Using doping superlattices to study transient-enhanced diffusion of boron in regrown silicon

K. S. Jones
Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

R. G. Elliman and M. M. Petravic'
Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

P. Kringhøj
University of Aarhus, Institute of Physics and Astronomy, NY Munkegade DK, 8000 Aarhus C, Denmark

(Received 28 November 1995; accepted for publication 20 March 1996)

A boron-doped silicon superlattice consisting of three boron spikes separated by 1700 Å of undoped silicon has been grown by molecular beam epitaxy and used to study the evolution of point defects following an amorphizing implant of Si^+. After MBE growth, the wafer was implanted at 77 K with either 146 or 292 keV Si^+ at a dose of $5\times10^{15}/cm^2$. These implants produced amorphous layer depths that coincided with the depths of either the middle B peak or just below the deepest B peak. The samples were then annealed at 800 °C in an Ar ambient. Secondary-ion-mass spectrometry and transmission electron microscopy were used to monitor the diffusion of the boron spikes upon annealing and the evolution of the extended defects upon annealing, respectively. For the lower-energy sample, an enhancement in the B diffusivity of over 500× was observed for both the surface B spike and the deepest B spike. The higher-energy implant shows conclusively that the back flow of interstitials into the regrown region is coming from the end-of-range damage just below the amorphous/crystalline interface. These results show that for these implant conditions the end-of-range damage does not act as a barrier to flow of interstitials to the surface. In addition it is noted that boron in the regrown silicon does not cluster whereas the boron below the amorphous crystalline interface does. Both of these features must be accounted for when modeling boron diffusion in regrown silicon. © *1996 American Institute of Physics*. [S0003-6951(96)01622-1]

In order to produce shallow junctions during integrated circuit device manufacturing, it is necessary to minimize the random channeling of ion-implanted dopants. For light ions like boron, this is most commonly done by preamorphizing the surface with Si^+ or BF_2^+. A number of studies have looked into the diffusion of boron after solid-phase epitaxial regrowth (SPER) of the amorphous layer.[1–11] Most agree that if the boron comes to rest below the amorphous/crystalline interface then enhanced diffusion is observed for this deeper tail.[4,7,9–12] This enhanced diffusion lasts for a limited time at typical annealing temperatures and is referred to as transient-enhanced diffusion (TED). TED is generally attributed to interactions between B and excess Si interstitials, where the source of interstitials is the end-of-range (EOR) damage that exists just below the amorphous/crystalline interface. What is not agreed upon is whether there is any enhanced diffusion of boron in the regrown silicon (i.e., above the amorphous/crystalline interface). Several papers have reported enhanced diffusion of boron in the regrown silicon.[2,3,13] For example, Kim *et al.*[2] report enhanced diffusion but only for 1150 °C anneals not 1000 °C anneals. Nishikawa *et al.*[13] reported that enhanced diffusion of boron in the regrown silicon can be retarded by carbon implantation, a well-known trap for interstitials.

On the other hand, there are many papers that report little or no enhanced diffusion of boron in regrown silicon.[1,5,6,8,14,15] Several of these papers have reported retarded diffusion of boron in the regrown layer which is attributed to a buildup of vacancies in the regrown Si because of the forward projected momentum transfer of the incoming ions.[5,10] To explain why the end-of-range damage, which consists of a high concentration of interstitials, does not flow back into the regrown silicon, it has been proposed that the end-of-range dislocations act as a barrier.[1]

The one common feature these experiments had was that they relied on the use of implanted boron as the detector for any enhanced diffusion. Because of its low mass, producing abrupt boron doping profiles by implantation is virtually impossible. In addition, many of the published experiments looking for enhanced diffusion in the regrown silicon suffered because the implanted boron diffused into the end-of-range loops. This could result in gettering of either the boron or the paired interstitial by the loops, complicating the interpretation of the boron diffusivity data. In order to circumvent these problems, a doping superlattice, grown by molecular beam epitaxy (MBE), was used to study the redistribution of point defects after SPER of an implantation-induced amorphous layer. It is shown conclusively, that for the amorphization conditions used in this experiment, there is a very large flux of interstitials from the end-of-range damage that flows towards the surface, resulting in transient-enhanced diffusion of boron in the regrown layer.

In this experiment a three spike boron-doped superlattice (DSL) was grown by MBE at 500 °C on a 4 in. (100) silicon wafer. The DSL consisted of boron spikes doped to a peak concentration of $1\times10^{20}/cm^3$ with a full width half maximum of about 100 Å. First, a 4200 Å buffer layer was grown followed by the boron spikes which were space 1700 Å apart

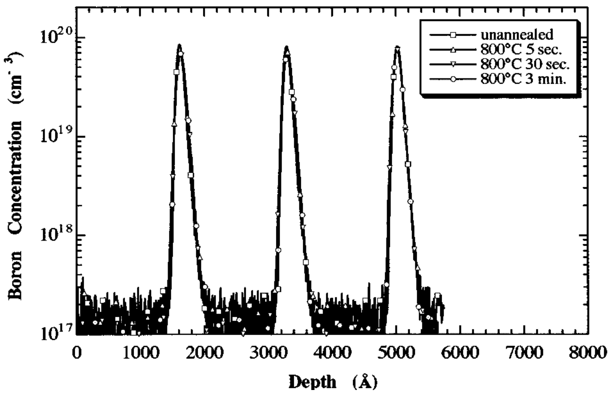

FIG. 1. SIMS profile of unimplanted boron-doped superlattice after annealing at 800 °C in argon.

with a final 1700 Å of undoped silicon on top. The DSL's were implanted at 77 K with Si^+ to a dose of $5\times10^{15}/cm^2$. The implant energy was chosen to amorphize either down to the middle spike (146 keV) or to just below the deepest spike (292 keV). Cross-sectional TEM confirmed that the amorphous layers were continuous to the surface and were 3240 Å (146 keV) and 5750 Å (292 keV) deep. The dose rate for the implants was 0.5–1 $\mu A/cm^2$. Annealing was done either by rapid thermal annealing (RTA) (≤ 30 s anneals) or by furnace (<30 s anneals) in an Ar ambient. The secondary-ion-mass spectrometry (SIMS) was done on a Riber MIQ 256 instrument using a 7 keV O_2^+ incident beam at 35° from the surface normal. Ions were collected from the central 10% of the sputtered crater to avoid edge effects and the Si signal was monitored to ensure no changes occurred in the sputtering rate during profiling.

Figure 1 shows the effect of 800 °C annealing on the as-grown (unimplanted) DSL. Very little diffusion was observed for diffusion times up to 3 min. This is to be expected since extrapolation of, for example, Fair's[16] diffusivity for boron gives a diffusivity of only 4×10^{-17} cm^2/s at 800 °C. This yields a $2\sqrt{Dt}$ value of only 17 Å if high concentration effects are ignored. It is also clear from Fig. 1 that grown-in defects from MBE are not yielding any significant diffusion over this time-temperature cycle.

Figure 2 shows the effect of the 146 keV implant on the DSL after the same annealing treatments used for the reference sample in Fig. 1. The position of the amorphous/crystalline interface prior to annealing is shown. The middle spike shows little diffusion because of boron gettering to the end-of-range defects combined with B clustering driven by the very high interstitial supersaturation.[17] It is very obvious that the spike closest to the surface, which was in the regrown Si, has diffused as much as the deepest spike which remained in unimplanted material. This implies that there was a high supersaturation of point defects in both regions. It should also be noted that the boron spike in the regrown silicon exhibited no clustering whereas the deepest spike did cluster. This will be discussed further in the next section.

The enhancement is diffusivity for both spikes is shown in Fig. 3, where the enhancement is defined as the ratio of the diffusivity in the ion-implanted material D_B to the boron diffusivity in the unimplanted material D_B^*. The values plotted are the enhancements for each time interval, not the time-averaged value for the whole anneal. There is some error in the absolute magnitude of these numbers due to the effect of dividing the implanted spike diffusivity by the very small control diffusivity. However, both spikes show a similar enhancement at each time interval implying they were the same distance from the source of the point defects. There was some question as to whether the enhancement in boron diffusivity could result from vacancies in the regrown silicon, because boron diffusion is known to have a small vacancy mediated component. In order to test whether the enhancement was mediated by vacancies or interstitials, phosphorus, which is believed to diffuse purely by interstitials, was implanted into the amorphous layer and annealed. It too showed enhanced diffusion. Thus, the enhanced diffusion of the B peak in the regrown DSL silicon is believed to be from excess interstitials. The interstitial source is transient, as is apparent from Fig. 3, having stopped somewhere between 3 and 60 min. This is consistent with the results of Listebarger *et al.*[18] who showed that the supersaturation of interstitials from end-of-range damage decays over times of between 5 and 30 min at 800 °C. In a paper soon to be published[19] it is shown that (311) defects,[20] and possibly in this case, boron interstitial clusters (BIC's) appear to be the sources of inter-

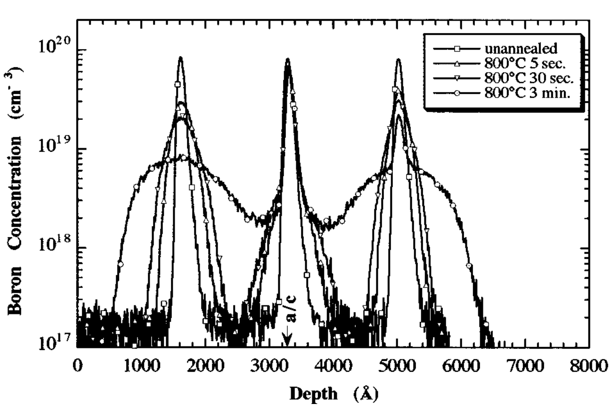

FIG. 2. SIMS profiles of boron-doped superlattice after implantation with 146 keV $5\times10^{15}/cm^2$ Si^+ and annealing at 800 °C in Ar. Amorphous/crystalline interface was about 3240 Å deep. Note enhanced diffusion in regrown Si.

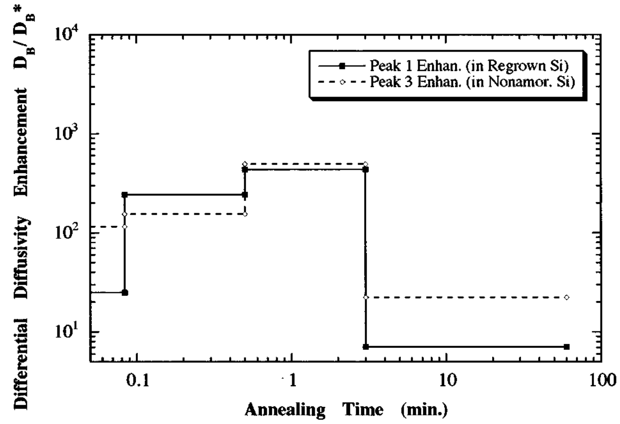

FIG. 3. Enhancement in boron diffusivity relative to the control for the shallowest (1) and deepest (3) boron spikes after 146 keV implantation and annealing at 800 °C.

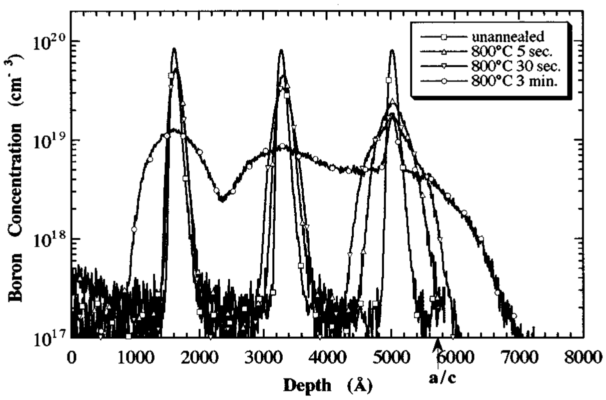

FIG. 4. SIMS profiles of boron-doped superlattice after implantation with 292 keV $5\times10^{15}/cm^2$ Si^+ and annealing at 800 °C in Ar. Amorphous/crystalline interface was bout 5750 Å deep. Note flow of interstitials from the end-of-range damage into the regrown silicon.

stitials from the end-of-range damage. All of these findings suggest that the end-of-range damage is the source of the interstitials for the TED of B in the regrown silicon.

To further investigate the role of the end-of-range damage, B diffusion was also examined in samples amorphized with 292 keV Si^+, where the amorphous layer extended from the surface to 5400 Å, or just beyond the third B spike. Figure 4 shows the effect of annealing on this sample. Again enhanced diffusion was observed in the regrown silicon. It is also obvious that the enhancement decreases with increasing distance from the end-of-range damage, providing additional evidence that the EOR damage is the source of the TED in the regrown silicon. Thus, for our loop density which by TEM was measured to be about $4\times10^{10}/cm^2$, the end-of-range damage does *not* act as a barrier to the flow of interstitials toward the surface during loop formation.

It should also be noted that despite having a high point defect supersaturation and a high boron concentration, no clustering of the shallower two B spikes was observed. The deepest peak did show an immobile B fraction, which was estimated to be as high as 21% after 3 min annealing. Cross-sectional TEM showed that most of the end-of-range loops formed on this boron spike, not 400 Å deeper as expected from the amorphous/crystalline interface position. This is very unusual and is probably due to the strong propensity of boron to getter and complex with interstitials.[21] At this point it is not possible to tell if the immobile fraction of the deepest peak is due to clustering or simply gettering to the EOR dislocations. The reason for the lack of clustering of the other two peaks is unclear. Stolk *et al.*[17] proposed a series of defect reactions that involved the reaction of both boron interstitial pairs and substitutional boron to get clustering. It is possible that after regrowth there is not enough interstitial backflow to get clustering.

The reason that TED in regrown silicon is observed by some authors and not by others may be related to the density of end-of-range loops. Because our implants were done at 77 K, the end-of-range loop density was lower ($4\times10^{10}/cm^2$) than usually observed for room-temperature implants (for example,[22] $1-2\times10^{11}/cm^2$). One could argue that the situation goes from a diffusion limited regime, in terms of the point defect/dislocation loop interaction kinetics, to a reaction rate limited regime, and that loops are therefore no longer acting as an effective barrier to interstitials. TED has been seen in regrown Si after room-temperature Ge preamorphizations which had EOR loop densities well above $1\times10^{11}/cm^2$. Thus it remains unclear why previous authors did not see TED in regrown silicon. Finally, there was concern as to how much diffusion was occurring in the amorphous layer during SPER. Low-temperature anneals did reveal that there was a very small amount of diffusion (<100 Å) after 600 °C solid-phase epitaxial regrowth.

In conclusion, it has been shown through the use of doping superlattices that transient-enhanced diffusion of boron can occur in regrown silicon. The end-of-range damage provides the source of interstitials for this TED. This is in direct contradiction to previous models which relied on the end-of-range damage to act as a diffusion barrier to the flow of interstitials toward the surface. In addition, no clustering is observed for boron in regrown silicon despite having adequate B peak concentration and interstitial supersaturation. It is suggested that the lattice site location of the boron after SPER may reduce its tendency to cluster.

The authors would like to thank Warren Lawrence, Mark Law, and Jim Williams for the many useful discussions with the assistance of VB, MB. This work was supported by a contract from SEMATECH and the Australian National University.

[1] T. O. Sedgwick, A. E. Michel, V. R. Deline, S. A. Cohen, and J. B. Lasky, J. Appl. Phys. **63**, 1452 (1988).
[2] Y. M. Kim, G. Q. Lo, D. L. Kwong, H. H. Tseng, and R. Hance, Appl. Phys. Lett. **55**, 2316 (1989).
[3] R. G. Wilson, J. Appl. Phys. **54**, 6879 (1983).
[4] R. B. Fair, J. Electrochem. Soc. **137**, 667 (1990).
[5] S. Solmi, R. Angelucci, F. Cembali, M Servidori, and M. Anderle, Appl. Phys. Lett. **51**, 331 (1987).
[6] S. Peterstrom and B. G. Svensson, J. Appl. Phys. **71**, 1215 (1992).
[7] R. Angelucci, P. Negrini, and S. Solmi, Appl. Phys. Lett. **49**, 1468 (1986).
[8] M. Servidori, R. Angelucci, F. Cembali, P. Negrini, S. Solmi, P. Zaumseil, and U. Winter, J. Appl. Phys. **61**, 1834 (1987).
[9] A. C. Ajmera, G. A. Rozgonyi, and R. B. Fair, Appl. Phys. Lett. **52**, 813 (1988).
[10] M. Servidori, Z. Sourek, and S. Solmi, J. Appl. Phys. **62**, 1723 (1987).
[11] A. Claverie, C. Bonafos, A. Martinez, and D. Alquier, Solid State Phenomena **47-48**, 195 (1996).
[12] Y. Kim, H. Z. Massoud, and R. B. Fair, J. Electron. Mater. **18**, 143 (1989).
[13] S. Nishikawa, A. Tanaka, and T. Yamaji, Appl. Phys. Lett. **60**, 2270 (1992).
[14] T. E. Seidel, IEEE Electron Device Lett. **4**, 353 (1983).
[15] F. Cembali, M. Servidori, S. Solmi, Z. Sourek, U. Winter, and P. Zaumseil, Phys. Status Solidi A **98**, 511 (1986).
[16] R. B. Fair, in *Impurity Doping Processes in Silicon*, edited by F. F. Y. Wang (North Holland, New York, 1981), Chap. 7.
[17] P. A. Stolk, H. J. Gossmann, D. J. Eaglesham, D. C. Jacobson, J. M. Poate, and H. S. Luftman, Appl. Phys. Lett. **66**, 568 (1995).
[18] J. K. Listebarger, H. G. Robinson, K. S. Jones, M. E. Law, D. D. Sieloff, J. A. Slinkman, and T. O. Sedgwick, J. Appl. Phys. **78**, 2298 (1995).
[19] K. S. Jones, L. Zhang, M. Law, D. S. Simons, L. Rubin, and R. G. Elliman, Appl. Phys. Lett. (submitted).
[20] D. J. Eaglesham, P. A. Stolk, H.-J. Gossman, and J. M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).
[21] L. H. Zhang, K. S. Jones, P. H. Chi, and D. S. Simons, Appl. Phys. Lett. **67**, 2025 (1995).
[22] J. Liu, M. E. Law, and K. S. Jones, Solid State Electron. **38**, 1305 (1995).