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Role of fluorine in suppressing boron transient enhanced diffusion in preamorphized Si

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We have explained the role of fluorine in the reduction of the self-interstitial population in a preamorphized Si layer under thermal treatment. For this purpose, we have employed a B spike layer grown by molecular-beam epitaxy as a marker for the self-interstitial local concentration. The amorphized samples were implanted with 7×10^{12}, 7×10^{13}, or 4×10^{14} F/cm^2 at 100 keV, and afterwards recrystallized by solid phase epitaxy. Thermal anneals at 750 or 850 °C were performed in order to induce the release of self-interstitials from the end-of-range (EOR) defects and thus provoke the transient enhanced diffusion of B atoms. We have shown that the incorporation of F reduces the B enhanced diffusion in a controlled way, up to its complete suppression. It is seen that no direct interaction between B and F occurs, whereas the suppression of B enhanced diffusion is related to the F ability in reducing the excess of silicon self-interstitials emitted by the EOR source. These results are reported and discussed. © *2004 American Institute of Physics.*
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The shrinkage demanded for future complementary metal-oxide-semiconductor devices will require the confinement of dopants in regions even shallower than 10 nm.[1] In Si crystals, the doping process is usually carried out through ion-implantation, resulting in a supersaturation of self-interstitials (Is) in the implanted crystal.[2,3] This fact, combined with the post-implantation annealing needed for the electrical activation of the dopant, leads to a rapid spread of the implanted atoms, that can diffuse at a rate of several orders of magnitude higher than their normal thermal diffusion. This effect, known as transient enhanced diffusion (TED), is particularly dramatic in the case of *p*-type doping with boron.[3–5]

The implantation of BF_2^+ molecular ions is one of the methods used in microelectronic manufacturing in order to fabricate shallower junctions.[6,7] This method permits the implantation of B closer to the surface, since the projected range for B from BF_2 molecules is smaller than that of atomic B at the same energy. Moreover, the more massive BF_2^+ ions cause an amount of damage that can, to some extent, reduce the undesirable B channeling tail.[8] In recent years, it has been found that the addition of F to previously BF_2^+- or B^+-implanted Si can decrease the boron TED.[9] However, this latter effect might be connected with the extra damage caused by the F implantation. In order to distinguish damage effects, BF_2^+ and $B^+ + F^+$ have been implanted into Si preamorphized with Si implants.[9] The subsequent recrystallization by solid phase epitaxy (SPE) leaves structural defects beyond the original amorphous–crystalline (*a*–*c*) interface, which are commonly referred to as the *end-of-range*

defects (EOR). Upon further thermal annealing, Is diffuse outwards from the EOR region, inducing the dopant TED.

Up to now, the mechanism whereby fluorine slows down the boron TED has not been unambiguously explained. On the one hand, it has been argued that the fluorine does not affect the evolution of the EOR damage, but interacts with the Is after their release from the EOR region.[9,10] On the other hand, very recently, Mokhberi *et al.*[11] have claimed that the presence of F has no bearing on the point-defect population, but that there should be instead a strong B–F chemical interaction leading to the boron TED drop. This controversy demonstrates that the precise role of F on boron TED remains unclear and that further investigations are demanded.

We studied the effect of fluorine on the Is population in a preamorphized Si layer. To this aim, we have used a B spike layer grown by molecular-beam epitaxy (MBE) as a marker for the Is local concentration.[3,12] To our knowledge, this is the first time that such a clean method is applied to ascertain the real role of F in the reduction of boron TED. From our results we conclude that there is a strong F–I interaction, and rule out B–F chemical bonding as responsible for boron TED decrease.

The samples were prepared by MBE on a 5 in., 2×1 reconstructed, Si (100) substrate. They consisted of a 650-nm-thick Si film with a B spike inserted at a depth of 240 nm (peak concentration of $\sim 7 \times 10^{18}$ B/cm^3, full width at half maximum of ~ 8 nm). During growth, the base pressure was 5×10^{-11} mbar, the substrate temperature was kept at 450 °C, and the Si rate deposition was 1 Å/s. Afterwards, the samples were cut into several pieces, which were then amorphized from the surface to a depth of ~ 550 nm by implanting Si$^-$ ions (3×10^{15} ions/cm^2 at 250 keV, plus 2×10^{15} ions/cm^2 at 40 keV) at liquid nitrogen temperature.

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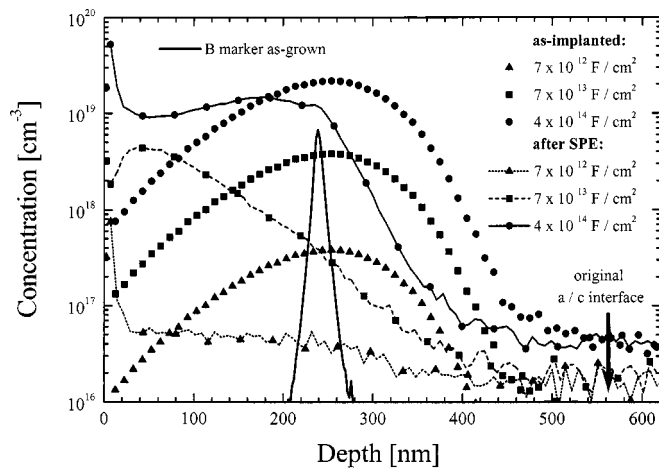
FIG. 1. F profiles as-implanted (symbols) and after solid phase epitaxy (SPE) (lines plus symbols) for the three different F doses, and B spike profile in the as-grown sample.
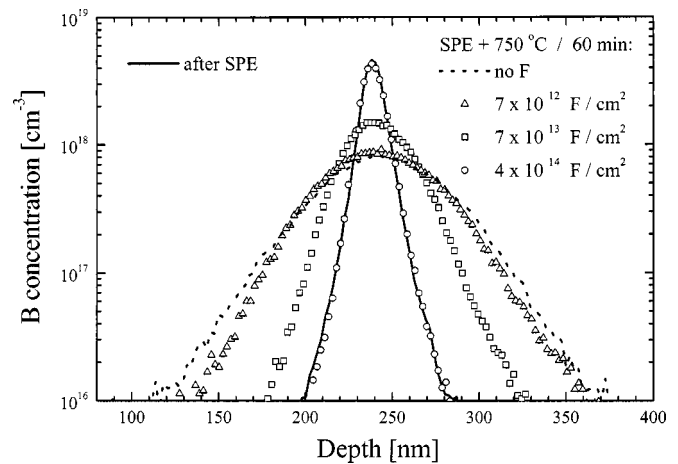

FIG. 2. B diffused profiles for the three different doses of F implantation after SPE plus thermal anneals (open symbols) at 750 °C/60 min. B profile for a similar sample without F is also shown for reference (dashed line).

The amorphized samples were next enriched in fluorine by implanting 100 keV F ions at different doses: 7×10^{12}, 7×10^{13}, and 4×10^{14} ions/cm^2. The implanted energy was chosen so that the F projected range coincides with the B spike position.[2] Some of the amorphized samples were not implanted with F, to be used as reference samples. In order to induce SPE, and taking into account the decrease of the SPE velocity by F,[13] we annealed all the amorphized samples at 450 °C for 30 min plus 700 °C for 80 s in N$_2$ atmosphere. By means of Rutherford backscattering spectrometry (RBS) in channeling geometry, we verified that the above-mentioned thermal process produced a complete regrowth with a good crystalline quality of the regrown layer. Finally, the regrown samples were treated by rapid-ramp thermal anneal in N$_2$ atmosphere, at 750 °C for 1 h or at 850 °C for 10 min,[14] in order to induce the defects release from the EOR region and thus study the B spike diffusion as a function of F amount. The concentration depth profiles of B and F were obtained by secondary ion mass spectrometry (SIMS), using a CAM-ECA IMS-4f instrument, by collecting F$^+$ and B$^+$ secondary ions while sputtering with a 3 keV O$_2^+$ analyzing beam.

Figure 1 shows, with symbols, the as-implanted F profiles at different doses (▲ 7×10^{12}, ■ 7×10^{13}, ● 4×10^{14} ions/cm^2), and the profiles after SPE for the same doses by line plus respective symbols. It is interesting to note the F segregation toward the surface after SPE. This anomalous redistribution can be explained assuming that the moving a–c interface pushes F atoms ahead during the SPE process, until saturation in the local F concentration is attained. Indeed, for the high implant-dose sample, we can see a wide plateau at a concentration level of $\sim 10^{19}$ F/cm^3, while for the medium implant dose, this saturation is not yet achieved. For both samples, the F dose remaining after SPE is about 75% of the original implanted dose. Instead, the low implant-dose sample underwent a substantial F outdiffusion. Note that the rise of F signal near the surface is presumably an artifact which is frequently observed in SIMS spectra obtained from silicon samples by collecting positive secondary ions. In addition, we indicate in Fig. 1 both the original a–c interface (arrow) and the profile of the B spike as grown (solid line).

In order to study the boron TED as a function of F dose, we performed thermal treatments at 750 and 850 °C on the regrown samples, inducing in this way the Is release from the EOR defects and subsequent TED on the B spike. In Fig. 2, we report the B profile after SPE as well as those after SPE followed up with annealing at 750 °C for 1 h and for different amounts of F. The solid line represents the B spike in the regrown sample, whereas the dashed line displays the B spike after the anneal on the reference sample (without F). Since the equilibrium diffusion would be negligible,[15] it is evident that the thermal process induced a significant Is release from the EOR, causing a huge enhanced diffusion of B. The B diffusion in F enriched samples is described by open symbols (△, □, ○) for the different implant doses. A boron TED decline with increasing F dose can be clearly seen, until a complete TED suppression is achieved for the high F dose. In this case, no B diffusion is observed at all. Analogous results were obtained for the annealing at 850 °C (not shown here), which demonstrates that the F ability in reducing boron TED is present at higher temperature as well.

The F profile evolution during the post-SPE thermal processes is reported in Fig. 3, for the medium and high implant doses. Open symbols are used for the annealing at 750 °C
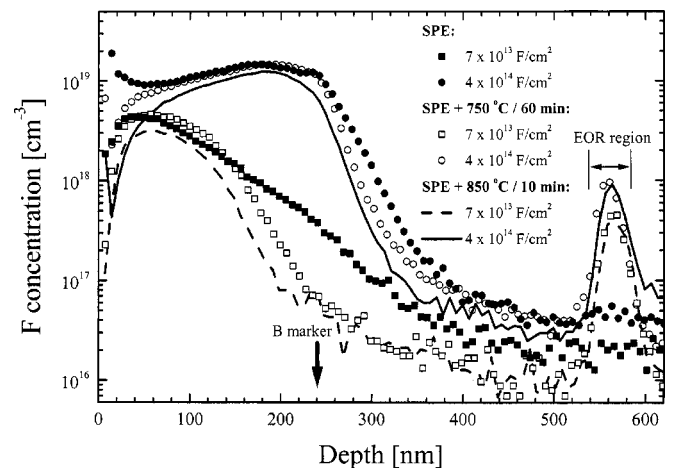

FIG. 3. F profiles after SPE (closed symbols), SPE plus thermal anneal at 750 °C/60 min (open symbols) or 850 °C/10 min (lines) for the two highest F implanted doses.

and lines for the 850 °C one. We can note a F diffusion toward the surface and the bulk, particularly for the higher temperature. Moreover, it can be seen that a clear F long-range diffusion has occurred with subsequent accumulation in the region that corresponds to the position of the EOR. The depth of the EOR zone was measured by transmission electron microscopy (not shown here), and indicated in Fig. 3.

Figure 3 reveals several interesting features. First of all, after both thermal processes, at the B spike depth, the F concentration for the medium implant dose is about two orders of magnitude lower than the B one. In spite of this, a consistent boron TED reduction is observed (Fig. 2). Moreover, the F diffusion profiles after both anneals are not affected by the presence of B. In fact, a homogeneous decrease by about one order of magnitude is observed in the F profile around the B marker with no evidence for F accumulation at the B depth. These two facts indicate that there is no direct interaction between B and F, and then a B–F chemical bonding cannot be responsible for the boron TED slowing down. On the other hand, the presence of the F peak at the EOR region allows us to claim a strong interaction between F atoms and EOR defects. In addition, the amount of F in this peak seems to be independent of the annealing temperature, while it seems to be a function of the implant dose. This feature might indicate that the F migration toward the EOR region takes place in the very early stages of the annealing process and with a low energy barrier. In particular, the amount of fluorine trapped in the EOR region has been found to be 1.3 and 2.9×10^{12} F/cm^2 for medium and high doses, respectively.

The data shown so far strongly support the idea that boron TED is suppressed by inhibiting the Is flux from the EOR region toward the surface. In principle, F reaching the EOR region could stabilize those defects thus avoiding the emission of Is. Alternatively, F might capture Is emitted by EOR defects during thermal treatments immediately after emission, forming F–I complexes. Though the microscopic mechanism of F interaction requires further investigations, it is clear that the origin of boron-TED suppression is a F-defect interaction.

In conclusion, the effect of F on boron TED was studied. We have seen that an anomalous segregation of F occurs during SPE of the amorphous Si layer. The presence of fluorine also suppresses the TED of boron. We have demonstrated that this effect cannot be ascribed to a chemical bonding between F and B atoms, while a strong interaction of F with Is is evidenced, causing a consistent reduction of the Is flux released during thermal treatments. These results have strong implications for the fabrication of ultrashallow junctions in future generation devices.

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