Effect of fluorine on the diffusion of boron in ion implanted Si

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Ion implants of 1 keV $^{11}B^+$ and 5 keV BF_2^+, to a dose of $1\times10^{15}/cm^2$ at a tilt angle of 0°, were implanted into preamorphized (Si^+,70 keV, $1\times10^{15}/cm^2$) wafers. These samples were rapid thermal annealed in an ambient of 33 ppm of oxygen in N_2 at very short times (<0.1 s spike anneals) at 1000 and 1050 °C to investigate the effects of the fluorine in BF_2 implants on transient enhanced diffusion (TED). By using a relatively deep preamorphization of 1450 Å, any difference in damage between the typically amorphizing BF_2 implants and the nonamorphizing B implants is eliminated because the entire profile (<800 Å after annealing) is well contained within the amorphous layer. Upon annealing, the backflow of interstitials from the end-of-range damage from the preamorphization implant produces TED of the B in the regrown layer. This allows the chemical effect of the fluorine on the TED of the B in the regrown Si to be studied independent of the damage. The secondary ion mass spectroscopy results show that upon annealing, the presence of fluorine reduces the amount of B diffusion by 30% for the 1000 °C spike anneal, and by 44% for the 1050 °C spike anneal. This clearly illustrates there is a dramatic effect of F on TED of B independent of the effects of implant damage. Analysis of the temperature dependence of the enhancement factors point to transient enhanced diffusion not boridation as the source of the interstitials. © *1998 American Institute of Physics.* [S0003-6951(98)03035-6]

It has been previously reported that BF_2 yields shallower junctions than B when implanted into single crystal Si at the same effective energy.[1–4] In addition, it was shown that adding F to B and BF_2 implants reduced diffusion.[5] However, as with all comparisons of BF_2 and B at higher doses, the effects of F could be interpreted as the result of either the increased damage/amorphization from the F or a chemical species effect from the F. In an effort to eliminate the damage effect, B and BF_2 comparisons into preamorphized layers were studied.[1,2] These results showed in layers which were preamorphized with 30 keV Ge^+ at a dose of $5\times10^{14}/cm^2$ that BF_2 yields shallower junctions than B at the same effective energy.[1,2] Unfortunately the amorphous layer was very shallow and thus the B diffusion overlapped with the end-of-range (EOR) damage. Also, the presence of Ge may also complicate the interpretation of the results. The purpose of this experiment is to use Si to produce a sufficiently deep amorphous layer such that the B can diffuse without encountering the EOR loops. By using implant conditions for which the loop density is not too high, a sufficient backflow of interstitials for transient enhanced diffusion (TED) is observed.[6,7] It is shown that by using the proper combination of implant and annealing conditions[8] fluorine does indeed show a chemical effect on the TED of boron.

For the experiment, the Varian VIISion-80 PLUS ion implanter was used to implant 200 mm, ⟨100⟩, *n*-type wafers with an amorphizing implant of $1\times10^{15}/cm^2$,70 keV Si^+ at a tilt/twist of 5°/180°. Following preamorphization a $1\times10^{15}/cm^2$, 1.0 keV $^{11}B^+$,or 5.0 keV $^{49}BF_2^+$ was implanted at a tilt/twist of 0°/180° (at these doses and energies, as expected, atomic force microscopy revealed no sputter etching for B and BF_2 nor reactive ion beam etching[9] for the BF_2 implant).[10] The temperatures of the Si preamorphizing implant was maintained at <36 °C, and the peak beam current density was maximized at over 2 mA/cm^2. These conditions produced an amorphizing layer of 1450 Å, and hence optimized the interstitial backflow into the regrown Si from the EOR damage. After implant, samples were rapid thermal annealed (RTA) in a STEAG AST Elektronik SHS-2800ϵ in 33 ppm of O_2 in N_2[7–9] at 550 °C 30 s+1000 °C, ~0 s (spike anneal), at 550 °C, 30 s+1050 °C, ~0 s, and at 1050 °C, ~0 s. The ramp-up rate was 50 °C/s, and the ramp-down rate was 86 °C/s for the high temperature anneal steps. It has been shown by us[4,8,9] that the presence of oxygen enhances boron diffusion by oxidation enhanced diffusion (OED) and/or other oxygen related diffusion phenomena, such as the formation of an SiB_4 layer.[10] Thus by keeping the oxygen concentration in the anneal ambient low for this experiment, the effect of oxygen on boron diffusion was minimized. The choice of spike anneals[4] minimizes the thermal diffusion component. The minimization of these diffusion components therefore yields a clearer illustration of the effects of fluorine on TED. After anneal, the wafers were measured by secondary ion mass spectrometry (SIMS) using a Physical Electronics Model Phi 6600 Quadrapole-SIMS System. The transmission electron microscopy (TEM) analysis was done on a

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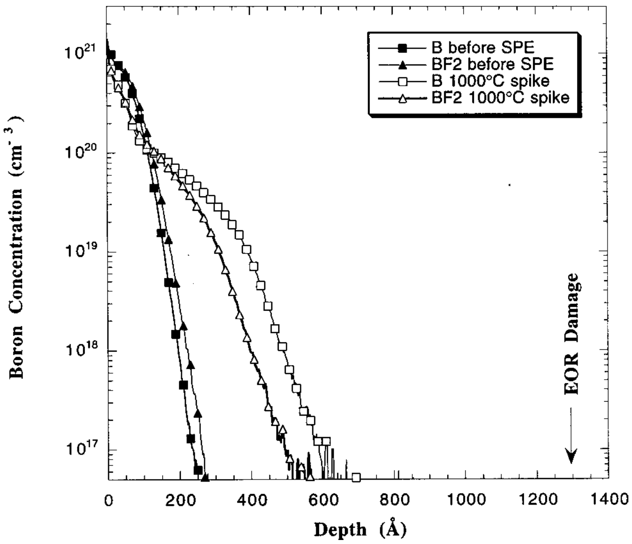

FIG. 1. Effect of F on B TED. SIMS of preamorphized silicon implanted with either 1 keV ^{11}B or 5 keV BF_2 profiles annealed at 550 °C for 30 s then at 1000 °C, 0 s in 33 ppm O_2+N_2.

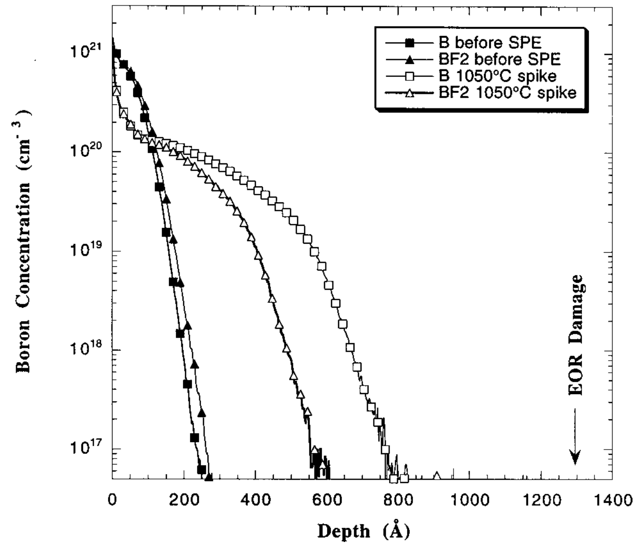

FIG. 2. Effect of F on B TED. SIMS of preamorphized silicon implanted with either 1 keV ^{11}Bor 5 keV BF_2 profiles annealed at 550 °C for 30 s then 1050 °C, 0 s in 33 ppm O_2+N_2.

JEOL 200 CX at an accelerating voltage of 200 kV.

An overlay of the ^{11}B and $^{49}BF_2$ profiles annealed at 550 °C, 30 s followed by the 1000 °C spike anneal is shown in Fig. 1. Cross-sectional TEM confirmed that the anneal of 550 °C, 30 s does not regrow the amorphous layer (thus these profiles are the same as the ''as-implanted'' profiles). While the B profile starts off at similar depths (230–250 Å at $1\times10^{17}/cm^3$, with BF_2 slightly deeper), after the spike anneal at 1000 °C the boron profile has moved 350 Å to a depth of 600 Å while the BF_2 profile has moved only 230 Å to a depth of 480 Å. The as-implanted and postanneal profiles of F in BF_2 implants have been researched extensively.[4] For this case, the as-implanted depth of the F is (at $1e17/cm^3$) at 1050 Å [after the 1050 °C RTA anneal employed in this experiment, the F junction is reduced to 215 Å with subsurface peaks at the original B peak and at the amorphous–crystalline (a–c) interface, with 7.25% of the implanted F remaining].[4] After a 1050 °C spike anneal (Fig. 2), the difference in the amount of diffusion between the B and BF_2 profiles is even greater. The B profile has diffused 530 Å to a depth of about 780 Å, while the BF_2 profile has diffused only 295 Å to a depth of 550 Å. This clearly illustrates there is a dramatic effect of F on TED of B, independent of the effects of implant damage.

For modeling purposes it is assumed that the time at temperature for the spike anneal has an upper limit value of 0.1 s. The profile motion from thermal diffusion was simulated using the process simulator FLOOPS. For a 0.1 s anneal the expected motion from pure thermal diffusion is anticipated to be about 80 Å at 1000 °C and 250 Å at 1050 °C. This is much less than the observed motion for the B of 350 Å at 1000 °C and 530 Å at 1050 °C, and hence is consistent with enhanced B diffusion. This enhancement in B diffusion may arise from several sources. It has been previously demonstrated that the interstitial backflow from the EOR region, just below where the amorphous–crystalline interface existed prior to annealing, induces TED in the regrown layer.[6,7] TED exhibits a negative temperature dependence, becoming smaller at higher temperatures. It has also been shown that at high B concentrations, the diffusivity of B can also be enhanced by the formation of a second phase.[11] This phenomenon has been termed boron enhanced diffusion (BED). The dose of the boron employed in this experiment is at the lower limit of where BED has been reported. It has been shown that BED exhibits a positive activation energy with annealing temperature, i.e., the effect is greater as the temperature increases.[12] In order to distinguish between these two phenomena, the enhancement factor was estimated at both 1000 and 1050 °C, assuming the motion can be approximated by $[2(DT)^{1/2}]$and the redistribution is Gaussian. The B enhancement factor D_B/D_B^* (where D_B is the diffusivity of B in the implanted sample and D_B^* is the intrinsic diffusivity of

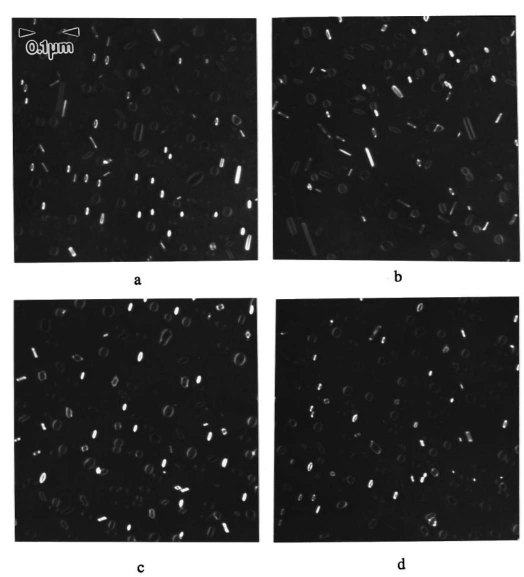

FIG. 3. Plan-view TEM of the evolution of the 70 keV Si^+ $1\times10^{15}/cm^2$ EOR damage after (a) 1 keV B^+ implant $1\times10^{15}/cm^2$ and 1000 °C spike anneal (b) 5 keV BF_2^+ implant $1\times10^{15}/cm^2$ and 1000 °C spike anneal (c) 1 keV B^+ implant $1\times10^{15}/cm^2$ and 1050 °C spike anneal (d) 5 keV BF_2^+ implant $1\times10^{15}/cm^2$ and 1050 °C spike anneal.

boron) was determined for the B implant to be about 20 at 1000 °C and only about 5 at 1050 °C. The higher enhancement at lower temperatures supports the premise that the enhancement is from TED not BED. Similar analysis for the BF_2 implants suggests the enhancement of the B is only 8 after 1000 °C annealing and between 1 and 2 after 1050 °C. It should be emphasized that while the relative shifts in the magnitude are believed to be reasonably accurate, the absolute value of these enhancements are estimates because the thermal diffusion component is difficult to determine for such short time anneals.

To investigate the mechanism for the F effect on boron TED, measurements of {311} and dislocation loop densities were made by TEM of the EOR damage after RTA. Figures 3(a) and 3(b) shows that there were still elongated loops (from the {311} unfaulting process) after the 1000 °C RTA. These loops were located at a depth of 1450–1650 Å. After 1050 °C RTA the loops had decreased in density and become more circular. The loop density in Figs. 3(a) and 3(b) was $1.60\times10^{10}/\mathrm{cm}^2\pm2\times10^8/\mathrm{cm}^2$ for both the BF_2 and B implants. The loop density in Figs. 3(c) and 3(d) decreases to $1.33\times10^{10}/\mathrm{cm}^2\pm2\times10^8/\mathrm{cm}^2$ after 1050 °C for both B and BF_2 samples. The loop density (not shown) was exactly the same after 1050 °C RTA with or without a preanneal of 550 °C, 30 s. Because of the elongated shape of the loops after the 1000 °C RTA it is difficult to quantify the interstitial release that occurs between 1000 and 1050 °C spike anneals but a rough estimate is about $3\times10^{13}/\mathrm{cm}^2$. These results indicate that the presence of fluorine does not affect the evolution of the EOR damage, which was the source of the interstitials. Thus, the fluorine must either affect the diffusion/concentration of interstitials after their release from the EOR region or affect the ability of the interstitial to bind/kickout the boron.

In conclusion it has been shown that preamorphization of Si can be used to separate the chemical and damage effects of fluorine on TED of boron. Independent of the effect of damage, the presence of F at concentrations of $1\times10^{21}/\mathrm{cm}^3$ during the annealing of implant damage reduces the TED of boron. The effect is greater at lower temperatures, consistent with the fluorine affecting the interstitials inducing TED diffusion. The exact role of the fluorine on TED is unclear and is the subject of ongoing investigations.

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