Diffusion of ion implanted boron in preamorphized silicon

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Transient enhanced diffusion of boron in preamorphized and subsequently regrown Si was studied by secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM). A comparison of 4 keV, $1\times 10^{14}/\mathrm{cm}^2$ boron implants into crystalline and Ge^+ preamorphized silicon was undertaken. Upon annealing the B^+ implant into crystalline material exhibited the well-known transient enhanced diffusion (TED). In this case the peak of the boron distribution was relatively immobile and only B in the tail showed TED. In the second set of samples, the surface was first preamorphized by a 180 keV, $1\times10^{15}/\mathrm{cm}^2$ Ge^+ implant which produced an amorphous layer 2300 Å deep, which then was implanted with boron. After implantation the tail of the B distribution extended to only 700 Å. Upon annealing, TED of the boron in the regrown Si was also observed, but the diffusion profile was very different. In this case the peak showed no clustering, so the entire profile diffused. The time for the TED to decay was around 15 min at 800 °C. TEM results indicate that the (311) defects in the end of range damage finish dissolving between 10 and 60 min at 800 °C. These results indicate that for these Ge preamorphization conditions, not only do the end of range defects not block the flow of interstitials into the regrown silicon, the (311) defects in the end of range damage act as the source of interstitials. In addition, boron does not appear to cluster in regrown silicon. © *1996 American Institute of Physics*. [S0003-6951(96)02519-3]

There has been a long standing controversy over whether there is a flow of interstitials from the end of range damage into the regrown silicon after amorphization by ion implantation and subsequent annealing. Several authors have reported that the end of range damage acts as a barrier to the flow of interstitials toward the surface.[1–6] This model has been widely accepted as true for all implant conditions. However, it was recently shown, using doping superlattices, that for high energy Si implants done at 77 K the end of range not only makes a poor barrier to the back flow of interstitials toward the surface, it appears to be the source of transient enhanced diffusion in the regrown Si.[7] It should be noted, however, that these studies were done using molecular beam epitaxy (MBE) material which can behave differently from conventional Si because of changes in impurity concentrations. In addition the boron for these layers starts out substitutional unlike implants of boron. Finally the end of range defect density was low ($4\times10^{10}/\mathrm{cm}^2$) relative to that produced by typical commercial implant conditions which result in end of range dislocation loops at concentrations closer to $1\text{–}2\times10^{11}/\mathrm{cm}^2$. The present experiments were designed to determine if conditions closer to those used in manufacturing also result in transient enhanced diffusion (TED) in regrown Si. It is shown that even when using Ge implants at room temperature and low energy B^+ implants, TED in the regrown silicon still occurs and that (311) defects in the end of range damage appear to be the source of the TED.

The substrates in these experiments were 150 mm, *n*-type (phosphorus) (100) Czochralski-grown Si wafers with a resistivity of 8–20 Ω cm. B^+ implants of 4 keV, $1\times10^{14}/\mathrm{cm}^2$ and Ge^+ implants of 180 keV, $1\times10^{15}/\mathrm{cm}^2$ were done at room temperature using water cooling. The implanter was an Eaton NV/GSD No. 104 with the beam stationary and the wafers spinning to minimize beam divergence. The tilt/twist angles were 5°/0° and the beam current was 0.69 mA for B^+ and 3.0 mA for Ge^+. These implants were subsequently annealed in nitrogen at 800 °C for times between 4 min and 4 h. Depth profiling of the boron was done on a Cameca IMS-3*f* ion microscope using a 5 keV O_2^+ primary beam and positive, $^{11}\mathrm{B}^+$ detection. The primary beam of 200–300 nA was focused and rastered over a 250 μm×250 μm area. The secondary ions were extracted from a circular area 60 μm in diameter. The depth scale was established from the crater depth measured by a stylus profilometer. TEM was done on a JEOL 200CX. Both bright field and weak beam dark field $\mathbf{g}_{220}$ micrographs were taken.

Figure 1 shows the TED characteristics of the 4 keV, $1\times10^{14}/\mathrm{cm}^2$ $^{11}\mathrm{B}^+$ implant into crystalline silicon after fur-

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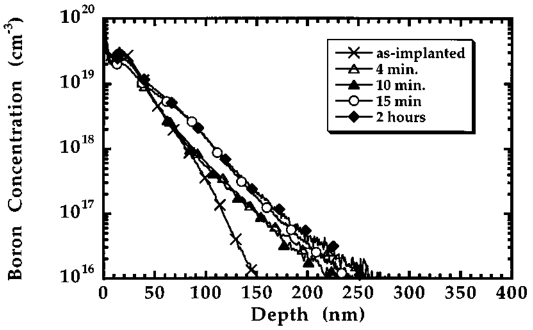


FIG. 1. SIMS profile of 4 keV 1×10^{14}/cm^2 ^{11}B$^+$ implant into crystalline silicon after annealing at 800 °C. Note the TED and lack of peak motion.

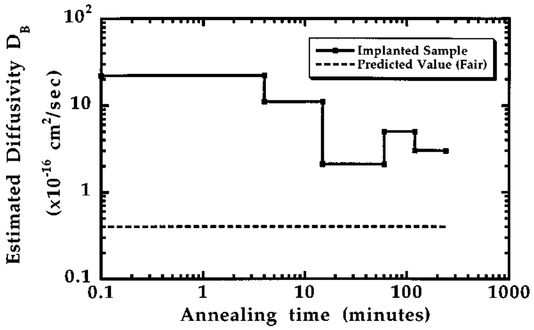


FIG. 3. Estimated B diffusivity in the regrown Si as a function of annealing time at 800 °C for the sample in Fig. 2. Also plotted are the estimates from the TEM micrographs of trapped interstitial concentration in (311) defects in the EOR damage.

nace annealing at 800 °C. These implant conditions resulted in no (311) defect formation as determined by plan-view and cross-sectional TEM. The TED that is observed saturated after 15 min. In this case the source of interstitials for the transient enhanced diffusion is believed to be boron/interstitial clusters (BICs).[8] It should be noted that for the most part the peak of the boron implant is immobile as has been previously observed by many groups. It was proposed that the lack of mobility on the peak was attributed to the high concentration of positively charged interstitials which exhibit a lower diffusivity than the neutral interstitial. Thus the breakpoint between the mobile tail and immobile peak appeared to follow the intrinsic carrier concentration n_i. However, our low energy implant results show the breakpoint to be considerably above n_i.[8] Since it was shown that the extent of TED is reduced with decreasing energy, presumably because of the role the surface plays in recombination, there appear to be fewer interstitials in the tail for the lower energy implants. This dependence of the breakpoint on the concentration of interstitials is inconsistent with the Fermi level model. A more plausible model is that the high concentration of interstitials is causing clustering of the peak as has been seen in doped superlattices.[9] It is possible that during annealing a small fraction of the clustered boron (BICs) breaks up and provides the interstitials for TED. It may also be that during cluster formation there are interstitials released as proposed by Stolk *et al.*[9] and these excess interstitials then provide the interstitials for TED.

Figure 2 shows the diffusion of boron implanted under the same conditions as in Fig. 1, only this time into a Ge$^+$ preamorphized sample. The 180 keV, 1×10^{15}/cm^2 Ge$^+$ amorphization produced an amorphous layer which was 2300 Å deep as indicated in the figure. Compared to Fig. 1, the diffusion characteristics are obviously very different for boron in regrown silicon. In this case the peak is clearly not clustered. In fact there is a loss of boron to the surface. In order to determine if the diffusivity is changing with time, the diffusivity was estimated assuming the simple redistribution of a Gaussian at the concentration of 1×10^{18}/cm^3 for each time interval. Figure 3 shows a plot of this diffusivity as well as the extrapolated value from Fair.[10] It is clear that the diffusivity is enhanced by a factor of 50 above the predicted value for the first 4 min then decays by an order of magnitude over the next 11 min. This reduction in the diffusion enhancement is roughly the same as that observed using doped superlattices.[7] In this reference it was concluded that the end of range damage is the source of the interstitials for the TED observed in the regrown silicon.

In order to study this further, plan-view TEM was needed to study the evolution of the EOR damage during 800 °C anneals. It has been shown that it is possible to quantify the number of interstitials bound by both the dislocation loops[11] and (311) defects.[12] Figure 4 shows plan-view TEM studies of the end of range damage upon annealing at 800 °C. After 4 min there is a collection of fine rods which are the (311) defects and small loops. Cross-sectional TEM confirms all of the damage is at 2300 Å, in the end of range region. After 10 min many of the smaller (311)'s have disappeared and the loops are getting larger as are the remaining (311)'s. However, between 10 and 60 min most of the (311)'s in the end of range damage have dissolved and most of the remaining defects are loops. The dissolution of (311) defects in the end of range damage corresponds to the same time interval as TED. When the (311)'s are gone TED slows down, which is consistent with (311)'s in EOR damage being the source of the interstitials.

A recent paper studying TED in regrown Si using DSL's showed a very large amount of backflow of interstitials into the regrown Si.[7] This was for a 77 K Si$^+$ implant and as such the EOR loop density was in the 10^{10}/cm^2 range. From this experiment, it would appear that increasing the end of range dislocation loop density to about 7×10^{11}/cm^2 also does not completely stop the backflow of silicon interstitials into the regrown silicon, but the enhancement (<100 relative to

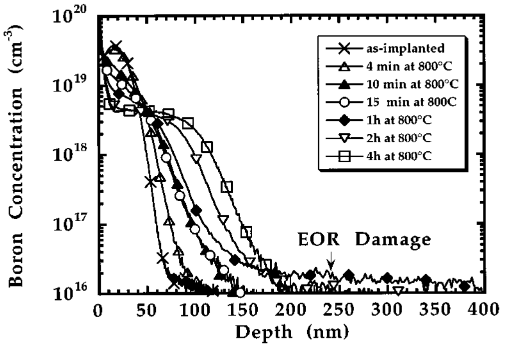
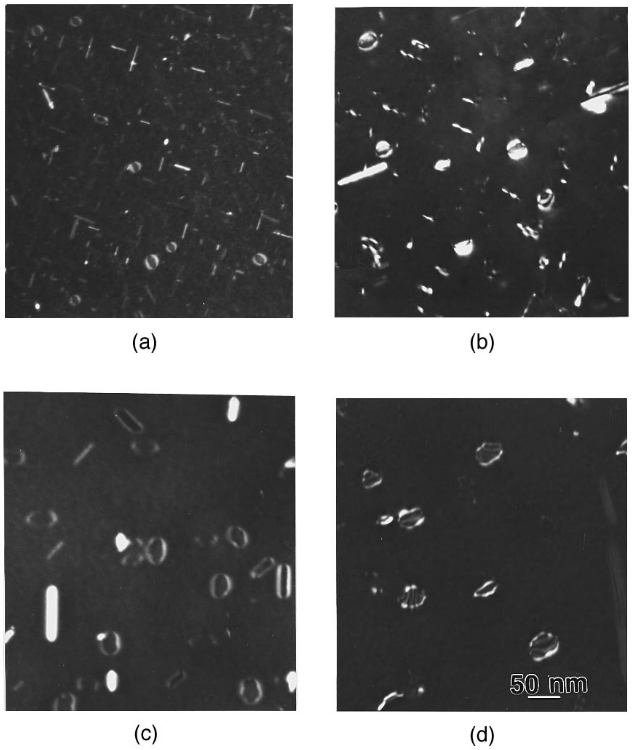


FIG. 2. SIMs profiles of 4 keV 1×10^{14}/cm^2 ^{11}B$^+$ implant into a Ge$^+$ preamorphized layer after annealing at 800 °C. Note the high diffusivity and the peak motion.



(a) (b) (c) (d)

FIG. 4. Weak beam dark field TEM micrographs of the end of range damage evolution upon 800 °C annealing of the B implanted sample in Fig. 2 for (a) 4 min, (b) 10 min, (c) 1 h, and (d) 4 h. Note the loss of (311) rodlike defects between 10 and 60 min.

Fair's value) appears reduced from the D_B/D_B^* value of >500 observed for the DSL study. Thus the amount of backflow may in fact depend on the end of range loop density with less backflow occurring as the EOR loop density increases. Further experiments into the nature of this TED are in progress. It remains unclear why boron implanted into crystalline Si is susceptible to clustering whereas boron in regrown silicon did not show clustering in this experiment. It is well known that boron appears to be highly active after solid phase epitaxial regrowth[13] whereas boron implanted into crystalline Si begins relatively inactive and exhibits the classic reverse annealing peak during activation (see, for example, Seidel *et al.*[14]). Based on Stolks[9] argument that clustering is assisted by both substitutional boron and high concentrations of boron interstitial pairs, one would expect just the opposite clustering behavior. It is also possible the boron did not cluster because of the combination of a relatively low B peak concentration and the relatively low (<100) interstitial supersaturation from the backflow. Further electrical investigations into crystallographic atom location of boron during annealing are needed. Studies into the activation energy associated with the saturation time for TED in regrown silicon are in progress. If the (311) defects are controlling the TED then one would expect an activation energy of around 3.6 eV, as was reported for TED from (311) defects for nonamorphizing implants.[15,16]

In conclusion, it has been shown that there is a marked difference in the diffusion characteristics of boron in crystalline versus regrown silicon. In crystalline silicon, TED is observed in the tail of the boron distribution while most of the peak remains immobile. It has also been shown that TED can occur in regrown silicon but that B does not cluster in this case. The end of range loops do not prevent the flow of interstitials into the regrown silicon and the (311) defects in the end of range damage appear to be the source of interstitials for the TED process.

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[1] T. O. Sedgwick, A. E. Michel, V. R. Deline, S. A. Cohen, and J. B. Lasky, J. Appl. Phys. **63**, 1452 (1988).

[2] S. Solmi, R. Angelucci, F. Cembali, M. Servidori, and M. Anderle, Appl. Phys. Lett. **51**, 331 (1987).

[3] S. Peterstrom and B. G. Svensson, J. Appl. Phys. **71**, 1215 (1992).

[4] M. Servidori, R. Angelucci, F. Cembali, P. Negrini, S. Solmi, P. Zaumseil, and U. Winter, J. Appl. Phys. **61**, 1834 (1987).

[5] T. E. Seidel, IEEE Electron Device Lett. **4**, 353 (1983).

[6] F. Cembali, M. Servidori, S. Solmi, Z. Sourek, U. Winter, and P. Zaumseil, Phys. Status Solidi A **98**, 511 (1986).

[7] K. S. Jones, R. G. Elliman, M. Petravic', and P. Kringhøj (unpublished).

[8] L. H. Zhang, K. S. Jones, P. H. Chi, and D. S. Simons, Appl. Phys. Lett. **67**, 2025 (1995).

[9] P. A. Stolk, H. J. Gossmann, D. J. Eaglesham, D. C. Jacobson, J. M. Poate, and S. Luftman, Appl. Phys. Lett. **66**, 568 (1995).

[10] R. B. Fair, in *Impurity Doping Processes in Silicon*, edited by F. F. Y. Wang (North Holland, New York, 1981), Chap. 7.

[11] H. L. Meng, S. Prussin, M. E. Law, and K. S. Jones, J. Appl. Phys. **73**, 955 (1993).

[12] D. J. Eaglesham, P. A. Stolk, H.-J. Gossman, and J. M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).

[13] M. Y. Tsai and B. G. Streetman, J. Appl. Phys. **50**, 183 (1979).

[14] T. E. Seidel and T. Macrae, in *First International Conference on Ion Implanting*, edited by F. Eisen and L. Chadderton (Gordon and Breach, New York, 1971).

[15] P. A. Stolk, H.-J. Gossmann, D. J. Eaglesham, D. C. Jacobson, H. S. Luftman, and J. M. Poate, Mater. Res. Soc. Symp. Proc. **354**, 307 (1995).

[16] D. J. Eaglesham, P. A. Stolk, H. J. Gossmann, T. E. Haynes, and J. M. Poate, Nucl. Instrum. Methods B (in press).