation-enhanced diffusion in MBE-grown superlattices,²⁸ but are orders of magnitude lower than diffusivities derived from metal diffusion studies^{15,68} and exhibit

FIG. 14. Boron diffusion profiles after TED ($5 \times 10^{13}/\text{cm}^2$, 40 keV Si implant; 670 °C, 1 h anneal) for delta-doping superlattices with B peak concentrations of (a) $10^{18}/\text{cm}^3$ and (b) $10^{19}/\text{cm}^3$.

a higher effective activation energy of 3.8 ± 0.5 eV compared to 1.2–1.8 eV.^{15,68} These discrepancies can be reconciled on the basis of trap-limited interstitial diffusion resulting from the high carbon concentration in the presently studied MBE material. It should be noted that this carbon level is not necessarily representative for the material quality obtained by MBE growth.^{19,27} It is remarkable that the FZ marker layers (Fig. 13) give similar values for D_I^{eff} , whereas the C content of FZ silicon is expected to be well below $10^{17}/\text{cm}^3$. Presumably, additional impurities or vacancy-type defects were introduced during the amorphization and/or regrowth steps in preparing the FZ marker layers, thereby hampering interstitial diffusion. Section VI discusses in detail how C is thought to affect the diffusion of Si self-interstitials.

V. BORON CLUSTERING

A. Results

The marker layer experiments of Fig. 11 show that a considerable portion of the B spike located next to the damage region remains immobile during annealing, whereas the deeper B spikes exhibit regular broadening without a signature of immobile B. Figure 14 demonstrates how this effect changes upon reducing the maximum B level in the superlattice from 10^{19} to $10^{18}/\text{cm}^3$. Transient diffusion was induced in both samples by annealing a 40 keV Si, $5 \times 10^{13}/\text{cm}^2$ implant at 670 °C for 1 h. Analysis of the diffused spikes shows that the interstitial diffusion profiles in both samples are nearly identical. Yet, the diffused profile in the high concentration sample [Fig. 14(b)] shows a clear distinction between mobile and immobile B in the second dop-

FIG. 15. Temporal evolution at 550, 670, 720, and 790 °C of the clustered B fraction in the second doping marker, derived from Gaussian fits to diffusion profiles as in Fig. 11(b).

ing spike, whereas this dual behavior is not observed in the low concentration sample. Figure 15 shows that the immobile fraction of the second B doping spike in high-concentration samples (10^{19} B/cm³) ranges from ~ 0.5 at 550 °C to ~ 0.25 at 790 °C. The immobile fraction remains at the initial level upon continued annealing in the temperature range from 550 to 720 °C, whereas it decays on a time scale of ~ 10 h at 790 °C.

B. Discussion

The observations made on the basis of Fig. 14 indicate that the formation of immobile B requires a relatively high concentration of both interstitials and substitutional B. Apparently, the clustering of multiple B atoms is facilitated when sufficient B atoms are driven out of solution by Si self-interstitials. Electrical measurements show that the immobile B peaks are electrically inactive, which is indeed consistent with B clustering. Presumably, the clustering process involves mobile B atoms B_I and a possible set of reactions which describes the generation and clustering of B_I is given by

where B_c refers to immobile clusters containing $m+1$ B atoms, and n is the number of interstitials ejected upon clustering to allow for stress relief. While reaction (4a) sustains the interstitial-enhanced diffusion of B_s , reaction (4b) provides a channel through which B_s becomes immobile at concentrations below the solubility limit, as observed. Figure 15 demonstrates that the B clusters are metastable and dissolve upon continued annealing at sufficiently high temperatures.

In an attempt to further identify the clustering mechanism, the diffusion behavior of an ion-implanted B superlattice annealed at 670 °C for 1 h was numerically modeled (Fig. 16). The diffusivity D_{B_s} of unclustered, substitutional B is enhanced by the local interstitial concentration $[I]$ according to

FIG. 16. SIMS measurements (solid circles) of an ion-damaged B marker superlattice annealed at 670 °C for 1 h and the corresponding best fit (solid line) obtained by modeling interstitial-enhanced clustering of B.

$$D_{B_s} = \left(1 + \beta \frac{p}{n_i}\right) D_B^x \frac{[I]}{[I^*]}, \quad (5)$$

where $D_B^x = D_B^*/(1 + \beta)$, $p = n_i$ for $[B_s] < n_i$, and $p = [B_s]$ for $[B_s] > n_i$,²⁸ with n_i the intrinsic carrier concentration and $\beta = 0.2$ at 670 °C. Assuming that the pairing reaction of B_I and B_s is diffusion-limited, the formation of B_c clusters is governed by the following rate equation:

$$\frac{d[B_c]}{dt} = 4\pi a_c D_{B_I} [B_I] [B_s], \quad (6a)$$

where D_{B_I} is the diffusivity of B_I , a_c is the pairing radius, and $[B_c]$ and $[B_I]$ are the concentrations of B_c and B_I , respectively. It should be noted that Eq. (6a) ignores the dissolution of clusters for $T = 670$ °C in agreement with Fig. 15. The product $D_{B_I} [B_I]$ reflects the B diffusion capacity and is equal to $D_{B_s} [B_s]$. Therefore, Eq. (6a) can be rewritten as

$$\frac{d[B_c]}{dt} = 4\pi a_c D_{B_s} [B_s]^2. \quad (6b)$$

The concept of Eq. (6b) can be readily extended to include higher order clustering reactions (e.g., pairing of B_I and B_c).

The above approach was used to calculate the evolution of the as-deposited B superlattice profile in response to diffusion and clustering of B under the wind of interstitials. The interstitial concentration $[I(x)]$ was fixed at the steady-state profile of Eq. (3) using the fitted values for $[I^0]$ and L_I [Fig. 12(b)]. Satisfactory agreement was obtained by taking two clustering reactions into account (i.e., B_I-B_s and B_I-B_c pairing), both with the same pairing radius a_c . The solid line in Fig. 16 represents the best fit to the diffusion data using $a_c = 0.5$ Å, a value which seems reasonable in comparison to the interatomic distance in Si. Similar values were derived from analyzing data for diffusion at 670 °C, 15 min. Modeling the data for 720 and 790 °C would require more elaborate calculations to account for the non-stationary interstitial profiles, which is beyond the scope of this simple analysis. Yet, the results in Fig. 16 suggest that the static peaks ob-

served in the marker experiments can indeed be attributed to the clustering of a few (two or three) B atoms induced by excess Si interstitials.

This notion is further corroborated by the result of Fig. 8, which illustrates that increasing the B background concentration leads to a reduction in the number of interstitials contained in $\{311\}$ defects during annealing. Presumably, this interstitial loss arises from the trapping of interstitials during the B clustering process.⁶⁹ The data in Fig. 8 can be analyzed in detail by assuming that a fixed density of interstitials, $[I_{311}]_0$, is shared in quasiequilibrium between an unsaturable sink S (i.e., $\{311\}$ defects) and a population of small B clusters (assumed to be B_I-B_s pairs). This assumption implies that

$$[B_I] = k_1 [B_s], \quad (7a)$$

$$[B_I B_s] = k_1 k_2 [B_s]^2, \quad (7b)$$

with $k_1 = \exp(-\Delta E/kT)$ and $k_2 = [N_s]^{-1} \exp(E_2/kT)$. Here ΔE denotes the energy difference between an interstitial trapped at a sink and an interstitial paired with a B atom, k is Boltzmann's constant, N_s is the Si atom density ($5 \times 10^{22}/\text{cm}^3$), and E_2 is the effective binding energy between two B atoms in a B_I-B_s pair. The areal density of interstitials trapped by one or more B atoms is given by

$$[I_{\text{trap}}] = \Delta X ([B_I] + [B_I B_s]), \quad (8)$$

where ΔX is the width of the region in which interstitials and B atoms interact, which should be roughly equal to the width of the as-implanted damage peak. Equations (7) and (8) yield the following expression which describes the $\{311\}$ interstitial density $[I_{311}]$ as a function of the total B concentration $[B_{\text{tot}}]$:

$$\frac{[I_{311}]_0 - [I_{311}]}{\Delta X} = \frac{[B_{\text{tot}}]}{2} - \frac{k_1^2 - 1}{8k_1 k_2} \left[1 - \left(1 + \frac{8k_1 k_2}{(k_2 + 1)^2} [B_{\text{tot}}] \right)^{1/2} \right]. \quad (9)$$

Equation (9) was fitted to the data in Fig. 8 yielding $\Delta X = 500$ Å, $\Delta E = 0.3$ eV, and $E_2 = 0.9$ eV for the free parameters. Also shown is a quadratic model which is obtained from the above equations in the limit of dilute interstitial concentrations.⁶⁹ It is obvious that the above model for interstitial trapping during B clustering satisfactorily reproduces the measurements in Fig. 8.

The B_I-B_s pair has been shown by deep-level transient spectroscopy (DLTS) to be stable up to temperatures of at least 400 °C.⁷⁰ Diffusion anomalies in earlier marker layer experiments⁷¹ were also explained in terms of B_I-B_s pair formation,⁷² although the evidence was not as obvious as in the present experiments. The pairing reaction has been successfully applied in modeling TED for a small variety of implant and diffusion conditions.⁷³ Recent first-principles calculations⁷⁴ have been used to identify the atomic structure of the B_I-B_s pair, and the activation barrier H_{br} to breaking this pair into two separate B_s atoms and one I was determined to be ~ 3 eV. To first order, the average time τ_{br} for dissolving a B_I-B_s pair can be estimated on the basis of the

activation barrier by assuming $\tau_{br} = 10^{-13} \exp(H_{br}/kT)$ s. This yields $\tau_{br} = 16$ s at 790 °C, which is much shorter than the measured dissolution time of ~ 10 h (see Fig. 15). This suggests that higher-order, more stable B-B agglomerates are involved in the clustering process.

The present observations support the earlier suggestion¹⁰ that interstitial-driven B clustering might be responsible for the fact that the peak of implanted B profiles is static during TED and remains electrically inactive (see Fig. 1). The static B peak was observed¹⁰ to dissolve on a time scale of >4 h during post-TED annealing at 800 °C, which is indeed consistent with the data in Fig. 15. The present study also shows that the pinning of the B concentration during TED does not necessarily require the presence of extended defects such as rodlike defects or stacking faults, in contrast to what was proposed in the literature.⁹ Furthermore, earlier studies²⁰ have pointed out that the demarcation level between mobile and immobile B appears to be correlated with the intrinsic carrier concentration n_i . This observation has occasionally been used as a reference point in process simulations to model the immobile B fraction during TED. However, the present study has shown that the demarcation levels may vary from spike to spike within one single sample (see, for instance, Fig. 11), which implies that the apparent correlation with n_i is fortuitous.

Finally, the present data indicate that Si self-interstitials become incorporated into the B clusters (i.e., when $n < m$), leading to a local reduction in the interstitial concentration. This feature is further supported by *in situ* electron microscopy measurements.⁷⁵ It is noteworthy in this respect that the annealing of shallow B implants was found not to be accompanied by the formation of {311} defects, while TED remained.⁷⁶ In this case, the interstitial content is presumably reduced to below the threshold for {311} defect formation as a result of the consumption of interstitials by B clustering, combined with an increased interstitial loss due to the surface proximity.

In the present marker layer experiments, the flux of interstitials is not detectably perturbed by the clustering process. This is evident from, for instance, the fact that the interstitial diffusion profile at 670 °C is not significantly affected upon reducing the peak B concentration by one decade (Fig. 14). One explanation is that the level of trapped interstitials is too low to affect the interstitial population in the local vicinity of the B doping spike. Alternatively, recent superlattice studies seem to indicate that B clustering is initiated during the very early interstitial "burst" of TED, before the {311}-controlled diffusion process is established.⁷⁷

VI. CARBON SUPPRESSING TRANSIENT ENHANCED DIFFUSION

A. Results

On the basis of interstitial diffusion data it was speculated in Sec. IV B that C could act as a trap for Si self-interstitials. To investigate this notion in more detail, the effect of C doping on interstitial-enhanced B diffusion was studied by growing two different B superlattices by MBE (see Sec. II): one with a background C level of $10^{18}/\text{cm}^3$

FIG. 17. Secondary-ion-mass spectrometry measurements of B diffusion profiles in MBE-grown superlattices containing substitutional C levels of (a) $10^{18}/\text{cm}^3$ and (b) $2 \times 10^{19}/\text{cm}^3$. Profiles are shown for unimplanted and ion-damaged ($5 \times 10^{13}/\text{cm}^2$, 40 keV Si) superlattices after diffusion at 790 °C for 10 min.

grown under standard conditions, and one with an intentionally raised C level of $2 \times 10^{19}/\text{cm}^3$ grown under a background acetylene pressure of 10^{-7} Torr. Figure 17 shows SIMS measurements of the B profiles for unimplanted and implanted ($5 \times 10^{13}/\text{cm}^2$, 40 keV Si) superlattices after annealing. The B diffusion in the superlattice containing $10^{18}/\text{cm}^3$ [Fig. 17(a)] is strongly enhanced with respect to thermal diffusion, and the behavior is similar to the previous superlattice measurements. The B diffusion in the ion-damaged superlattice with $2 \times 10^{19}/\text{cm}^3$ [Fig. 17(b)], on the other hand, shows no significant enhancement relative to thermal diffusion. TEM micrographs demonstrate that the formation of {311} interstitial defects is fully suppressed in C-rich Si samples. This illustrates that the effect of C is to eliminate the source of TED, rather than to limit B diffusion by trapping the dopant atoms.

Figure 18 compares TED for a $1.5 \times 10^{14}/\text{cm}^2$, 30 keV B implant in C-lean FZ silicon (prepared by amorphization and SPE) and C-rich FZ silicon with a uniform level of $4\text{--}6 \times 10^{18}/\text{cm}^3$ in the near-surface region (prepared by amorphization, C implantation, and SPE; see Sec. II). The diffused B profiles in the C-lean reference sample exhibit all the features characteristic to TED (see Fig. 1): Boron in the tail of the implanted profile has undergone enhanced diffusion over a distance of ~ 700 Å upon annealing at 800 °C for 35 min, while the peak portion of the profile above $10^{18}/\text{cm}^3$ has remained immobile due to the clustering of B driven by the excess interstitials. The diffusion behavior for the C-rich substrate is very different, as shown in Fig. 18(b). First, the diffusion length of B in the tail of the B profile stays well below ~ 700 Å at both 800 and 950 °C. In addition, there is no pronounced signature of immobile B in the peak of the

FIG. 18. SIMS measurements of B profiles after implantation ($1.5 \times 10^{14}/\text{cm}^2$, 30 keV B) and after subsequent annealing. Prior to B implantation, the float-zone Si sample in (b) was amorphized to a depth of $2 \mu\text{m}$ by Si ion implantation, enriched with C by multiple implants to a level of $4\text{--}6 \times 10^{18}/\text{cm}^3$ over $1 \mu\text{m}$, and regrown at 500°C for 1 h, 600°C for 2 h, and 900°C for 15 min. Sample (a) was prepared as sample (b), but without the C implants.

profile. Again, this demonstrates that C acts as traps for interstitials thereby suppressing both the enhanced B diffusion and the interstitial-driven clustering of B. In Fig. 19 the as-prepared and diffused C profiles are compared, which shows that a considerable portion of the C has diffused from the peak of the B implant to a depth of $\sim 2000 \text{ \AA}$ after the high-temperature anneal. This indicates that C diffusion is enhanced by the injected interstitials, as is discussed in Sec. VI B.

The spreading resistance measurements of Fig. 20 show that the major part ($\sim 80\%$) of the B profile is electrically active after the 950°C annealing step. In addition, Hall measurements on B profiles in *n*-type, C-rich substrates show that the electrically active fraction after diffusion at 800°C is

FIG. 19. Carbon depth profiles in C-rich FZ silicon [as Fig. 18(b)] after preparation of the sample, and after annealing an implant of $1.5 \times 10^{14}/\text{cm}^2$, 30 keV B at 800°C for 35 min and 950°C for 15 min.

FIG. 20. Comparison of atomic and electrical B profiles in *p*-type, C-rich FZ silicon [as Fig. 18(b)] obtained after annealing an implant of $1.5 \times 10^{14}/\text{cm}^2$, 30 keV B at 800°C for 35 min and 950°C for 15 min.

approximately 60% and increases to $\sim 85\%$ upon further annealing at 950°C , consistent with Fig. 20. The sheet resistance is 800 and $620 \Omega/\square$ after annealing at 800 and 950°C , respectively. Comparable values were found for B profiles implanted into FZ substrates and annealed under the same conditions. These electrical measurements therefore show that the presence of C and/or C-interstitial agglomerates does not deteriorate the doping efficiency to unacceptable levels; however, preliminary ion-implanted diode structures prepared in wafers with relatively high C concentrations indicate enhanced junction leakage. This is in line with electrical measurements on C-implanted Si samples.^{78,79} Further studies are required to investigate whether C incorporation in silicon precludes the formation of high-quality devices.

In order to assess the details of how C affects the flux of interstitials from a near-surface implant, superlattice structures were prepared which contain a nonuniform profile of substitutional C. To this end, MBE-grown B-doped *c*-Si superlattices were amorphized to a depth of $2 \mu\text{m}$, implanted with 115 keV C to a dose of $9 \times 10^{13}/\text{cm}^2$, and thermally regrown. Figure 21 shows the B and C profiles in C-rich superlattices (CSPE) and reference superlattices without C (SPE) after implantation and annealing. The injection of interstitials from the ion damage in sample SPE leads to diffusion and clustering of the B markers near the damage source. Figure 21(b) shows that the $10^{18} \text{ C}/\text{cm}^3$ in sample SPE has redistributed under the injection of interstitials, analogous to the result of Fig. 19. The decoration of the B peaks with C could indicate that part of the mobile C is gettered at the B clusters. The substitutional C which was incorporated into superlattice CSPE consists of a peak of $5 \times 10^{18}/\text{cm}^3$ at a depth of $\sim 3000 \text{ \AA}$ [Fig. 21(b)]. Figure 21(a) shows that the injection of interstitials in sample CSPE also enhances B diffusion, but the broadening of the B peaks in the C-rich region is much less pronounced than in reference sample SPE.

Figure 22 summarizes the values for $\langle D_B^{\text{int}} \rangle$ as a function

FIG. 21. SIMS measurements of (a) boron and (b) carbon depth profiles after diffusion at 790 °C for 10 min. CSPE refers to a MBE-grown B doping superlattice which was amorphized using Si implants, implanted with 115 keV C to a dose of $9 \times 10^{13}/\text{cm}^2$, and regrown at 500 °C for 1 h, 600 °C for 2 h, and 790 °C for 15 min. SPE was prepared as CSPE, but without the C implantation step. The damaging implant consisted of $5 \times 10^{13}/\text{cm}^2$, 40 keV Si.

of depth derived from the diffusion profiles in Figs. 11 and 21(a). The interstitial diffusion profile in sample SPE is significantly steeper than in the as-grown MBE sample, indicating a lower interstitial diffusivity. This suggests that the amorphization and/or SPE-regrowth steps have raised the level of interstitial traps in the superlattice. One possible mechanism could be the knock-on of carbon from deposited hydrocarbons on the sample surface during the relatively long (~ 1 h) amorphizing implant at liquid-nitrogen temperature. In addition, vacancy-type defects could have been introduced during SPE. The deviation between the diffusion

FIG. 22. Depth dependence of the intrinsic B diffusivity showing the effect of solid-phase epitaxy and C incorporation on the interstitial diffusion profile in MBE-grown superlattices. Data were obtained by analyzing the B diffusion profiles in Figs. 11(a) and 21.

FIG. 23. (a) Boron diffusion profiles and (b) intrinsic B diffusivities for a MBE-grown superlattice containing a buried spike of substitutional C. Transient enhanced diffusion (TED) was induced by annealing a $5 \times 10^{13}/\text{cm}^2$, 40 keV Si implant at 810 °C for 15 min in vacuum. Oxidation enhanced diffusion (OED) was induced by repeating the same diffusion anneal for an unimplanted sample in a dry oxygen ambient.

profiles for samples SPE and CSPE demonstrates that the interstitial-enhanced diffusion of B is reduced by a factor of ~ 10 at the peak of the C profile (~ 3000 Å deep). Beyond a depth of ~ 4500 Å, however, the values for $\langle D_B^{\text{int}} \rangle$ are nearly identical for both samples, indicating that the interstitial diffusion profile is only perturbed in the local vicinity of the incorporated C.

Figure 23 shows measurements of TED and oxidation-enhanced diffusion (OED) for a B-doped superlattice which contains of a narrow C spike at a depth of ~ 2300 Å. This structure was grown by briefly leaking C_2H_2 into the MBE chamber in between the growth of the second and third B doping spike. As is obvious from the diffusion enhancements in Fig. 23(b), the implantation damage is a more efficient source for interstitials at 810 °C than the oxidizing surface. For both TED and OED, the third B spike shows significantly less broadening than the two spikes adjacent to the source of interstitials. In particular, the interstitial-enhanced diffusion is fully suppressed at the wing of the third doping spike that is contained within the buried C spike [see Fig. 23(a)]. On the other hand, the deepest marker layer exhibits at least as much broadening as the preceding spike, and the diffusion is a factor of 5 above D_B^* . Analogous to the results in Figs. 21 and 22, this indicates that the incorporation of C leads to a local reduction of the interstitial concentration without fully obstructing the flow of interstitials to the bulk of the material.

B. Discussion

The results in the previous subsection have shown that raising the C concentration in Si from 10^{18} to $10^{19}/\text{cm}^3$ reduces the strength of interstitial-enhanced B diffusion. The straightforward explanation is that the interstitials driving TED are captured by substitutional C (C_s) through the following well-known replacement reaction:^{80,81}

The thus formed highly mobile C_I complex can pair with another substitutional C atom to yield a more stable complex ($C_I C_s$),^{82,83}

The ability of C_s to absorb interstitials is believed to play a crucial role in the coprecipitation of C and oxygen in Si at high temperatures,⁸⁴ although the detailed kinetics of this process are still under debate.^{85–87} The formation of C_I pairs through the replacement reaction of Eq. (10) reduces the amount of interstitials available for pairing with substitutional B, thereby lowering the B diffusivity. The density of interstitials that is bound in {311} defects in the early annealing stages of TED was found to decrease linearly with increasing C level (Fig. 9), consistent with C–I pairing.

In the case of an initially uniform C distribution, the continuous exchange between C and I will impose a gradient in C_I which follows the diffusion profile of I. Since C_I is highly mobile,^{81,84} this gradient will result in a net transport of C from the ion-implanted region to the adjacent region, as observed in Fig. 19. For comparison, it has been shown that the injection of interstitials during P in-diffusion yields a similar diffusion behavior in the near-surface region of C-rich Si samples.⁸⁸ In the case of a localized C peak (Figs. 21–23), the interstitials that are paired with C will be liberated when C_I diffuses out of the high-concentration region. This explains why the presence of C only causes a local reduction in the B diffusivity without fully suppressing the interstitial population at greater depths.

In addition to the effects of C–I pairing, part of the mobile C_I species will interact with remaining substitutional C atoms through, for instance, reaction (11). These C-related trapping reactions affect measurements of the interstitial diffusivity D_I in Si. Figure 24 compares typical values for D_I from metal diffusion studies¹⁵ with results obtained from the present experiments using MBE-grown B superlattices (Sec. IV B). The values for D_I at 800 °C vary from 10^{-6} to 10^{-12} cm^2/s , while the activation energies for diffusion range from ~ 1 to ~ 3.5 eV. Also, the diffusion range of interstitials in Si superlattices grown by chemical-vapor deposition has been shown to be much larger than in MBE-grown Si.²⁷ This discrepancy between the various experiments has been ascribed to the fact that the migration of self-interstitials is perturbed by the presence of interstitial traps in Si,^{18,19} and presumably C is the dominant impurity as demonstrated above.

The presence of trapping sites (T) will impose a local equilibrium between free (I) and trapped interstitials (IT) according to

$$[IT] = k_T [I] ([T] - [IT]). \quad (12)$$

FIG. 24. Interstitial diffusivities in silicon. Solid lines refer to data derived from metal diffusion studies (Ref. 15), whereas points are from MBE marker layer experiments (Sec. IV and Ref. 35). The dashed lines refer to model fits of trap-limited diffusion assuming immobile traps, Eq. (13).

Constant k_T can be approximated by $k_T \approx N_s^{-1} \exp(E_T/kT)$, with E_T the energy difference between the free and bound states of I . For immobile traps, the interstitial diffusion flux J_I is entirely carried by the mobile species I , and the effective diffusivity D_I^{eff} for the total interstitial distribution $[I] + [IT]$ is defined through

$$J_I = -D_I \nabla [I] = -D_I^{\text{eff}} \nabla ([I] + [IT]).$$

For a uniform distribution of traps ($\nabla[T] = 0$), the evaluation of this definition yields

$$D_I^{\text{eff}} = \frac{D_I}{1 + k_T [T] / \{1 + k_T [I]\}}. \quad (13)$$

Equation (13) was fitted to our TED and OED measurements of the interstitial diffusivity in Fig. 24 by taking D_I and $[I^*]$ from the metal diffusion experiments of Ref. 15. Furthermore, $[T]$ was fixed at $10^{18}/\text{cm}^3$ to match the C content in our samples, and the average interstitial concentration in the TED and OED experiments was taken as $1000 \times [I^*]$ and $10 \times [I^*]$,²⁸ respectively. Using $E_T = 2.1$ eV, the calculations for D_I^{eff} indeed reconcile the discrepancy between metal diffusion studies and our experimental data.

A severe limitation of the above analysis, however, is the simplifying assumption of immobile traps, whereas C–I pairing through reaction (10) leads to the formation of mobile C_I complexes. This implies that the interstitial flux J_I is actually carried by the migration of both I and C_I . In order to evaluate the effect of trapping reactions (10) and (11) on the diffusion of free interstitials, the full set of coupled diffusion and trapping equations was solved using the process simulator PROPHET.^{49,89} The diffusivity of C_I was taken as $D_{C_I} = 2.5 \times 10^{-3} \exp(-H_{C_I}^m/kT)$ cm^2/s , with $H_{C_I}^m = 0.8$ eV.⁸¹ The trapping enthalpies for reactions (10) and (11) were assumed to be 1.7 and 0.9 eV, respectively, in accordance with recent first principle calculations.⁷⁴

Figure 25 shows the evolution of the distributions of I , C_I , $C_I C_s$, and C_s at 800 °C. These profiles were calculated by assuming an interstitial injection level of $1000 \times [I^*]$ at

FIG. 25. Profiles of Si self-interstitials I , carbon-interstitial complexes C_i , C_iC_s pairs, and substitutional C during diffusion at 800 °C, which were obtained by using the numerical calculations.

the surface, typical of TED. It is obvious that the simultaneous migration of I and C_i introduces a strong concentration dependence in the interstitial diffusion profile, which unfortunately obstructs the extraction of effective interstitial diffusivities for comparison with experimental data. Nevertheless, the important conclusion from Fig. 25 is that the apparent interstitial diffusivity in marker layer studies will depend critically on how the experimental conditions (e.g., interstitial injection levels and C content) modify the relative strength of I and C_i diffusion.

Carbon should also affect the analysis of metal diffusion studies. In an extensive number of experiments (e.g., Refs. 15 and 68), the diffusion profiles of various metals in Si (Au, Zn, and Pt) have been used to derive values for D_I and $[I^*]$. It was shown almost 20 years ago⁹⁰ that increasing the C concentration in Si accelerates the in-diffusion of interstitial Au (Au_i), which was ascribed⁸⁴ to C trapping the interstitials formed in the kick-out reaction,

where Au_s denotes Au incorporated on substitutional sites. In most papers on metal diffusion, the C- I interaction is fully ignored in spite of the fact that the C content in "standard" Si wafers could be as high as $\sim 10^{17}/\text{cm}^3$. Therefore, Zn diffusion data from Ref. 15 were reanalyzed by explicitly in-

cluding the trapping of interstitials at immobile, nonannihilating traps into our process simulator.⁸⁹ Independent of the trap concentration $[T]$, excellent fits to the measured diffusion profiles of Zn are obtained.⁸⁹ The extracted value for $[I^*]$ varies inversely with $[T]$, while the product of $[I^*]$ and D_I remains constant. This implies that metal diffusion experiments only provide direct information on the Si self-diffusion coefficient, that is, $[I^*]D_I$. The separate determination of $[I^*]$ and D_I , on the other hand, requires detailed knowledge about the interaction of I with C or other impurities. Further experiments and analyses are required to solve this enigma.

VII. PHYSICAL MODELING

A. Monte Carlo simulations

The experiments in Secs. III and IV have shown that the rate and strength of interstitial injection during TED is controlled by the evaporation of $\{311\}$ defects, that is, for the implantation regime presently explored. Implementation of this concept into process modeling tools requires a detailed understanding of the kinetics and parameters that are involved in the formation and annealing of implantation damage. For instance, it is *a priori* not clear how the as-implanted population of vacancies and interstitials develops into a distribution of rodlike interstitial clusters in the early stage of annealing. To help elucidate these processes, an atomistic process simulator was developed.⁶³ This simulator includes a Monte Carlo diffusion code coupled to the MARLOWE⁹¹ computer code, which employs the binary collision approximation to estimate ion-induced defect formation in silicon. The parameters used in the Monte Carlo simulations were derived from molecular dynamics calculations using the Stillinger-Weber potential for Si.⁹² More details about the new simulator have been given in a recent article by Jaraíz *et al.*⁶³

The simulation of a typical room-temperature implant of $5 \times 10^{13}/\text{cm}^2$, 40 keV Si into Si(100) indicate that ~ 520 Frenkel pairs are generated per implanted ion. Approximately 70 interstitials per ion survive room-temperature recombination of interstitials and vacancies during and after implantation, which is implicitly accounted for in the modeling. The resulting defect population consists of small interstitial and vacancy clusters, which are distributed according to the initial MARLOWE depth profile of interstitials and vacancies.

For a subsequent anneal at 815 °C, free vacancies are emitted from their clusters, while the more tightly bound interstitials remain immobile in their small clusters. The random walk of the vacancies annihilates most of the interstitials. Although the dominant annihilation process is bulk recombination, some vacancies reach the surface (assumed to be a perfect sink) and annihilate there, leaving an excess of interstitials. Figure 26 shows the cumulative number of vacancies V_{surf} and of interstitials I_{surf} annihilated at the surface, per implanted ion, as a function of simulation time. The emission from the vacancy clusters can be easily identified as an increase in V_{surf} , especially after 10^{-3} s, when the larger clusters break up. At ~ 1 s, all of the vacancies have disappeared with the overwhelmingly dominant mechanism being

FIG. 26. Monte Carlo calculations of damage annealing in ion-implanted silicon (40 keV Si, $5 \times 10^{13}/\text{cm}^2$). Comparison between the number of interstitials recombined with vacancies in the bulk and the number of vacancies V_{surf} and interstitials I_{surf} annihilated at the surface.

bulk recombination; only 1% of the vacancies diffuse to the surface.

Figure 27 plots the net excess of interstitials (interstitials minus vacancies), per implanted ion, throughout the anneal. The starting value (1.3) corresponds to the situation after the room-temperature implant, and includes the contribution of the implanted ion (the true +1), the sputtered Si atoms (-0.3), the trapping of vacancies at oxygen traps (+0.3), and the surface contribution (0.3) due to the fact that vacancies diffuse faster than interstitials and are on average slightly closer to the surface. The number of interstitials remaining when all the vacancies have disappeared is ~ 1 per implanted ion, in agreement with the measurements in Fig. 7. It is quite remarkable that the full blown calculation, with the sputtering and surface terms, gives such a good approximation of the +1 model.

FIG. 27. Monte Carlo calculations of the net excess of interstitials per implanted ion during the 815 °C anneal. The solid points represent experimental data from TEM measurements of {311} defects (Fig. 5). Also shown is the average interstitials cluster size.

Upon continued annealing, small interstitial clusters undergo an Ostwald ripening process (Fig. 27, dashed line), analogous to the observed dynamics for {311} defects in Fig. 4. Eventually, the large clusters dissolve by emitting interstitials that subsequently annihilate at the front surface. The effect of trapping centers is almost negligible because of their low concentration relative to the interstitial concentration in the ion-implanted region. The dominant initial process during the high-temperature anneal is interstitial-vacancy recombination in the bulk of the material. Consequently, the imbalance in the interstitial and vacancy concentration arising from the implanted ion (the +1 model) dominates the excess interstitial concentration. This was confirmed by a simulation where the implanted ion was intentionally removed from the diffusion process. In that case the simulation yields +0.3 for the excess interstitial level, as opposed to +1.3. The clustering mechanism only establishes the time scale as was shown by an annealing simulation without clusters ($E_{\text{bind}}=0$ for all clusters), in which case the vacancies disappear in 5×10^{-6} s, leaving +1.3 interstitials per implanted ion. The +1 model is, therefore, physically plausible because of the dominant role of bulk recombination, with only minor deviations due to sputtering and surface annihilation. This feature makes it a particularly robust approximation for process simulation tools, only weakly sensitive to changes in the implant or anneal parameters.

Finally, the implications of these results for TED can be assessed. A close correlation between the excess interstitials and the induced TED can be drawn from the free interstitial distribution, time-integrated throughout the anneal. It is found that most of the TED occurs after the vacancies have fully disappeared,⁶³ which explains why continuum simulators yield reasonable predictions using the +1 model in this damage regime. However, simulations for implant doses as low as $5 \times 10^9/\text{cm}^2$ demonstrate that TED predominantly takes place before all vacancies have recombined. In this case, the probability of an interstitial interacting with a dopant atom has become greater than with a vacancy, because of the dilute interstitial and vacancy population.^{26,93} This notion could explain the observation that the total broadening of B marker layers induced by TED declines with decreasing implantation dose, saturating at a fixed, nonequilibrium level for low doses.²³

Although the +1 model seems to be appropriate for sufficiently high implantation doses ($> 5 \times 10^{12}/\text{cm}^2$), successful implementation of this model into process simulators requires detailed description of how interstitial clusters (i.e., {311} defects and dislocation loops) decay as a function of the implant (energy, dose) and annealing conditions (time, temperature). One example will be given in the following subsection. Modeling for lower doses should also include the fact that the average number of interstitial diffusion steps prior to recombination progressively increases with decreasing ion dose, leading to a more efficient damage-dopant coupling.

B. Process simulations

The concept of interstitial clustering has been incorporated into the process simulator PROPHET.^{49,94} The basis of

the model is that an interstitial in a cluster may spontaneously escape at a rate given by the interstitial hopping frequency and the binding energy to the cluster, while the clusters grow whenever diffusing interstitials are trapped by a cluster. The overall equation governing cluster kinetics is given by

$$\frac{d[I_{cl}]}{dt} = 4\pi\alpha a D_I [I][I_{cl}] - [I_{cl}] \frac{D_I}{a^2} \exp\left(-\frac{E_b}{kT}\right), \quad (15)$$

where $D_I = D_0 \exp(-E_m/kT)$ is the interstitial diffusivity, a is the average interatomic spacing, α is the capture radius expressed in units of a , $[I_{cl}(x,t)]$ is the concentration of interstitials trapped in clusters, and $[I(x,t)]$ is the concentration of free interstitials. Whenever free interstitials are numerous, the first term dominates and $[I_{cl}]$ grows exponentially until it is balanced by the evaporation flux. Equating the first and second terms in Eq. (15) yields the following expression for the interstitial concentration $[I_e]$ in equilibrium with the defect clusters:

$$\frac{[I_e]}{[I^*]} = \frac{1}{4\pi\alpha\Gamma} \exp\left(\frac{E_f - E_b}{kT}\right), \quad (16)$$

where E_f is the formation energy of the interstitial and Γ is defined by the interstitial formation entropy through $\Gamma = \exp(S_f/k)$. As is obvious from the above equation, the interstitial supersaturation during TED is set by the balance between cluster evaporation and growth, provided that the initial interstitial level is high enough for stable clusters to be formed.

The evaporation rate of clusters after self-implantation can be estimated by assuming that the excess interstitial dose ($Q \approx +1$) immediately condenses into clusters upon annealing. The loss of interstitials from the cluster region is controlled by the diffusive interstitial flux to the surface, which can be approximated by $D_I[I_e]/R_p$, where R_p is the projected ion range. Substituting the supersaturation of Eq. (16), the effective time needed to dissolve the clusters is given by Eq. (17). Thus, the evaporation time is thermally activated according to

$$\tau = \frac{4\pi\alpha R_p Q}{D_0 N_s} \exp\left(\frac{E_m + E_b}{kT}\right). \quad (17)$$

This model reproduces TEM observations that the {311} decay rate decreases with increasing ion dose and energy.^{60,64} Applying this model to the $5 \times 10^{13}/\text{cm}^2$, 40 keV Si implants of Figs. 2–5, assuming $\alpha=1$, and using the most recent experimental values of D_I and $[I^*]$,¹⁵ yields $\tau=42$ s at 815 °C and $\tau=14\,600$ s at 670 °C, in perfect agreement with the experiments in Fig. 5. The activation energy $E_b + E_m$ was taken to be 3.57 eV, in accordance with the TED time constants in Fig. 6 and in Ref. 11. A more exact calculation was carried out using the PROPHET simulator with the above numerical values to solve the differential equations for interstitial transport, recombination, and reaction with clusters in space and time. The result is shown in Fig. 28. The detailed calculation confirms the initial impression that the model captures the time and temperature dependence of {311} cluster evaporation. There is some discrepancy in the shape of the evaporation curves in that the simulated curves are more

FIG. 28. Simulation of the number of interstitials contained in clusters, as a function of time, at various annealing temperatures. The experimental data are reproduced from Fig. 5. The simulation model predicts the time and temperature dependence of {311} evaporation.

abrupt than the experimental ones. Apart from the possibility of an experimental artifact (see Sec. III A), this dissimilarity is probably due to ignoring the dependence of the binding energy on cluster size. Including Ostwald ripening in a more sophisticated model with a distribution of cluster sizes would probably improve the evaporation behavior; yet, it is satisfying that this single population model already predicts the time to remove a given dose of interstitials with an error of only 30%.

Having established $E_b + E_m = E_{\text{evap}} = 3.57$ eV, and knowing the interstitial self-diffusion energy $E_f + E_m = E_{\text{SD}}$, then the formation energy per atom of a {311} cluster is given by the difference $E_{311} = E_{\text{SD}} - E_{\text{evap}} = E_f - E_b = 1.38$ eV (see Fig. 29). This is in very satisfactory agreement with recent predictions of E_{311} from molecular dynamics calculations (~ 1.3 eV),⁹² and tight binding calculations (0.7–0.9 eV).⁹⁵ The formation energy per atom is also the activation energy of the interstitial supersaturation in Eq. (16), allowing the interstitial supersaturation during TED to be estimated as ~ 4000 at 800 °C and ~ 400 at 1000 °C. Typical experimental numbers are in the range of ~ 1000 – $10\,000$ at 800 °C,^{7,10,11,96} and 20–200 at 1000 °C.^{10,11} The experimental values are generally underestimates since they attribute the diffusive motion

FIG. 29. The average energy of an interstitial in a {311} cluster is found to be 1.38 eV. This estimate is independent of the particular experimental values taken for D_I and $[I^*]$, as it comes out as the difference of the $D_I[I^*]$ product, which is in good agreement between various studies and the {311} evaporation time activation energies.

to the entire annealing time, whereas the transient vanishes some intermediate time during the anneal. From the interstitial profile in Fig. 12(b) it was derived that $[I_e]/[I^*]$ is fixed at $(7.7 \pm 3.8) \times 10^3$ during TED at 670 °C. This yields $E_{311} = 1.3 \pm 0.1$ eV upon substitution in Eq. (16), in good agreement with the above numbers. It thus appears that the above model provides a self-consistent way of dealing with the clustering and injection of interstitials during TED, which can be efficiently implemented into process simulation programs.

A simple model of boron clustering can be developed on the following lines. One imagines a distribution of clusters, containing 2,3,4, etc., boron atoms. A cluster may shrink by spontaneously emitting a mobile boron-interstitial pair, or it may grow by capturing a free boron-interstitial pair. This yields rate equations which are analogous to those of Eq. (6a), but now with the addition of a decay term,

$$\frac{dN_3}{dt} = \frac{-N_3}{\tau} + 4\pi a_c D_{B_I} [B_I] N_2, \quad (18a)$$

$$\frac{dN_4}{dt} = \frac{-N_4}{\tau} + 4\pi a_c D_{B_I} [B_I] N_3, \quad \text{etc.}, \quad (18b)$$

where N_i is the number of clusters of size i and τ is a spontaneous decay time. Multiplying each equation by i and summing over i ,

$$\frac{d}{dt} \left(\sum_i i N_i \right) = \frac{-\sum_i i N_i}{\tau} + 4\pi a_c D_{B_I} [B_I] \sum_i i N_i. \quad (19)$$

The rate equation for the total number of boron atoms in clusters, $B_c = \sum_i i N_i$, is then

$$\frac{d[B_c]}{dt} = -\frac{[B_c]}{\tau} + 4\pi a_c D_{B_I} [B_I] [B_c]. \quad (20)$$

This result relies on the approximations that τ and a_c are independent of cluster size, and that the average cluster contains at least three or four boron atoms. Making one final assumption that the pairing reaction for forming B_I [Eq. (4a)] is in equilibrium,

$$\frac{d[B_c]}{dt} = -\frac{[B_c]}{\tau} + k_f [B_s] [I] [B_c], \quad (21)$$

with k_f a rate constant expressed in cm^6/s . The equation predicts that when the number of interstitials is large, the second term will dominate and lead to an exponential growth in $[B_c]$. The exponential growth will continue until the second term is reduced and the first term increased to bring them into balance. When this occurs,

$$\frac{1}{\tau k_f [I]} = [B_s]. \quad (22)$$

That is to say, the free boron concentration $[B_s]$ will be lowered until it reaches a quasisolubility which is inversely related to the interstitial concentration $[I]$. This is consistent with the observation that the apparent solubility in each superlattice spike is inversely related to the amount of diffusion seen in that spike (see, for instance, Fig. 11).

FIG. 30. PROPHET simulation of TED for the experiment of Fig. 1 ($1.5 \times 10^{14}/\text{cm}^2$, 30 keV ^{10}B implant diffused at 800 °C for 35 min). A comparison is made between the default diffusion model (PROPHET-1) and the new model including interstitial and B clustering (PROPHET-2). This figure clearly illustrates the improvements that have been made.

The above approaches for dealing with interstitial and boron clustering were implemented into PROPHET and used to simulate the initial TED experiment of Fig. 1. It was required to take the net interstitial excess at +0.5 instead of +1.0 to match the diffusion in the tail of the profile. A similar effect has been seen in other work⁷¹ where implanting B and Si at the same dose and energy gave identical TED in buried markers. Since the B is implanted more deeply, one would expect more TED than from the Si implant. That one does not is an indication that the net interstitial excess is smaller with B implants than Si implants. Alternatively, this discrepancy could reflect the trapping of some of the interstitials in B clusters (Fig. 8). As can be seen from Fig. 30, the fit to the B profile has greatly improved as a result of the physical insights presented in this article. Of course, more simulations are required to test the present model for a wider range of implant and annealing conditions.

VIII. SUMMARY: THE LIFE OF THE INTERSTITIAL

This article has dealt with clustering and diffusion phenomena involving dopants and defects which are activated in ion-implanted silicon during annealing. The common microscopic agent of these processes is the Si self-interstitial, and the physical mechanisms which control transient enhanced dopant diffusion can be summarized in a qualitative manner by following the life of the interstitial.

Ion implantation leads to an athermal generation of interstitials and vacancies through the collisional displacements of lattice atoms. The average number of Frenkel pairs that is generated per incoming ion depends on the ion species and energy, and may vary from tens to thousands for keV implants of atoms such as B, Si, or P. The Monte Carlo simulations in Sec. VII A have shown that a fraction of the Frenkel pairs recombines during and after implantation at

room temperature, and the remaining interstitials and vacancies are contained in small clusters. Upon annealing, these clusters will dissolve by emitting point defects (interstitials and/or vacancies), which will eventually recombine with their free or clustered counterparts, annihilate at the surface, or diffuse into the bulk. It was demonstrated by TEM measurements in Sec. III that for sufficiently high damage levels (40 keV Si, $>1 \times 10^{13}/\text{cm}^2$), the resulting excess number of interstitial atoms approximately equals the imbalance in the interstitial and vacancy concentrations resulting from the extra implanted atom (the +1 model). This suggests that $I-V$ recombination is the dominant decay mechanism in the initial annealing stage, as reconfirmed by the Monte Carlo simulations in Sec. VII A.

The excess interstitials are contained in {311} defect clusters for doses in the range from 5×10^{12} to $1 \times 10^{14}/\text{cm}^2$, and these defects sustain a local supersaturation of interstitials by emitting and recapturing interstitials during continued annealing (Ostwald ripening). Interstitials are gradually lost from the damage region through diffusion into the bulk and to the surface, the latter most likely being the dominant loss mechanism.³¹ The rate at which this decay occurs is determined by the average binding energy of interstitials at {311} (~ 1.3 eV), the proximity of the surface, and the initial interstitial concentration as it is set by the implant dose. For sufficiently high doses ($>1 \times 10^{14}/\text{cm}^2$) and annealing temperatures, {311} defects may unfault into more stable dislocation loops which will change the kinetics of interstitial injection.

Those interstitials which have escaped from the damage region into the bulk of the material may pair with dopants such as B and P, or with impurities such as C. The first interaction causes the local dopant-interstitial pair concentration to increase above the equilibrium level, thereby causing enhanced diffusion. For sufficiently high B levels, the wind of diffusing interstitials drives substitutional B into metastable clusters at concentrations below the solid solubility limit. This clustering process is most likely accompanied by the trapping of interstitials, which perturbs the interstitial flow.

The coupling of interstitials with C leads to the formation of highly mobile C_i pairs. This process reduces the amount of interstitials available for pairing with dopants, leading to a strong reduction in the enhanced diffusion and clustering of B for sufficiently high C concentrations ($\sim 10^{19}/\text{cm}^3$). The rapidly migrating C_i pairs, which carry part of the net interstitial diffusion flux, can undergo further trapping reactions with ubiquitous impurities in Si such as substitutional C. The resulting retardation of the interstitial transport depends critically on the injected level of interstitials and on the concentrations of C_s , a notion which would explain the large variation in published interstitial diffusivities. Eventually, interstitials trapped in B- and C-related clusters will be reemitted and will continue to migrate through trapping and detrapping, until the equilibrium between free interstitials and vacancies is fully recovered.

Some caution is required with respect to the modeling of TED of ion-implanted B. When the high B concentration is contained inside the ion-damaged region, some fraction of

the interstitial-enhanced B diffusion and clustering may actually occur as the interstitial and vacancy population collapses. This would require a full-blown evaluation of the coupled defect-defect and defect-dopant interactions to assess the B profiles and the defect distribution before the {311}-controlled diffusion regime kicks in. This is just one question which remains to be answered among many others: By which microscopic mechanism does B diffuse? Can the various published diffusivities of Si indeed be reconciled on the basis of C-interstitial trapping reactions? How do {311} defects evolve into dislocation loops, and how does this process affect the interstitial injection kinetics? Do the interstitial and vacancy populations behave independently for high-energy implants? These and related issues will certainly provide a challenge to the silicon research community for many years to come.

ACKNOWLEDGMENTS

A large number of people has contributed significantly to the present work in the form of discussions and technical support. Among them are J. L. Benton, T. Boone, G. S. Higashi, and F. C. Unterwald at Bell Laboratories, T. Diaz de la Rubia and J. Zhu at Lawrence Livermore National Laboratories, and N. E. B. Cowern at Philips Research Laboratories. A portion of this work was sponsored by the U.S. Department of Energy, Office of Energy Research, Laboratory Technology Applications Division and the Division of Materials Sciences under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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(Received 4 April 1996; accepted for publication 4 June 1996)

Boron implantation into silicon offers a unique system for studying the gettering mechanisms of Fe. Using deep level transient spectroscopy to monitor the remaining Fe in the gettered region and secondary-ion-mass spectroscopy to measure the concentration of Fe redistributed to the B region, we show that the gettering mechanisms can be quantitatively described. A combination of Fermi-level-induced Fe^+ charge-state stabilization and Fe^+-B^- pairing acts to lower the free energy of Fe in p^+ regions. This can lead to Fe partition coefficients as high as 10^6 at a p^+/p interface at temperatures below $\approx 400^\circ\text{C}$. The dynamic response of the system is diffusion limited during the cooling cycle. B gettering is more effective than gettering produced by Si implantation damage and more effective than trapping by a neutral impurity such as C. These mechanisms also make a large contribution to the effective gettering of Fe by p/p^+ epitaxial silicon wafers. The Fermi-level/pairing gettering mechanism is also expected to operate for Cr and Mn. © 1996 American Institute of Physics. [S0021-8979(96)00718-9]

I. INTRODUCTION

Every Si integrated circuit processing fabrication line has in place an accepted gettering technique. Gettering is defined¹ as a process through which impurities in the device region are reduced by localizing them in predetermined, passive regions of the Si wafer. The gettering technique can represent up to 10% of the total integrated circuit manufacturing costs. New clean room practices, advances in tool design, and increased implementation of statistical process controls have reduced metal contamination during device manufacture to the required levels; however, the industry continues to depend on gettering strategies to ensure the maintenance of high yield in the event of process variations. In particular, transition metals such as Fe and Cu are detrimental impurities because of their likely presence in the processing environment and their high diffusivities in Si. Most transition metals are known to introduce deep levels inside the Si band gap,²⁻⁵ which adversely affect minority carrier lifetimes and junction leakage. In addition, Fe contamination levels as low as $1 \times 10^{11} \text{ cm}^{-3}$ have been reported to degrade the performance of thin gate oxides.⁶ Extrapolations suggest that the $0.18 \mu\text{m}$ generation of devices will require the impurity levels in active device regions to be reduced below $1 \times 10^{10} \text{ cm}^{-3}$, and materials specifications may be as low as

10^8 per cm^2 (SIA Roadmap). The quantitative predictions of the gettering effectiveness has thus become a major issue in specifying the materials and process for future generations of Si product. Despite this, we have to date only a qualitative understanding of the mechanisms involved in gettering. In this article we compare the effectiveness of various gettering techniques and offer the first quantitative model of Fe gettering by B in Si.

There have been many attempts to describe and classify the physical mechanisms responsible for the observed metal gettering, but the general consensus in the published literature has been to use the terms relaxation gettering and segregation gettering. Relaxation gettering⁷ is defined as a non-equilibrium mechanism, occurring during the cooling period at the end of any high-temperature processing step, and the accepted explanation is heterogeneous precipitation of contaminants at gettering sites, resulting from supersaturation of metals at low temperatures. Segregation gettering⁸ is presented as an equilibrium, high-temperature process and the mechanism is described as a solubility enhancement of the metallic impurities in the gettering region. A wide variety of gettering techniques has been divided into these two categories with the implication that the underlying physical phenomena are understood. In general, a combination of mechanisms is in effect and, in particular, equilibrium mechanisms can occur during cooling. Gettering at dislocations may be due to heterogeneous precipitation, segregation to a Cottrell cloud, or a combination of both mechanisms. Any "segregation" mechanism must have an inherent activation energy in order to overcome the entropy associated with uniform distribution. Thus, by definition a segregation mechanism oper-

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ates more effectively at low temperature and cannot be easily distinguished from a "relaxation" mechanism. Gettering by epitaxial $p/p+$ wafers involves both processes. In other examples, neither of these mechanisms describes the physics. The boron ion-implantation gettering mechanisms described in this work cannot be adequately understood by using either of these terms. We would suggest, therefore, that these terms have outlived their usefulness, and that in the future the various atomistic trapping mechanisms be defined specifically.

Although a wide variety of gettering schemes has been developed for Si processing in the past decades,⁹⁻¹⁶ two approaches are dominant in the current technology. First, intrinsic or internal gettering (IG) is achieved in the interior of Czochralski (Cz) bulk Si wafers which have been subjected to a high-low-high annealing cycle. This procedure comprises a high-temperature anneal (1100 °C) for the out-diffusion of O from the near-surface region, a second low-temperature anneal (700 °C) to induce the precipitation of O inside the wafer, and an optional high-temperature anneal (1000 °C) to accelerate the growth of the O precipitates. The electronic devices are fabricated in the near surface, oxygen-denuded zones of these wafers. The gettering action results from the oxygen precipitates and/or oxidation-induced crystal defects (e.g., punched out dislocations) in the Cz substrates, which provide heterogeneous nucleation sites for metal precipitation.^{1,17} It has been shown that precipitation during IG at a given temperature only occurs when the metal concentration exceeds the solid solubility limit.¹⁸ This requirement may put a severe limit on the efficiency of IG at low contamination levels.

In a second gettering scheme devices are fabricated in lightly B-doped (p) epitaxial layers grown by chemical-vapor deposition (CVD) on highly doped ($p+$) Cz substrates. Although these structures were originally developed to enhance the latch-up resistance of complementary metal-oxide-semiconductor (CMOS) devices, they have also proven to exhibit good gettering characteristics. It has been demonstrated in recent experiments^{19,20} that the high B-doping level in $p+$ substrates enhances the removal of Fe contamination from the epitaxial Si layers. This enhanced gettering is consistent with the observation²¹ that raising the B-doping level in Si increases the solubility of Fe, thereby providing a driving force for Fe to pile up in the $p+$ substrate. However, there have been no attempts until now to quantify the separate contributions of B doping and O precipitates to gettering in $p/p+$ structures.

In this article high-energy boron ion implantation is used as a model system to study a specific gettering process—the enhanced trapping of Fe at a highly doped B region in Si. Implantation is used to introduce precisely controlled concentrations of B in well-defined regions. The gettering effectiveness of this dopant is compared with implanted C, a neutral impurity, and is also compared to damage sites introduced by Si implantation. We show that a region of high B concentration provides enhanced gettering of Fe, which can be explained by electronic interactions between interstitial Fe and the dopant B ions, controlled by the temperature-dependent Fermi-level position. Iron, $\text{Fe}^{0/+}$, diffuses interstitially and is known to have either a neutral or positive charge

state regulated by the Fermi-level position in the host silicon.^{3,4} When the Fe species is in the neutral state, no preferential gettering occurs, however, when the Fermi level is below $E_V + E_T = 0.39$ eV, the positive charge state of the Fe interstitial atom exhibits enhanced gettering. It is shown in this article that the gettering of Fe in B-doped Si can be quantitatively understood in terms of previously identified electronic interactions between Fe and B.^{22,23}

We have introduced gettering layers into Fe-contaminated Si wafers by means of high-energy ion implantation. These experimental results establish a foundation for an evaluation of high-energy ion implantation as a gettering technique in device fabrication. The presence of regions of high B concentration effectively reduce the residual Fe concentration in the lower-doped device regions which will have a positive impact on carrier lifetime and device leakage characteristics. It is suggested that high-energy B implantation into bulk Si substrates offers promise as a method for replacing the use of $p/p+$ epitaxial layers, which could lead to significant cost reductions in Si processing.

This article is organized as follows. In the following section we present the experimental approach through which the gettering mechanisms were investigated. The subsequent section discusses our data on the gettering efficiencies of ion-implanted B, C, and Si in Fe-contaminated Si. On the basis of these results we discuss the various gettering mechanisms in Sec. IV, and present a quantitative explanation of the mechanism of Fe gettering in B-doped Si.

II. EXPERIMENT

Figure 1 is a schematic representation of the Fe and B distributions within the Si and the experimental conditions measured in this work. Uniformly contaminated wafers were obtained by implanting double-polished float-zone (FZ) Si(100) wafers (500 μm thick, B doped, 20 Ωcm) on the backside of the samples with 500 keV ^{54}Fe or ^{56}Fe to a dose of $1 \times 10^{13} \text{ cm}^{-2}$. For comparison, crucible-grown, Cz, and $p/p+$ epitaxial Si substrates were also contaminated and measured. All samples were annealed at 1000 °C for 1 h to remove implantation damage and to uniformly distribute the Fe throughout the Si at a concentration of $2 \times 10^{14} \text{ Fe/cm}^3$. It should be noted that this contamination level is slightly below the solid solubility limit of Fe at 1000 °C.^{4,18}

Gettering layers were introduced on the front side of the contaminated wafers by implanting ^{10}B , ^{12}C , ^{16}O , or ^{28}Si at energies ranging from 0.5 to 7 MeV. The implanted samples were annealed at 1000 °C for 1 h in a tube furnace under He flow to induce gettering. The sample temperature T_s during and after annealing was monitored by means of a thermocouple mounted in a quartz rod attached to the sample holder. The temperature evolution during cool down from 1000 °C can be well described by a stretched-exponential decay

$$T_s(t) = T_f + (T_i - T_f) \exp[-(t/\tau)^\beta]$$

for $t \leq 1200$ s, with $T_i = 1000$ °C, $T_f = 141$ °C, $\tau = 67$ s, and $\beta = 0.71$. The measured temperature during the cooling down and the fit to the data points are presented in Fig. 2. A subset

FIG. 1. Schematic representation of the Fe and B distributions during these experiments and an indication of the sample regions probed by DLTS and SIMS.

of the samples received additional anneals in the temperature range from 600 to 1000 °C after the initial annealing step.

The accumulation of Fe in the implanted region at the front of the samples was detected by means of secondary-ion-mass spectrometry (SIMS). The analyses were performed on a Cameca 3f system employing an O_2^+ sputtering beam. High-resolution mass detection was applied to avoid interference of $^{10}\text{B-Si-O}$ trimers (54 u) with the ^{54}Fe signal, or interference of Si-Si dimers (56 u) with the ^{56}Fe signal. The SIMS sensitivity was limited to $\sim 1 \times 10^{15} \text{ cm}^{-3}$ for ^{54}Fe and $\sim 1 \times 10^{16} \text{ cm}^{-3}$ for ^{56}Fe . To take advantage of the higher measurement sensitivity, the majority of our samples were implanted with ^{54}Fe ions. Figure 3 illustrates the misleading results obtained by the low mass resolution SIMS profiles of Fe. The aliasing of ^{54}Fe with $^{10}\text{B-Si-O}$ leads to an exaggeration of the Fe in Fig. 3(a).

The depletion of Fe from the near-surface region and from the bulk of the wafer was measured by deep-level tran-

FIG. 2. Measurements of the temperature during cooling after heat treatment at 1000 °C and the theoretical fit to the data discussed in Sec. II of this work.

sient spectroscopy (DLTS) using a BioRad DL8000 spectrometer. Titanium was evaporated through a shadow mask to make the Schottky contacts for the DLTS measurements. The average Fe concentration within the probe region of the measurement (1–3 μm from the surface) was obtained by adding the DLTS signals from the levels that are associated with interstitial iron atoms (Fe_i) and with $\text{Fe}_i\text{-B}_i$ pairs.

FIG. 3. Comparison of (b) high mass resolution SIMS results with (a) standard measurements using an O_2^+ sputtering beam. The $^{10}\text{B-Si-O}$ trimer (54 au) produces a SIMS artifact which mimics the ^{54}Fe signal leading to misleading Fe concentration profiles.

FIG. 4. Solubility of Fe in Si [solid line: this work; dashed line: Aoki co-workers (Ref. 18)]. The solid circles are data using precipitates of β -FeSi₂ as Fe source; the other data points are from the annealing behavior of uniformly distributed Fe concentrations of $2 \times 10^{14} \text{ cm}^{-3}$ in FZ silicon (open circles) and in Cz silicon (triangles).

These signals are located at 0.39 and 0.10 eV from the valence band, respectively.^{22,23} Implantation energies were chosen to ensure that the gettering layer and possible implantation damage on the front side of the wafers were introduced deep enough, $\sim 4 \mu\text{m}$, to allow for unperturbed DLTS measurements in the near-surface region. Some of the samples were thinned by mechanical polishing in order to measure Fe_i and Fe_i-B_s concentrations through the thickness of the wafer.

This equipment set was also used to obtain self-calibrated reference data on the equilibrium solubility of Fe in Si. To this end, 500- μm -thick double-polished FZ Si pieces were implanted with $4 \times 10^{17} \text{ cm}^{-2}$, 300 keV, ⁵⁶Fe at a temperature of 350 °C to obtain a buried layer of FeSi₂ precipitates.²⁴ Cross-section transmission electron microscopy (TEM) indeed confirmed the formation of a band of precipitates of β -FeSi₂. Individual samples were annealed at temperatures in the range from 600 to 1000 °C in order to dissolve Fe from the silicides into the bulk of the wafers. The annealing times ranged from 18 h at 600 °C to 1 h at 1000 °C, allowing full Fe equilibration in the sample through diffusion. The Fe concentration in equilibrium with the silicide layer was measured after diffusion by performing DLTS on the side of the wafer opposite the implanted silicide. Figure 4 (solid circles) shows these results compared with the previously published solubility (dashed line) of Fe in Si.^{4,18}

III. RESULTS

A. Boron dose dependence of Fe gettering in Si

Si samples which were contaminated with a uniform concentration of $2 \times 10^{14} \text{ Fe cm}^{-3}$ were implanted with $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV, ¹⁰B and then heat treated at 1000 °C for 1 h. The total Fe concentration, measured by DLTS before and after the B gettering implant and anneal, is shown in Fig. 5. Prior to the B gettering treatment, the Fe concentration in the near-surface region is detected as the sum of the Fe_i-B_s and Fe_i signals. After the high-energy B ion implan-

FIG. 5. DLTS, $\tau_r = 9 \text{ ms}$, showing the initial Fe concentration throughout the sample after 500 keV ion-implanted Fe at a dose of $1 \times 10^{13} \text{ cm}^{-2}$ and heat treatment of 1000 °C, 1 h (solid line) and after a gettering implant of 3.3 MeV, $4 \times 10^{14} \text{ B cm}^{-2}$ and anneal of 1000 °C, 1 h. The residual Fe in the near-surface region after gettering is below the detection limit of $1 \times 10^{10} \text{ cm}^{-3}$.

tation and gettering anneal, the Fe concentration in the 1–3 μm region below the surface is less than the DLTS detection limit of $1 \times 10^{10} \text{ Fe cm}^{-3}$. This demonstrates that the high-energy B implant produces a dramatic reduction in the Fe concentration in its immediate proximity. SIMS data on a companion sample with the same initial Fe contamination, B implant, and anneal, shows that the Fe has redistributed to the B profile [Fig. 3(b)]. The peak concentration of ⁵⁴Fe gettering at the range of the B is $\sim 2 \times 10^{16} \text{ cm}^{-3}$, which is two orders of magnitude above the initial contamination level. The integrated ⁵⁴Fe dose at the implanted B peak is $5 \times 10^{11} \text{ cm}^{-2}$, indicating that 5% of the total contamination in the Si sample is collected in the B-doped region. It is important to note that the gettered Fe does not mirror the B profile, but is narrower by a factor of 2. This nonlinearity is fully predicted by the gettering model that is presented in Sec. IV.

The effectiveness of the gettering of Fe by the implanted B is a function of the B dose. Figure 6 shows that the total Fe

FIG. 6. Gettering effectiveness of B, C, and Si as a function of ion-implantation dose, measured by DLTS. The concentration of Fe remaining in the near-surface region is two orders of magnitude less after B gettering at high doses than after Si gettering. Dislocations are observed in transmission electron micrographs in the Si-implanted samples.

FIG. 7. Comparison of the integrated amount of Fe which is collected at 2.2- μm -deep B (solid triangles) and C (open circles)-implanted layers as a function of ion dose. The initial Fe concentration was $2 \times 10^{14} \text{ cm}^{-3}$ and all samples received 1000 °C for 1 h.

concentration remaining in the near-surface region of the Si after the gettering implant and anneal, 1000 °C for 1 h, decreases with increasing B dose. At a value of $1 \times 10^{14} \text{ B/cm}^2$, the Fe concentration is reduced to below the DLTS sensitivity; at implantation doses $> 1 \times 10^{15} \text{ B cm}^{-2}$, corresponding to a peak B concentration $> 3 \times 10^{19} \text{ cm}^{-3}$, extended defects remain in the measurement volume producing broad dislocation signals in the DLTS spectra²⁵ which prevent the detection of the Fe-related peaks. SIMS measurements indicate that as the B dose is raised, more Fe is trapped in the implanted region. Figure 7 shows the integrated amount of Fe that is collected at 2.2- μm -deep B layers introduced by 1.5 MeV implants. The gettered Fe dose increases with increasing B dose reaching a level of $\sim 10^{13} \text{ cm}^{-2}$ at a B dose of $1 \times 10^{15} \text{ cm}^{-2}$. For each of these doses the implanted B is expected to be incorporated onto substitutional sites within the first seconds of the annealing step,^{26,27} yielding full electrical activation.

DLTS measurements on the backside of the wafers opposite to the B implants reveal Fe concentrations remaining at the initial levels of $2 \times 10^{14} \text{ cm}^{-3}$ after gettering, even for the highest B doses. These results indicate that the gettering process is only effective in the close vicinity of the implanted B layer. In order to establish the range over which gettering occurs, DLTS was performed on samples that were thinned to various depths by mechanical polishing. The solid circles in Fig. 8 show the Fe concentration as a function of depth after gettering at 1000 °C with $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV B. The Fe concentration increases from the fully gettered level ($\leq 1 \times 10^{10} \text{ cm}^{-3}$) near the implanted layer to $1 \times 10^{14} \text{ cm}^{-3}$ at a depth of $\sim 50 \mu\text{m}$. The diffusion length for Fe in Si, 1000 °C, 1 h, is $\approx 1000 \mu\text{m}$, or more than twice the thickness of the sample: The diffusion length for Fe in Si during the quench, integrating over the full cooling curve as shown in Fig. 2, is 67 μm . Therefore, the DLTS measurements at both surfaces of the samples allows simultaneous monitoring of the diffusion-limited gettering during cool-down (front-side) and Fe solubility at the annealing temperature (back-side). These results demonstrate that a high-energy B implant leads to a strong reduction in the Fe concentration in its

FIG. 8. DLTS depth profiles of Fe-contaminated samples, given a 3.3 MeV B, $1 \times 10^{14} \text{ cm}^{-2}$ gettering implant and 1000 °C anneal, followed by 1000 °C, 1 h (solid circles); 800 °C, 2 h (open circles); or 600 °C, 18.5 h (solid triangles) additional heat treatments.

immediate proximity, and that the gettering is occurring during the cooling cycle.

B. Temperature dependence of B gettering of Fe in Si

The above experiments illustrate how a single annealing cycle at 1000 °C affects the Fe gettering behavior. In order to investigate whether the accumulation of Fe at an implanted B layer can be enhanced by further annealing at lower temperatures, ^{56}Fe -contaminated samples were implanted with $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV ^{10}B and gettered at 1000 °C for 1 h. Then samples were heat treated at lower temperatures for times sufficiently long to allow for Fe diffusion over the entire thickness of the sample. Representative results are also plotted in Fig. 8. Fe concentrations at 500 μm (backside) are all consistent with the published solubility results and are plotted in Fig. 4 (open circles).^{4,18} In all cases, the Fe has been gettered to well below the solubility limit from the front 3 μm of the samples.

Comparison of SIMS profiles of the Fe concentration in samples implanted with $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV ^{10}B and heated to 1000 °C, 1 h with samples given an additional heat treatment at 800 °C for 2 h, Fig. 9, demonstrates that the amount of Fe at the gettering layer increases from 3×10^{12} to $9 \times 10^{12} \text{ cm}^{-2}$, indicating that at 800 °C almost the entire contamination dose is collected at the B implant. This effect is reversed by an additional annealing step at 1000 °C for 1 h, for the integrated Fe dose at the B implant returns to $2 \times 10^{12} \text{ cm}^{-2}$. Also, DLTS shows that the Fe contamination on the wafer backside is returned to $\sim 1 \times 10^{14} \text{ cm}^{-3}$ after the 1000 °C anneal. The high-dose B implant and its remaining associated lattice damage provide effective heterogeneous nucleation sites for Fe precipitation at temperature, pinning the concentration of Fe in solution throughout the entire sample to the solid solubility. It is interesting to note in Fig. 4, that the amount of Fe remaining in solution after heat treatment and fast cool to room temperature is somewhat lower in crucible-grown, Cz. material, $[\text{O}] \approx 10^{18} \text{ cm}^{-3}$, (tri-

FIG. 9. High-resolution SIMS measurement of ^{56}Fe profiles in Fe-contaminated Si samples that were implanted with $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV ^{10}B and gettered at 1000 °C for 1 h (solid line); given an additional heat treatment of 800 °C, 2 h (dotted-dashed line); and then given a third furnace anneal of 1000 °C, 1 h (dashed line). After 800 °C, more than 90% of the implanted Fe is collected at the B implant.

angles) than in FZ silicon, $[\text{O}] \approx 10^{16} \text{ cm}^{-3}$ (open circles). The Cz Si forms oxygen aggregates during high temperature cycling which provide a distribution of Fe precipitation nucleation sites throughout the sample. Therefore, the difference observed in the "solubility" curves is an indication of additional Fe precipitation occurring during the cool in the bulk of the silicon containing higher concentrations of O.

C. Comparison of gettering effectiveness of B, C, Si, and O

In order to understand the mechanisms responsible for B gettering of Fe, it is instructive to compare the high-energy B implantation layers with the gettering effectiveness of Si and C. These data are plotted in Fig. 6. Transmission electron micrographs in Fig. 10 prove that, in general, B or Si implants at doses $\geq 3 \times 10^{14} \text{ cm}^{-2}$ result in the generation of end-of-range dislocation loops. The high-energy Si-

FIG. 10. Cross-section TEM micrographs of ion-implanted Si showing dislocations after high-dose B or Si ion implantation. Sample surfaces are at the top of the figure.

implanted samples, therefore, provide examples of the effectiveness of crystal damage as a gettering scheme. Comparison of the Si dose dependence with the B data (Fig. 6) contributes evidence that it is the B species which is responsible for the enhanced gettering of Fe and not the related ion damage. Likewise, comparison of the B with the dose dependent gettering by C, a neutral trap for Fe, illustrates the added effectiveness of the electronic interactions between Fe and B.

It is worth considering the Si implant results in more detail. It is expected that ion damage will provide heterogeneous nucleation sites for metal precipitation in Si. For anneals where the Fe is supersaturated, precipitation at dislocations leads to gettering at the anneal temperature. The SIMS data of Fig. 9 show that for high-dose B ion implantation into a sample containing $2 \times 10^{14} \text{ cm}^{-3}$ Fe, most of the Fe in the sample ($\approx 9 \times 10^{12} \text{ cm}^{-2}$ out of a total dose of $1 \times 10^{13} \text{ cm}^{-2}$) is precipitating at the ion-damaged region during an 800 °C anneal. TEM shows that these samples contain dislocations at the B range.²⁸ It appears that Fe comes out of solution and forms precipitates at these dislocations during the second, lower-temperature anneal. The cross-section TEM micrographs of Fig. 10 show the damage created by a 1.5 MeV B implant for a dose of $3.5 \times 10^{14} \text{ cm}^{-2}$ and for a co-implant of 0.7 MeV Si, $3.0 \times 10^{14} \text{ cm}^{-2}$. There is no observable damage when the B dose is reduced to $3.5 \times 10^{13} \text{ cm}^{-2}$.

In principle, precipitation at dislocations should also lead to effective gettering during cooling. During the final part of our standard cool (Fig. 2), the Fe diffusion length is $> 3 \mu\text{m}$ even for temperatures below 400 °C. If rapid precipitation occurred at the band of dislocations, one would thus expect the near-surface Fe concentration to be close to the solid solubility of Fe at 400 °C (10^7 cm^{-3}), which is below the detection limit of DLTS. The observation that the Fe level in Si-implanted samples which contain dislocations is well in excess of the DLTS detection limit suggests that the gettering at dislocations is limited by nucleation rate rather than diffusion kinetics. The lower relative near-surface concentration of Fe which results from B gettering thus occurs because it is limited only by diffusion rates.

The amount of Fe remaining in the gettering region as measured by DLTS can be compared to the amount of Fe collected in the implanted region as measured by SIMS. Several ion implantation configurations were monitored by SIMS, including high-energy B only, high-energy Si only, spatially separated B and Si co-implants, and overlapping B and Si co-implants. The DLTS data, Fig. 6, reveal that the total remaining Fe concentration in the near-surface region, averaged over the area of the measurement diode, is two orders of magnitude less for a B gettering implant compared to a Si implant, i.e., B provides more effective "gettering." On the other hand, SIMS measurements show that the amount of Fe collected in the implanted region, Figs. 11(a) and 11(b), is the same for both B and Si ions. Note that the SIMS of collected Fe is dominated by the gettering in the initial stages of cooling, over long diffusion lengths ($\sim 60 \mu\text{m}$). When Si and B are co-implanted, Figs. 11(c) and 11(d), the position of the gettering Fe aligns with the dislocations

FIG. 11. SIMS profiles showing the redistribution of Fe after high-energy B and/or Si ion implantation followed by furnace anneal of 1000 °C, 1 h: (a) 1.5 MeV B, $6 \times 10^{13} \text{ cm}^{-2}$, only; (b) 2.1 MeV Si, $3 \times 10^{14} \text{ cm}^{-2}$, only with a range of 1.8 μm ; (c) 2.1 MeV Si, $3 \times 10^{14} \text{ cm}^{-2}$, and 0.45 MeV B, $3 \times 10^{13} \text{ cm}^{-2}$; (d) 2.1 MeV Si, $3 \times 10^{14} \text{ cm}^{-2}$, and 1.5 MeV B, $6 \times 10^{13} \text{ cm}^{-2}$.

introduced by the Si ion implantation. These SIMS results suggest that the dislocations provide the most effective nucleation sites for Fe precipitation at elevated temperatures, and the DLTS data indicate that the B profile provides a more homogeneous driving force for Fe diffusion on length scales less than 5 μm , i.e., in the final annealing stages.

IV. GETTERING MECHANISMS

A. Boron Ion Implantation

The above results imply that the most effective gettering is associated with the presence of a B-rich region, and that the Fe gettering occurs during the cooling cycle. This gettering behavior can be entirely explained in terms of Fe-enhanced segregation into the highly doped B regions controlled by the difference in the Fermi-level positions in the two regions of differing B concentrations.

Interstitial iron, $\text{Fe}_i^{0/+}$, in solution in a Si crystal is known to have either a neutral or positive charge state regulated by the Fermi-level position. In *p*-type material, the charge on the interstitial iron donor level, $E_v + 0.39 \text{ eV}$, will be positive when the Fermi level is below this deep level state. This Fermi-level-controlled fraction of Fe^+/Fe^0 as a function of temperature and B-doping concentration, shown in Fig. 12(a), is calculated from the relationship

$$\frac{[\text{Fe}^+]}{[\text{Fe}^0]} = 0.5 \exp\left(\frac{(E_T - E_F)}{kT}\right), \quad (1)$$

FIG. 12. (a) The fraction of positively charged interstitial Fe to neutral Fe plotted as a function of temperature and B doping level. (b) The calculated partition coefficient of the total Fe concentration redistribution for a region of $[\text{B}] = 1 \times 10^{18} \text{ cm}^{-3}$ adjacent to a region of $[\text{B}] = 1 \times 10^{15} \text{ cm}^{-3}$, as a function of temperature. The solid line shows the effects of Fermi-level-controlled Fe^+ redistribution and Fe^+B^- pairing. The dashed line shows neutral trapping of Fe at an impurity site with a binding energy of 0.65 eV.

where the square brackets denote the concentration of each species. When the Fe_i is positively charged, there is an association reaction driven by Coulomb attraction, to form the $\text{Fe}_i\text{-B}_j$ pair with the negatively charged boron acceptor,

The mass-action relationship for Fe^+ pairing with B^- is known from previous DLTS results²³ to be

$$\frac{[\text{Fe}^+\text{B}^-]}{[\text{Fe}^+][\text{B}^-]} = 10^{-23} \exp\left(\frac{0.65 \text{ eV}}{kT}\right). \quad (3)$$

In the situation where we have Fe distributed throughout Si which has two adjacent regions of differing B concentrations, the higher number of negative ions in the highly doped region will produce a Coulomb attraction between B^- and Fe^+ . At equilibrium, the ratio of Fe^+ in the highly B-doped region, $[\text{Fe}^+]_H$, to the Fe^+ in the region of less B, $[\text{Fe}^+]_L$, will be a function of the Fermi level difference ΔE_F according to the relation

$$\frac{[\text{Fe}^+]_H}{[\text{Fe}^+]_L} = e^{\Delta E_F/kT}. \quad (4)$$

Thus, both Fermi-level-induced Fe redistribution and Fermi-level-controlled Fe-B pairing provide mechanisms for the observed enhanced gettering.

The calculation, based on these two equilibrium mechanisms, for the partition coefficient, $[\text{Fe}^{\text{tot}}]_H/[\text{Fe}^{\text{tot}}]_L$, for a highly doped layer, $[\text{B}] = 10^{18} \text{ cm}^{-3}$, adjacent to a lower doped region, $[\text{B}] = 10^{15} \text{ cm}^{-3}$, is shown in Fig. 12(b). For temperatures above 600 °C, the electronic effects are too weak to produce appreciable redistribution of Fe. Below

600 °C, the partition function increases steeply. The calculation for neutral trapping of Fe at a B site is also plotted in Fig. 12(b) (dashed line), and illustrates the reduction in the partitioning at low temperatures without the Fermi-level-induced redistribution. Highly doped layers, $>10^{18}$ B/cm³, are extremely effective gettering regions, providing equilibrium partition coefficients for Fe of approximately 10^6 at low temperatures.

Since the equilibrium mechanisms are ineffective at high temperatures, in actual practice the nonequilibrium diffusion kinetics become the limiting factor, and gettering becomes dependent on cooling rates and Fe diffusivity. The calculations of Fig. 12(b) can be extended to predict the dynamic response to the nonequilibrium situation during cooling from high temperature. Our example uses the experimentally determined initial B-doping profile of Fig. 3(a), a uniformly distributed metal contamination of 2×10^{14} Fe/cm³, and the measured cooling curve of Fig. 2. At each temperature during the calculation, the B-doping profile is used to evaluate E_F as a function of depth, which allows the determination of the local volume concentration of neutral Fe⁰ and charged Fe⁺ from the entire Fe profile through Eq. (1). The kinetics of the redistribution of Fe can then be determined from the diffusion flux F , given by

$$-F = D^0 \nabla[Fe^0] + D^+ \nabla[Fe^+] + \frac{D^+}{kT} [Fe^+] \nabla(E_F - E_T), \quad (5)$$

where D^0 and D^+ are the diffusivities of Fe⁰ and Fe⁺ in Si.²⁹ The drift motion of Fe⁺ induced by the gradients in the Fermi level is represented by the third term in the equation. It is assumed that Fe⁺ pairs rapidly with B⁻ to set a local equilibrium according to Eq. (3). Previous DLTS experiments suggest that this should be a good approximation above ~ 200 °C.²³ This diffusion equation, Eq. (5), is coupled with the trapping equation, Eq. (3), and solved numerically to determine the redistributed Fe profile in response to the measured cooling curve. It should be stressed that no adjustable parameters are used in these calculations; the Fe donor level, the Fe-B binding energy, and the Fe⁰ and Fe⁺ diffusivities are all obtained from independent measurements in the literature. Figure 13 shows the calculated Fe profiles at several temperatures during cooling after a 1000 °C anneal. The results reproduce the depletion of Fe from the surface and the accumulation of Fe in the B-implanted layer. The final Fe distribution perfectly reproduces the experimental observations of both SIMS (solid circles) and DLTS (solid triangles). Moreover, calculations of the near-surface Fe depletion as a function of the B gettering dose reproduce the measurements in Fig. 6, within the experimental error of the measured Fe diffusivity, giving further support for this explanation of enhanced gettering.³⁰

The model gives a complete description of the redistribution of Fe by a B-implanted profile during heat treatment and subsequent cooling. It does not include nucleation kinetics or precipitate spatial inhomogeneities which control the position of the final gettered Fe profile.

FIG. 13. Measurements and calculations of the Fe impurity depth profile during and after gettering at an implanted B layer (4×10^{14} cm⁻², 3.3 MeV B). The solid points represent data of the final Fe profile obtained by SIMS, and the triangles are DLTS measurements. The calculated redistribution of Fe is solved numerically using the partitioning coefficient of Fig. 10 and the diffusion flux of Eq. (5).

B. $p/p+$ epitaxial silicon

The effective gettering of $p/p+$ epitaxial silicon wafers can also be explained by these results.^{25,20} Changing the starting B profile in the same iterative program discussed above allows the calculation of the expected gettered Fe concentrations in epitaxial Si. Representative results for an initial Fe concentration of 2×10^{14} atoms/cm³ and the cooling curve in Fig. 2 are plotted in Fig. 14. For a 7-μm-thick p -epitaxial layer doped with $[B] = 10^{15}$ cm⁻³ grown on a $p+$ substrate, $[B] = 10^{18}$ cm⁻³, the Fe remaining at room temperature in the gettered region is $< 10^{10}$ cm⁻³. To depict how the gettering is sensitive to the difference in the B concentrations, results for an epitaxial layer doped at 10^{17} B/cm³ are also plotted and show that the gettering effectiveness has

FIG. 14. Calculations of the redistribution of Fe after 1000 °C gettering treatment and fast quench for two different doping concentrations. $[B] = 10^{15}$ cm⁻³ (solid line) and $[B] = 10^{17}$ cm⁻³ (dashed line) in a 7 μm epitaxial layer on a $p+$ substrate. $[B] = 10^{18}$ cm⁻³.

been dramatically reduced. Experimental results verify this trend. Using this model system it is shown for the first time that the gettering of Fe in B-doped Si can be quantitatively understood in terms of the previously identified electronic interactions between Fe and B.

Typically, the thermal cycles used in epitaxial growth will also lead to O precipitation in the Cz substrate. This provides heterogeneous Fe precipitation sites within the $p+$ region. Thus, we anticipate that the O precipitates in $p/p+$ epitaxial wafers mimic the effect of dislocations in the high-dose B implants and in the B and Si co-implants. This would imply that intrinsic gettering requires slow cooling after high-temperature annealing steps for the process to be efficient at low impurity concentrations.

It appears that the same gettering mechanisms, i.e., Fermi-level-controlled Coulombic attraction between the interstitial Fe and the substitutional B, control the residual Fe concentration in the near-surface region for both B ion-implanted profiles and $p/p+$ epitaxial layers. It is useful to compare the two configurations as a function of quench rate. The gettering calculation is reproduced in Fig. 15 for two different initial concentrations of Fe contamination. The high-energy implanted sample is consistently more effective than epitaxial silicon in gettering Fe in these two examples.

Although increasing the doping level in the substrate would change this result, in practice, this is not practical for integrated circuit production because of the additional strain generated at the substrate/epitaxial layer interface by the lattice mismatch. It is also evident from the model results of Fig. 15 that the amount of Fe remaining after gettering scales

FIG. 15. Calculation of the amount of Fe remaining in the near-surface region of Si after 1000 °C, 1 h, anneal as a function of the quench rate for two different initial Fe concentrations. The solid lines are based on a 3.3 MeV B implant which gives a peak concentration of 1×10^{19} B/cm³, and the dashed lines are calculation for an epitaxial layer on a $p+$ substrate doped at 1×10^{18} B/cm³.

linearly with the Fe concentration present before gettering. This linear dependence was indeed observed by Aoki and co-workers.²⁰ These results suggest that it is extremely important to provide controlled nucleation sites for precipitation to maintain the lowest possible initial Fe in solution and to prevent undesirable Fe precipitation at the Si surface or Si-oxide interface. We propose that the oxygen in the Si substrates used for epitaxial growth fulfills this role. Previous

TABLE I. Experimentally determined properties^a of transition metals in Si.

Metal	Charge state	Activation energy (eV)	Pair	Charge state	Activation energy (eV)	Solubility (1100 °C) (cm ⁻³)	Diffusivity (1100 °C) (cm ² s ⁻¹)
Ti _i	+/++ DD 0/+ D -/+ A	H(0.28) E(0.28) E(0.08)	not seen			2×10^{13}	4×10^{-9}
V _i	+/++ DD 0/+ D -0 A	H(0.30) E(0.42) E(0.15)	V-B (?)			4×10^{12}	2×10^{-8}
Cr _i	0/+ D	E(0.22)	Cr _i -B _s	0/+	H(0.28)	3×10^{14}	2×10^{-6}
Mn _i	+/++ DD 0/+ D -0 A	H(0.25) E(0.42) E(0.11)	Mn _i -B _s	0/+	H(0.55)	3×10^{15}	4×10^{-6}
Fe _i	0/+ D	H(0.43)	Fe _i -B _s	0/+	H(0.10)	3×10^{15}	4×10^{-6}
Co _i	A AA	E(0.41) E(0.21)	Co-B (?)			4×10^{15}	6×10^{-5}
Ni	A A	E(0.43) H(0.22)	Ni _i -B _s	0/+	H(0.14)	5×10^{17}	4×10^{-5}
Cu _i	AA A	E(0.16) H(0.41)	Cu _i -B _s	0/+	H(0.22)	8×10^{17}	$> 5 \times 10^{-5}$
Zn _i	AA A	H(0.60) H(0.32)	Zn-B(?)		H(0.09)	2×10^{16}	10^{-7}

^aThe following definitions are used in this table: D: donor; A: acceptor; AA: double acceptor; *i*: interstitial; *s*: substitutional; E: activation energy measured from the conduction band; H: activation energy measured from the valence band.

FIG. 16. Calculations comparing the redistribution of Fe, Cr, and Mn following a $4 \times 10^{14} \text{ cm}^{-2}$, 3.3 MeV B gettering implant, and a 1000 °C, 1 h heat treatment, plus cool to room temperature using experimentally determined cooling curve shown in Fig. 2.

work shows that the Fe precipitation rate is controlled by the oxygen concentration in the Si.¹⁸

C. Gettering of other transition metals

The mechanism of Fermi-level-induced redistribution and pairing can be extended to other transition metals, and the expected effectiveness can be predicted based on known values of solubilities, diffusivities, and charge states of the interstitial atoms. Table I collates literature data on these parameters for a number of important transition metals.^{26,27}

Calculations comparing the high energy B gettered redistribution of Cr and Mn with that of Fe are shown in Fig. 16. Comparison of B gettering of Fe (dotted-dashed line) and Mn (dashed line), where solubilities and diffusivities are similar, illustrates the effect of the position of the donor states of the interstitial atoms in the gap relative to the Fermi level in *p*-type Si. Mn remains positively charged even at high temperatures as indicated in Table I; but, the Fermi-level mechanisms do not dominate until the lower temperatures which occur during cooling, and there is little difference in the final distribution of metals. Comparison of the Mn with the Cr calculation, where the charge states are the same but the diffusivities are different, illustrates that the diffusion kinetics at low temperatures limit the gettering effectiveness.

Ti and V have low diffusivities, so that any transport to B will be diffusion limited and gettering would be restricted to high temperatures, where Fermi-level mechanisms are less effective. The metals Co, Ni, Cu, and Zn exhibit very high diffusivities. Although the metal-B pairs for these four contaminants have been experimentally observed, the interstitial metal atoms have not been identified by DLTS, and little is known about the pairing mechanisms. For these four metals, gettering by X-B pairing cannot yet be predicted quantitatively.

V. CONCLUSIONS

High-energy B implantation is used as a model materials system to study the gettering mechanisms of Fe in B-doped

silicon. A quantitative explanation of the gettering mechanism is provided which shows that the enhanced diffusion of the Fe into the highly doped B regions is controlled by both Fermi-level-induced Fe redistribution and Fermi-level-controlled Fe-B pairing. This equilibrium partitioning of Fe is extremely effective at temperatures below 400 °C, and it is shown that the gettering occurs during sample cooling. The dynamic response of the system is diffusion limited. The effectiveness of B gettering of Fe depends on the boron doping level, on the difference in the Fermi-level positions in the two regions of differing B concentrations, on the starting Fe concentration and on the Fe diffusion kinetics during the cooling cycle. The principles of the model are extended to *p/p*+ epitaxial silicon.

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Efficient production of silicon-on-insulator films by co-implantation of He^+ with H^+

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(Received 20 October 1997; accepted for publication 2 January 1998)

We have investigated the process of thin film separation by gas ion implantation and wafer bonding, as well as the more basic phenomenon of blistering, on which the technique is based. We show that when H and He gas implants are combined they produce a synergistic effect which enables thin-film separation at a much lower total implantation dose than that required for either H or He alone. By varying the H and He implantation doses we have been able to isolate the physical and chemical contributions of the gases to the blistering processes. We find that the essential role of H is to interact chemically with the implantation damage and create H-stabilized platelet-like defects, or microvoids. The efficiency of H in this action is linked to its effective lowering of the silicon internal surface energy. The second key component of the process is physical; it consists of diffusion of gas into the microvoids and gas expansion during annealing, which drives growth and the eventual intersection of the microvoids to form two continuous separable surfaces. He is more efficient than H for this process since He does not become chemically trapped at broken bonds and thus segregates into microvoids more readily. In particular, we have demonstrated that a $1 \times 10^{16} \text{ cm}^{-2}$ He dose in combination with a $7.5 \times 10^{15} \text{ cm}^{-2}$ H dose are sufficient to shear and transfer a thin silicon film onto a handle wafer after bonding the two wafers together. © 1998 American Institute of Physics. [S0003-6951(98)01809-9]

There is at present a great deal of interest in the use of hydrogen ion implantation for synthesis of thin silicon-on-insulator (SOI) films.¹ It has been demonstrated that hydrogen implantation can be used to shear and transfer a thin silicon layer from an implanted wafer onto a supporting wafer after bonding the two wafers together and annealing.¹ This process potentially allows SOI wafers to be produced more economically than competing processes such as oxygen implantation or bonded etchback since the remaining sheared wafer can be re-polished and used again. The thin-film separation process was originally proposed based on the observation that implantation of high doses of hydrogen leads to the blistering of metal and semiconductor surfaces.^{2,3} Recently, it has been demonstrated⁴ that the hydrogen-induced thin-film separation process, and the more basic phenomenon of blistering^{2,3} on which it is based, involves a buildup of pressure of H gas trapped in microvoids during annealing. While it is clear that the thin film separation process with H^+ proceeds by both chemical interactions (bond breaking and internal surface passivation) and physical interactions (gas coalescence, pressure, and fracture) of implanted H with the Si substrate,⁴ it is difficult to isolate the contribution of each component to the overall process using implantation of H only. In this work, we have combined H and He gas implantation to decouple the physical and chemical contributions to

the blistering and thin film separation processes. We have observed that a combination of H and He gas implants results in a synergistic effect that allows the combined threshold dose for thin-film separation to be significantly reduced.

For the blistering experiments, Czochralski Si was implanted at room temperature with 30 keV H^+ and 33 keV He^+ singly, or in combination, to doses ranging from 1×10^{15} to $5 \times 10^{17} \text{ cm}^{-2}$. The samples were subjected to furnace annealing (FA) at 450 °C for 20 min, or rapid thermal annealing (RTA) at 750 °C for 20 s in flowing N_2 . All annealed samples were imaged using an optical microscope with Nomarski contrast capability. For thin-film separation experiments, 100 mm float zone (FZ) wafers polished on both sides were implanted with $6 \times 10^{16} \text{ cm}^{-2}$ H^+ only, or $7.5 \times 10^{15} \text{ cm}^{-2}$ H^+ with $1 \times 10^{16} \text{ cm}^{-2}$ He^+ , or $1 \times 10^{16} \text{ cm}^{-2}$ H^+ with $1 \times 10^{16} \text{ cm}^{-2}$ He^+ . The implanted wafers were then hydrophilically joined to "handle" wafers with a thermally grown 3400 Å oxide. After joining, the bonded pairs of wafers were cut with a high-speed diamond saw into $1 \times 1 \text{ cm}^2$ pieces for thin-film separation experiments. Pieces were also cut for transmission electron microscopy (TEM) studies. Cross-sectioned TEM samples were prepared by mechanical thinning and Ar^+ ion beam milling at 77 K. Extended defects were imaged using the weakly excited 220 and 400 reflections.

Figure 1 compares optical micrographs showing blistering in samples implanted with H^+ only, H^+ and He^+ together, and He^+ only, after annealing at 750 °C for 20 s. The typical pattern of blisters and flakes shown in Fig. 1(a) for a H dose of $6 \times 10^{16} \text{ cm}^{-2}$ is not observed for a H^+ dose of 4

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FIG. 1. Nomarski optical micrographs of the silicon surfaces after implantation with (a) $6 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$, (b) $4 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$, (c) $1 \times 10^{17} \text{ cm}^{-2} \text{ He}^+$, and (d) $1 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$ followed by $1 \times 10^{16} \text{ cm}^{-2} \text{ He}^+$, after annealing at 750°C for 20 s.

$\times 10^{16} \text{ cm}^{-2}$ [Fig. 1(b)] nor is it observed for a He^+ dose as high as $1 \times 10^{17} \text{ cm}^{-2}$ [Fig. 1(c)]. The blistering and flaking behavior is recovered however when a low He dose of $1 \times 10^{16} \text{ cm}^{-2}$ is co-implanted with a low H^+ dose of $1 \times 10^{16} \text{ cm}^{-2}$ [Fig. 1(d)]. These results imply that a He dose as small as $1 \times 10^{16} \text{ cm}^{-2}$ is able to compensate for the larger reduction in H dose of $5 \times 10^{16} \text{ cm}^{-2}$. Thus, a combination of the two species is capable of reducing the critical total dose below that which is necessary using either species alone. This synergistic effect is illustrated in Fig. 2 where the total dose necessary for blistering is plotted as a function of the fraction that is H^+ . Figure 2 illustrates two important features. First, the addition of a small fraction of H quickly reduces the critical total dose relative to that for He alone. Second, the effect is clearly non-additive demonstrating that He and H play different roles in the blistering process. The minimum total dose shown in Fig. 2 is $1.75 \times 10^{16} \text{ cm}^{-2}$, which in-

FIG. 2. Total ($\text{H}^+ + \text{He}^+$) implantation dose necessary for blistering as a function of the fraction that is H^+ .

FIG. 3. Weak-beam dark-field cross-sectional TEM images of samples implanted with (a) $6 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$ only, (b) $1 \times 10^{16} \text{ cm}^{-2} \text{ He}^+$ only, and (c) $1 \times 10^{16} \text{ cm}^{-2} \text{ H}^+$ followed by $1 \times 10^{16} \text{ cm}^{-2} \text{ He}^+$. All images are for as-implanted samples.

cludes a H dose of only $7.5 \times 10^{15} \text{ cm}^{-2}$, a factor of 3 smaller than the dose necessary when using H only.

Hydrogen is well known to chemically interact with broken silicon bonds, readily passivating unreconstructed dangling bonds on the surfaces or in the bulk.⁵ A consequence of this chemical interaction between H and Si is that when H is implanted into silicon it begins to pair immediately with the broken silicon bonds created during implantation. Figure 3(a) shows a TEM image of the buried layer of defects, located approximately $0.3 \mu\text{m}$ below the surface, which results from a $6 \times 10^{16} \text{ cm}^{-2} \text{ H}$ implant. High-resolution imaging reveals the buried layer to consist of a high density of well defined 3–10 nm platelet defects oriented on $\{100\}$ and $\{111\}$ planes. These extended defects are well known and have been shown to be H stabilized.⁶

Implantation of He leads to a very different defect morphology. Fig. 3(b) shows that for a $1 \times 10^{16} \text{ cm}^{-2} \text{ He}$ implant the buried layer contains relatively fewer defects $< 10 \text{ nm}$ but many platelets $> 300 \text{ nm}$. In weak-beam dark-field TEM imaging conditions strain contours are seen surrounding the large platelets indicating the presence of a large strain field around them. It can be inferred that this strain is due to pressure from He trapped within. Helium appears to diffuse and segregate into large platelets during the implantation itself, a behavior consistent with the lack of chemical interaction of He in Si . If the same dose of $1 \times 10^{16} \text{ cm}^{-2} \text{ He}$ is implanted after a $1 \times 10^{16} \text{ cm}^{-2} \text{ H}$ implant, a buried defect layer is observed [see Fig. 3(c)] that is similar to that of the sample implanted with $6 \times 10^{16} \text{ cm}^{-2} \text{ H}$ only [compare Figs. 3(c) and 3(a)], consisting of 3–10 nm platelet defects.

Based on these TEM observations, we explain the blistering behavior and the synergistic effect from H/He co-

implantation as follows. In general, exfoliation requires a gas pressure as well as a narrowly confined layer of cracks or microvoids into which the gas can segregate and expand during annealing, leading to growth and an eventual intersection of the microvoids to form two continuous internal surfaces. The essential role of H is to chemically interact with the implantation damage and to create a high density of microvoids (the H platelet defects) during the implant. While H is more efficient at forming the required high density of microvoids due to its chemical interaction with Si and especially due to dangling bonds, we argue that the same chemical interaction hampers segregation of H into the voids and formation of H₂ gas since all of the broken bonds created by the implantation compete for the available H, and furthermore, H diffusion in Si is severely limited by defect traps.⁷ Helium, on the other hand, being not so easily trapped by broken Si bonds, can more easily segregate and expand into the microvoids, thus playing a predominantly physical role to provide the force that drives crack growth leading to exfoliation. The presence of H is expected to aid the crack growth process by reducing the surface free energy density of the new internal surface area produced during crack growth. Such a model, and a comparison of Figs. 3(b) and 3(c), predict that He implantation before H would not be as efficient. Additional experiments have confirmed this prediction; doses of H and He that are just above the threshold for blistering when H was implanted first did not lead to blistering when He was implanted first.

Based on our findings with blistering experiments we have used a $7.5 \times 10^{15} \text{ cm}^{-2}$ H implant followed by a $1 \times 10^{16} \text{ cm}^{-2}$ He implant to successfully produce thin SOI films by wafer bonding, demonstrating that the total implantation dose can be reduced to $1.75 \times 10^{16} \text{ cm}^{-2}$, less than 30% of the $6 \times 10^{16} \text{ cm}^{-2}$ dose necessary when using H alone. A smaller implantation dose can potentially lead to more economical production of SOI films. The films separated by co-implantation of H with He have been characterized by atomic force microscopy (AFM); with a root-mean-square roughness of 60 Å they are comparable to films prepared using H⁺ alone.

In summary, we have observed a synergistic effect when H and He gas implants are combined. By taking advantage of

this synergy, the technologically important process of thin-film separation can be achieved with a total implantation dose that is at least three times smaller than that which is necessary using H alone. There appear to be two critical components to the blistering process: formation of a perforation layer that is sufficiently weakened by a high density of small microvoids, and gas diffusion and expansion to provide stress which drives crack growth in the microvoid layer. The synergy arises because H is more efficient in the first process, due to its chemical interaction with the implantation damage while He is more efficient at the second, primarily physical process. Therefore, the most efficient process occurs when the H dose is reduced to that which is just large enough to create a sufficient number of microvoids and by adding just enough He for gas expansion during annealing. We have demonstrated that a $1 \times 10^{16} \text{ cm}^{-2}$ He dose in combination with a $7.5 \times 10^{15} \text{ cm}^{-2}$ H dose is sufficient to produce a thin SOI film by wafer bonding.

The authors gratefully acknowledge Yves Chabal, Vittorio Marsico and Marcus Weldon for introducing the problem to us as well as for helpful discussions, Chung-Ming Hsieh for bonding the implanted wafers, and Stan Christman for patiently and expertly cutting them. This research was supported in part by an appointment to the Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute of Science and Education and Oak Ridge National Laboratory, and funded by the U. S. Department of Energy, Laboratory Technology Research Division under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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Damage, defects and diffusion from ultra-low energy (0–5 keV) ion implantation of silicon

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Abstract

Continued use of ion implantation for doping of silicon integrated circuits will soon require implantation energies below 5 keV to form electrical junctions less than 50 nm deep. At such low energies, dopant diffusion and formation of extended defects is modified by both the proximity of the surface and by the large volume concentrations of point defects and dopant atoms that arise from reduced range straggling. This brief review summarizes our recent experiments which measured defect formation and evolution, as well as enhanced diffusion, in silicon implanted with Si⁺ and B⁺ ions at energies as low as 0.5 keV. The results have demonstrated that {311}-type extended defects are generated from Si⁺ implants even within 3 nm of the surface. However, when these defects eventually dissolve, the surface acts as a perfect sink to efficiently annihilate the released interstitials. As a result, the amount of TED from Si⁺ implantation measured by epitaxially-grown B markers decreases approximately linearly with decreasing ion energy. For sub-keV B⁺ implants typical doses currently used for source-drain doping lead to a boron diffusion enhancement of 3–4× despite the proximity of the surface. Enhanced diffusion is also observed from molecular beam-deposited silicon layers containing a high boron concentration. This newly emerged diffusion enhancement mechanism, *boron-enhanced-diffusion* (BED), is associated with the formation of a fine-grain polycrystalline silicon boride phase in the implanted layer during activation annealing. These investigations of ultra-low energy (ULE) implantation have thus reinforced and validated our understanding of the role of implantation damage in enhancing dopant diffusion in silicon, while simultaneously revealing some important new materials issues which will impact semiconductor processing in coming device generations. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the challenges which must be met for the coming generations of silicon-based microelectronics is the development of a method to form extremely shallow junctions. For example, the industry's latest technology roadmap projects that junctions shallower than 30 nm

for transistors with 0.05 μm effective gate length will be required by the year 2012 [1]. Ion implantation at energies in the single-digit keV range has the potential to meet this requirement [1]. Consequently, equipment manufacturers have been aggressively developing equipment architectures to implant at energies as low as 250 eV [2]. Reducing the implantation energy is expected to reduce two contributions to the junction depth: the projected range of the dopant implant, R_p , as well as the transient enhanced diffusion (TED) of the dopant resulting from implantation damage, which occurs during activation annealing and becomes the

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dominant contribution to junction depth when R_p is reduced to depths of the order of 10 nm [3–7].

The defect formation and dissolution behavior for low-energy implants (i.e. 10–100 keV) has been quite intensively investigated [8]. It is now generally agreed that most of the implantation damage is removed during the early stage of annealing via point defect recombination, leaving excess interstitials, approximately equal in number to the implanted dose, which then coalesce into extended defects [4,5]. After short, or low-temperature, anneals (e.g. 15 s/750°C) these extended defects are primarily of the {311} type, consisting of interstitial condensates elongated in the (110) directions, and located on the {311} habit plane [8–10]. With further annealing, these {311} defects dissolve, releasing interstitials [8]. It is also well known that the interstitials released from these metastable extended defects are responsible for TED of dopants, such as boron, which diffuse by an interstitial mechanism in silicon [4,11–13]. Knowledge of defect formation and dissolution is thus necessary for understanding transient enhanced diffusion from very low energy implants and to enable successful predictions of dopant profiles by process simulations.

Until recently there was very little data on the damage, defects or diffusion from ultra-low energy (ULE) implantation. Of particular interest are: (1) the kinetics of growth and dissolution of defects such as {311}'s from very low energy implants, (2) the impact of the surface on annihilation of excess-interstitials and hence on TED and (3) the chemical effects due to the high concentrations of dopants in the implanted layer that result from reduced straggling at low implantation energies. For instance, based on reductions in TED observed after surface etching [14], it has been suggested that surface proximity increases point-defect annihilation leading to reduced TED. However, no direct measurements have tested this prediction for ULE implants. This paper reviews recent experiments [15–18] that address these issues, which are critical to successful use and implementation of ULE ion implantation for ultra-shallow junction formation. While many of the results are consistent with extrapolations based on studies at higher energies implantation, a couple of new phenomena have also been observed. For Si^+ implants a relatively stable species of {311}-type defects are observed when the volume concentration of implantation-induced interstitials exceeds 1%. Diffusion experiments with very low energy Si^+ implants have also confirmed that TED of boron markers decreases as the implant is moved closer to the surface at a rate consistent with the hypothesis that the surface is a perfect sink for interstitials. The most important new finding however is related to boron diffusion. It is found that amorphous layers containing high boron concentrations inject interstitials

during annealing, leading to enhanced diffusion of boron. This diffusion enhancement, which is in addition to the standard concentration dependence [19], is even produced by evaporated B layers. This phenomenon has been termed BED, or *boron-enhanced-diffusion* [18]. Included in this paper are the most recent data on BED in silicon, which demonstrate that BED occurs when the boron dose exceeds a threshold that corresponds to both amorphization during implantation and silicon boride phase formation during annealing. The limit on ULE B^+ implant doses which is implied by these findings is also discussed.

2. Interstitial defects from 1–5 keV Si^+ ion implantation

There are two principal consequences for the damage distribution when the implantation energy is reduced for a fixed dose: firstly, the implanted layer is brought closer to the surface and secondly, the ion straggling decreases such that the volume concentration of excess interstitials, C_i , within the layer becomes quite large for typical doses (e.g. C_i exceeds 1% of the atom density of silicon for a $3 \times 10^{14} \text{ cm}^{-2}$ Si^+ implant at 5 keV). Two new phenomena related to these aspects have been observed [15]: (1) {311}-type defects are formed despite the proximity of the surface (2.5 nm for a 1 keV Si^+) and (2) in samples where C_i exceeds $\approx 1\%$, a subset of the {311} defects consists of zig-zag {311} defects which alternate {113} habit planes [20]. The zig zag {311} defects have a corrugated appearance when viewed in cross-section along their long (110) axis and are wider than ordinary {311} defects when observed in plan-view. This second finding has particularly important consequences for TED since the zig zag {311} defects are more stable against dissolution and unfaulting than the ordinary {311} defects.

To investigate the defect microstructure in very low energy implants, epitaxially grown 200-mm Si wafers (p on p⁺) were implanted at room temperature with 1-, 2- and 5-keV Si^+ ions to doses of 1 and $3 \times 10^{14} \text{ cm}^{-2}$. Pieces were annealed at 750, 810 and 900 °C, using either rapid thermal annealing or a conventional furnace. Extended defects were imaged by plan-view transmission electron microscopy (TEM) using the weakly excited 220 and 400 reflections. The number of interstitials trapped in extended defects was estimated by counting and measuring {311} defects as described by Eaglesham et al. in Ref. [8] and assuming an interstitial density of the defect as given by Takeda in Ref. [10]. In samples having dislocation loops, the number of interstitials trapped in the loops did not exceed 10% of those trapped in {311}'s.

Implantation with 5-keV Si⁺ to a dose of 3×10^{14} cm⁻² produces an amorphous layer extending 6 to 8 nm from the surface [15]. The roughness of the amorphous-crystalline interface observed by TEM indicated that this dose is just slightly above the amorphization threshold; no amorphous layer is observed at the dose of 1×10^{14} cm⁻². After annealing at 750°C, both the low-dose and high-dose samples contained elongated extended defects. High-resolution TEM imaging confirmed that the defects have a {311} habit plane [15]. However, in plan-view, some of the defects in the high-dose sample were much longer and wider than any of those observed in the low-dose sample or in previous work [8]. In cross-section, the wide {311} defects were found to have a corrugated structure when viewed along their long [110] axis (Fig. 1). The same defects have previously been identified in the literature as 'zig-zag' defects [20]. They are related to the {311} defects usually observed from subamorphizing implants [8] in that their structure essentially consists of intersecting segments of {311} defects.

The time- and dose-dependence of the total number of interstitials trapped in {311} defects and/or zig-zag defects is shown in Fig. 2 for 5-keV Si⁺ implants [15]. For comparison, Fig. 2 also includes data from Ref. [8] for 40 keV Si⁺. Note first that when the time dependence of the interstitial concentration is extrapolated back to zero time, the initial interstitial concentration for the 5-keV implants is approximately equal to the implanted dose, just as it is for the 40-keV implants [8]. The interstitial dissolution rate for the low-dose samples annealed at 750°C is similar to that for 40 keV. However, the dissolution rate for the high-dose samples is ten times slower. The remarkable disparity

Fig. 1. High resolution cross-sectional TEM image showing a zig-zag {311} defect in (100) Si implanted with 3×10^{14} cm⁻² Si⁺ at 2 keV, annealed at 810°C for 600 s.

Fig. 2. Interstitials trapped in {311} defects as a function of annealing time at 750°C for 1 and 3×10^{14} cm⁻² Si⁺ at 5 keV. Earlier data from Ref. [8] for 5×10^{13} cm⁻² Si⁺ at 40 keV are also included for comparison (after Ref. [15]).

in dissolution rates is attributed to the presence of zig-zag {311} defects in the high-dose sample. After short anneals (20 s to 10 min at 750°C), the high-dose sample shows, predominantly, a very high density of ordinary {311} defects with only a small fraction of zig-zag {311} defects. After prolonged annealing (30 min to 48 h at 750°C) only the zig-zag {311} defects survive.

It has been proposed [15] that zig-zag {311} defects are formed in the early stages of annealing when neighboring {311} defects coalesce during growth. In this case, the formation of zig-zag defects would depend critically on the density of the precursor {311} defects, and therefore on the interstitial concentration. Assuming that all vacancies and recoils created during the implant annihilate quickly at the start of annealing, an excess interstitial profile can be estimated from Monte Carlo simulations, e.g. using TRIM'95 [21]. For 5-keV Si⁺, C_1 is $\approx 1\%$ at the peak of the profile (located approximately 10 nm below the surface) for 3×10^{14} cm⁻² and $\approx 0.3\%$ for 1×10^{14} cm⁻². Therefore, a minimum value of C_1 of $\approx 1\%$ appears to be necessary for formation of zig-zag {311} defects. To check this point, we examined defects from a 40-keV Si⁺ implant with a dose of 8×10^{14} cm⁻² (corresponding to $C_1 \approx 1\%$). Indeed, zig-zag {311} defects were observed [15]. The same defects were also observed when the same implant was performed at 150°C to prevent amorphization, thus ruling out amorphization/recrystallization as a possible explanation for formation of the zig-zag {311} defects.

The zig-zag {311} defects grow to enormous lengths due to their enhanced stability. Fig. 3 shows the average {311} length as a function of annealing time [15]. The data is grouped by the orientation of the long {110} axis of the {311} defects relative to the surface.

Fig. 3. Comparison of average length of {311} defects elongated in (110) directions parallel and inclined to the (100) surface. Samples were implanted with $3 \times 10^{14} \text{ cm}^{-2} \text{ Si}^+$ at 5 keV and annealed at 750°C (after Ref. [15]).

There are two different (110) axes that lie parallel to the (100) wafer surface and 4 different (110) axes inclined at an angle of 45°. The inclined zig-zag {311} defects are at most $\approx 20 \text{ nm}$ long, while the parallel defects grow to lengths $> 60 \text{ nm}$. The limit on growth in the inclined direction is determined by the narrow width of the C_1 profile. For instance, in the $8 \times 10^{14} \text{ cm}^{-2} \text{ Si}^-$ implant at 40 keV, which has a broader C_1 profile, inclined defects grew to lengths of $\approx 100 \text{ nm}$. All {311} defects that survive beyond 30-min annealing at 750°C, i.e. parallel to the surface, are zig-zag {311} defects.

3. Reduction in TED from 1–5 keV Si^+ implants due to surface proximity

High-resolution TEM images reveal the formation of {311} defects from even a 1-keV Si^- implant after annealing at 810°C, 20 s [15]. It is clear that although the surface is only 3 nm away from the implanted region for 1 keV Si^- , excess interstitials are not annihilated faster than they can coalesce into {311} defects. In a recent investigation [16], we have varied the distance of the implanted layer from the surface by varying the ion implantation energy and measuring the enhanced diffusion of buried boron marker layers to monitor the flux of interstitials injected into the bulk at 810 to 1050°C. By varying the ion implantation energy, interstitial annihilation at the surface was quantified as a function of the distance of excess interstitials from the surface while maintaining the same surface condition for all samples.

Boron-doping superlattices (B-DSL's) were grown by low temperature molecular beam epitaxy [22]. Each B-DSL consisted of six 10-nm wide B spikes doped to a concentration of $1 \times 10^{18} \text{ cm}^{-3}$ and spaced 100 nm

apart; the shallowest spike was 50 nm below the surface. The B-DSL's were implanted at room temperature with $1 \times 10^{14} \text{ cm}^{-2} \text{ Si}^+$ at 1, 2 and 5-keV for annealing at 810°C for 600 s or 1050°C for 10 s, and with 0.5, 1, 2, 5, 10 and 20-keV for annealing at 950°C for 30 s. The B-DSL's were analyzed by secondary ion mass spectroscopy (SIMS) using 2-keV Cs^+ or O^- primary ion bombardment with positive secondary ion detection.

Fig. 4 compares typical boron depth profiles obtained by SIMS for an unimplanted sample with one that has been implanted with $1 \times 10^{14} \text{ cm}^{-2} \text{ Si}^-$ at 5 keV and annealed for 600 s at 810°C. For each broadened peak in Fig. 4 the time-averaged boron diffusivity (D_B) and its error were extracted by fitting the experimental data with simulated diffused profiles using the process simulator PROPHET [23,24]. Dividing (D_B) by the equilibrium boron diffusivity [19], D_B^* , yields the diffusivity enhancement at each spike. Fig. 5(a) shows the enhancement data for 1050°C annealing as a function of marker depth. Two trends are evident: a smaller enhancement occurs at deeper spikes, and the enhancement at each spike decreases with decreasing Si^- implantation energy. The energy dependence is shown explicitly in Fig. 5(b), where the data for the second through fourth boron spikes has been replotted as a function of the projected ion range. Comparing data for the Si^- implanted and unimplanted samples it is evident that the enhancement is significantly reduced with diminishing implant energy. The same trends were observed in the depth dependent enhancement data at 810 and 950°C [16].

Since B diffusion is mediated by interstitials [13], the observed boron diffusivity is proportional to the number of hops made by the excess interstitials during annealing. From a simple random walk argument the total number of hops made by an interstitial before

Fig. 4. SIMS profiles comparing diffusion of boron spikes from a 600 s anneal at 810°C in unimplanted and implanted B-DSL's. The Si^- dose was $1 \times 10^{14} \text{ cm}^{-2}$ at 5 keV (after Ref. [16]).

Fig. 5. Boron diffusivity enhancement data from B-DSL's unimplanted and implanted with $1 \times 10^{14} \text{ cm}^{-2} \text{ Si}^-$ at 1-, 2- and 5-keV and annealed at 1050°C for 10 s, as a function of (a) depth and (b) R_p , the projected ion range (after Ref. [16]).

arriving at the surface is a quadratic function of its initial distance from the surface. Under conditions of perfect recombination at the surface (every interstitial is annihilated the very first time it reaches the surface), the diffusivity enhancement, related to the number of interstitial hops per lattice site, would be expected to have a linear dependence on the initial interstitial depth. Such a linear dependence is in fact observed at 1050°C (Fig. 5b), as well as 810 and 950°C [16]. The linear trends extrapolate to an enhancement factor of approximately unity (i.e. no enhancement) at $R_p = 0$. Therefore, TED from implantation-induced interstitials will vanish, as predicted, as the implant energy goes toward zero. Thus, while the defect formation study (see Section 2) confirms the existence of 'plus one' implantation-induced interstitials, these experiments show that the depth of the interstitials must additionally be taken into account to correctly simulate TED.

The reduction in diffusivity enhancement with decreasing energy demonstrated by the data in Fig. 5(b) is due to increased interstitial annihilation at the surface. By assuming a model for interstitial diffusion it is, in principle, possible to simulate interstitial diffusion profiles and compare with the experimental data to

quantify the efficiency of interstitial recombination at the surface. A discrete simulation as well as a continuum model (PROPHET [23, 24]) were used to extract the surface annihilation efficiency. Both simulations agree that the surface is effectively a perfect sink for interstitials [16].

4. Low energy boron implants and boron-enhanced-diffusion (BED)

In Sections 2 and 3 it has been shown that defects are formed even from very low energy Si^- implants and that the surface is a sink for interstitials. Both of these findings imply that the lower the dopant ion implantation energy is, the shallower a junction can be made. In the case of B^+ implants however, enhanced diffusion is still observed at energies as low as 0.5 keV [18, 25]. Fig. 6 shows diffused boron profiles from $1 \times 10^{15} \text{ cm}^{-2} \text{ B}$ implanted at 5, 2, 1 and 0.5 keV after annealing at 1050°C for 10 s. Even the 0.5-keV B profile shows significant diffusion. Diffusivity enhancements for the profiles in Fig. 6 have been extracted and compared with enhancement data from Si implants (Fig. 7). Fig. 7 illustrates the reduction in TED, at 1050°C (data from Fig. 5b) and at 950°C [16], which accompanies a reduction in the implantation energy down to 0.5 keV for a fixed Si^- dose of $1 \times 10^{14} \text{ cm}^{-2}$. Each data point corresponds to the diffusivity enhancement measured at a buried marker located 150 nm below the surface. In contrast to the reduction in enhancement to $1\times$ observed for ULE Si^- , a saturation in the reduction of diffusivity enhancement at $4\times$ is seen for the B^+ implants at 1 and 0.5 keV (Fig. 7). Extrapolation of this trend predicts that enhanced diffusion would be observed even if the implantation energy was reduced to a few eV. To confirm that the trend exhibited by the B^+ data

Fig. 6. SIMS profiles comparing diffusion of $1 \times 10^{15} \text{ cm}^{-2} \text{ B}$ implanted at 5, 2, 1 and 0.5 keV at from 1050°C 10 s annealing (after Ref. [18]).

Fig. 7. Summary of diffusivity enhancement data for ULE Si^+ and B^+ implants from Refs. [1,2], respectively. The Si^+ dose of 10^{14} cm^{-2} was implanted at 0.5, 1, 2, 5 or 10 keV for 950 C 30 s annealing, or at 1, 2 and 5 keV for 1050°C/10 s annealing; The B^+ dose of 10^{15} cm^{-2} was implanted at 0.5, 1, 2 and 5 for 1050 C 10 s annealing.

can be extrapolated to extremely low energies, we tested for a diffusivity enhancement from an evaporated surface B layer. Since the B atoms arrive at the surface with energies of the order of only ≈ 0.0001 keV, well below the displacement threshold, interstitial injection by Frenkel-pair defect generation is not possible. Fig. 8 compares diffusion from an evaporated B layer and from the $1 \times 10^{15} \text{ cm}^{-2}$, 2 keV B^+ -implant previously shown in Fig. 7. The junction depth in the two samples is surprisingly similar even though the evaporated-B sample does not contain any implant damage, which is the normal cause of TED. The diffusivity enhancement factor for evaporated B is $3.5 \times$, nearly the same as the enhancement in the implanted B layers. Also included in Fig. 7 is a simulated diffu-

Fig. 8. SIMS profiles comparing diffusion from an evaporated pure-B layer (capped with 10 nm of amorphous Si) with that from a $1 \times 10^{15} \text{ cm}^{-2}$, 2 keV B^+ implant, after 1050 C 10 s annealing. Also shown for comparison is a simulated diffusion profile which assumes only the standard concentration-dependent diffusivity.

sion profile from an infinite B source without any diffusion enhancement. The simulation includes the standard concentration dependence of boron diffusivity. The diffusion enhancement observed in both implanted and evaporated B layers is therefore neither conventional concentration-dependent diffusion nor TED. Since the effect is related to the presence of B, the term *boron-enhanced* diffusion, or BED has been used to describe this enhancement effect [18]. Comparison of the simulation in Fig. 7 with the experimental data illustrates the serious consequences of BED for forming shallow junctions.

The observation of enhanced diffusion for evaporated B suggests that there is another source of interstitials in the sample with evaporated B. This hypothesis was directly confirmed using MBE-grown boron markers separated from an evaporated surface boron layer. Fig. 9 compares diffusion of boron markers in samples with and without a pure B layer on the surface. It is clear from the data in Fig. 9 that marker diffusion is enhanced in the sample with the surface B. This implies that the surface B layer produces an interstitial supersaturation in the near-surface bulk during annealing. Evaporated surface layers containing 10 and 1% B were also grown on marker layer samples for comparison with the 100% B layer. The same enhancement was observed for the 10% B layer as for the 100% B surface layer, but there was no enhancement for the layer containing only 1% B (Fig. 10). These results clearly indicate that there exists a threshold concentration for the BED effect between 1 and 10% B.

A threshold concentration for the diffusion enhancement was also observed in the case of implantation of B^+ . Fig. 11 shows diffusivity enhancement data from 0.5-keV B^+ as a function of implanted dose. As before, each data point corresponds to the enhancement at a boron marker located 150 nm below the surface following implantation at doses from 1×10^{13} to

Fig. 9. SIMS profiles comparing diffusion of B markers with and without a layer of pure-B on the surface.

Fig. 10. SIMS profiles comparing diffusion of B markers with and without $6 \times 10^{20} \text{ cm}^{-3}$ B on the surface.

$2 \times 10^{15} \text{ cm}^{-2}$, and 10 s annealing at 1050°C . The diffusivity enhancements from doses of $3 \times 10^{14} \text{ cm}^{-2}$ and below are close to $1\times$ (no enhancement), consistent with the very shallow placement of the implant damage. However, between the doses of 3×10^{14} and $1 \times 10^{15} \text{ cm}^{-2}$, the diffusivity enhancement abruptly increases from approximately $1\times$ to $\approx 4\times$. This increase is due to the onset of the BED effect and the enhancement factor of $4\times$ is consistent with that observed for evaporated B. According to TRIM simulations [21], the peak B concentrations corresponding to the two doses that bracket the increase in enhancement are 1 and 3%. This threshold is also consistent with the evaporated-B threshold concentration of between 1 and 10%.

The possible chemical effect of high B concentration, in combination with the implant damage, from high dose ULE B implants is considered next. It was previously shown that fairly modest B^+ doses can amorphize the implanted layer at ULE energies, e.g. a dose of $5 \times 10^{15} \text{ cm}^{-2}$ at 2 keV [17]. The absence of an amorphous ring pattern from a dose of $2 \times 10^{15} \text{ cm}^{-2}$

B^+ at 2 keV, implies an amorphization threshold dose between 2 and $5 \times 10^{15} \text{ cm}^{-2}$ at 2 keV. While amorphization by boron has been reported previously ($6 \times 10^{16} \text{ cm}^{-2}$ at 60 keV [26]), there have been no previous reports of amorphization by conventional ion implantation at boron doses typical for source/drain formation (low 10^{15} cm^{-2} range). Electron diffraction analysis of the as-implanted amorphous layer, imaged in plan-view prior to annealing, reveals a ring pattern indistinguishable from that of amorphous silicon. Surprisingly, an amorphous layer persists after annealing at 550°C , temperatures at which solid phase epitaxial regrowth of amorphous silicon would occur easily. However, the diffraction pattern no longer corresponds to that of amorphous Si. For a detailed electron diffraction analysis of the amorphous phase formed from a high boron dose, samples containing a thicker boron-rich implanted layer of comparable composition were prepared by implantation of B^- at 10 keV, at doses from 1×10^{15} to $1 \times 10^{17} \text{ cm}^{-2}$. The electron diffraction patterns obtained from the amorphous phase in the 10-keV implanted samples above doses of $1 \times 10^{16} \text{ cm}^{-2}$ after annealing are similar to the one seen from the 2-keV B^+ implanted sample after annealing; an example is shown in Fig. 12. At least two additional rings appear in the diffraction pattern which do not correspond to any known interplanar spacings in silicon: one located inside the d_{111} polycrystalline silicon ring [27] and one just outside. These two additional rings correspond to d-spacings of 0.42 and 0.26 nm (for comparison, the d_{111} spacing is 0.314 nm). By comparison with X-ray diffraction data of known crystalline compounds in the silicon-boron system [28,29] the amorphous phase created in our samples has been identified as silicon tetraboride (SiB_4) [17].

It is important to determine precisely what processing conditions lead to BED. There are two distinct physical processes which precede the observation of BED in all of our experiments: creation of an amorphous silicon layer containing a high concentration of boron (either by implantation or by evaporation) and transformation of this amorphous silicon layer to a silicon boride phase during annealing. Strictly speaking, it is possible that both amorphization by boron implantation and the silicon boride phase transformation require different threshold boron doses. In the range of our experiments however, silicon boride phase transformation has only been observed when the layer was initially amorphous and the two processes appear to have the same threshold. The formation of silicon boride in crystalline silicon has been studied previously by Armigliato et al. [30]. Their work showed that precipitation of a silicon boride phase from boron-supersaturated polycrystalline silicon is quite slow, requiring several tens of hours, even at temperatures as high as

Fig. 11. Diffusivity enhancement from 0.5 keV B^+ implanted at doses from 10^{13} to $2 \times 10^{15} \text{ cm}^{-2}$.

Fig. 12. Electron diffraction pattern from a high concentration boron-implanted layer ($1 \times 10^{17} \text{ cm}^{-2}$, 10 keV B^+), after annealing at 1050 C for 10 s.

1000 C [30]. In contrast, the formation of silicon boride in amorphized silicon was observed within 10 s at 1050 C. This relatively rapid transformation suggests that the kinetic barrier to silicon boride phase formation may be considerably reduced in amorphous silicon as opposed to crystalline silicon. If so, it would provide a natural explanation for our observation that the threshold concentrations for boride phase formation and amorphization coincide. In other words, due to the slow kinetics of the boride phase transformation in crystalline silicon, the boride phase can form during typical anneals if and only if the implanted silicon layer is amorphous.

While it appears that the silicon boride phase transformation is responsible for BED, the exact atomistic mechanism that generates excess interstitials is not clear at this point. However, a variety of similar processes exist in which either the formation of another phase [31], e.g. oxidation or nitridation, or even the mere presence of another phase [32], e.g. TiSi_2 , leads to point defect injection into the bulk. BED thus belongs in the same category of point defect enhancement mechanisms.

The implication of BED for ultra-shallow junction processing is apparent: at ULE energies the B^+ implant dose needs to be lower than that which will result in amorphization of the implanted layer in order to avoid silicon boride phase formation and BED. We

now review the threshold doses to achieve amorphization by B^+ ion implantation at 10, 2 and 0.5 keV. At 10 keV the amorphization threshold dose is between 0.8 and $1 \times 10^{16} \text{ cm}^{-2}$. At 2 keV the threshold dose is between 2 and $5 \times 10^{15} \text{ cm}^{-2}$, corresponding to an atomic fraction of between 2 and 10% within the implanted layer. This concentration is also consistent with the boron concentration in the evaporated layers of between 1 and 10% for observation of BED. At 0.5 keV the amorphization dose was confirmed, by cross-section transmission electron microscopy, to be between 3×10^{14} and $1 \times 10^{15} \text{ cm}^{-2}$, which corresponds to a peak atomic fraction of between 1 and 3%, which clearly corresponds to this threshold for the onset of BED (Fig. 10).

5. Summary

We have summarized our recent TEM and SIMS data on transient enhanced diffusion and extended defects from ULE ion implantation at 0.5 to 5 keV. Despite the proximity of the surface, {311}-type defects are observed even for 1 keV Si implants. Moreover, when the peak concentration of excess interstitials exceeds $\approx 1\%$ of the atomic density a subset of the defects consist of the so-called zig-zag {311} defects which are corrugated across their width. The zig-zag

{311} defects form by coalescence of ordinary {311} defects as a consequence of the confinement of a high volume density of {311} defects within a very narrow implanted layer. Boron TED from a silicon implant decreases linearly with Si⁺ ion implantation energy and this reduction is due to increased annihilation of implantation-induced excess interstitials at the surface. Extrapolation predicts that the transient diffusion driven by implantation-induced excess interstitials disappears at sub-keV energies. A new diffusion enhancement mechanism referred to as BED (boron-enhanced-diffusion) was discussed: boron diffusion is enhanced in the proximity of a high-concentration boron-containing layer during annealing. This phenomenon is related to the formation of a fine-grain silicon boride phase when annealing an amorphous Si layer which contains a high B concentration. Formation of the silicon boride phase injects interstitials into the silicon bulk to enhance boron diffusion. The threshold B dose for the BED effect coincides with the amorphization threshold dose. At 0.5 keV the threshold implantation dose which leads to BED lies between 3×10^{14} and $1 \times 10^{15} \text{ cm}^{-2}$. Formation of the shallowest possible junctions by ULE 0.5 keV B⁺ requires that the implant dose be kept lower than this threshold.

Acknowledgements

We gratefully acknowledge John Jackson at Eaton Corporation for his assistance with ULE implants. This research was supported in part by an appointment to the Post-doctoral Research Associates Program administered jointly by the Oak Ridge Institute of Science and Education and Oak Ridge National Laboratory and funded by the U.S. Department of Energy, Laboratory Technology Research Division under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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