B profile alteration by annealing in reactive ambients

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Suppression or stimulation of B diffusion and activation in Si (coimplanted with F) has been investigated by anneals in a N2 ambient enriched with H2 or O2. The H2 rich ambient leads to B desorption and therefore stimulated diffusion toward the surface, thus effectively reducing indiffusion. Annealing in an O2 rich ambient promotes deeper B diffusion by injection of Si interstitials. The impact of these ambient can further be modulated by combining the B implant with a shallow or deep F coimplant acting as Si interstitial trap. Deep F coimplant and H2 rich ambient offer attractive B diffusion and activation. © 2009 American Institute of Physics. [DOI: 10.1063/1.3068756]

The studies on profiling and activation of dopants have attracted a lot of attention in the past1–3 in order to achieve desired junction and sheet resistance properties. For dopants that diffuse interstitially such as B, the thermal movement of Si interstitials (I) created during the implant is the main reason for the rapid B diffusion—transient enhanced diffusion (TED) (Ref. 4) especially in the tail of the profile. During this process B-I clustering also leads to B deactivation, thus limiting the high electrical activation. Many approaches have been presented to suppress the B deactivation and the TED. F5,6 or C7,8 coimplantation have been used for this purpose as these species trap the Si interstitials and prevent their interaction with the B atoms. Si surface treatment has been proven to affect B diffusion and activation and to accelerate damage removal.9 Hence the role of the ambient during anneal can play a crucial role as the B diffusion can be enhanced in the case of an ambient causing oxidation (enhanced diffusion by I injection)10 or NH3 treatment (reduced diffusion).11,12 An additional mechanism impacting the B diffusion is the role of surface reactions, as anneal in a H2 ambient leads to a strong surface desorption8 and an enhanced B diffusion toward the surface. The B desorption can be stimulated by the native oxide thinning or even its complete removal in an H2 rich ambient according to the following reaction13 at temperatures above 700 °C (typical for H2 prebake prior epideposition):

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\text{SiO}_2 + 2\text{H}_2 \rightarrow \text{Si (substrate)} + 2\text{H}_2\text{O}\]

Removal of native oxide has been proven to suppress B diffusion due to enhanced I recombination to the surface.9

Faced with the requirement for next generation technologies, to limit the B diffusion and smaller junction depths [less than 10–15 nm (Ref. 14) with spike rapid thermal anneal or submelt laser activation], the H2 rich ambient appears interesting as its B desorption process stimulates shallower and sharper dopant profile. The concurrent reduction in the B concentration (resulting from the dose loss) may also impact the (substrate oriented) diffusion flux, thereby reducing the observed junction depths (as compared to the one observed for the normal anneal in a N2 ambient). Hence junction control by reduced diffusion resulting from desorption process leading to the dynamic reduction in the B dose during the activation anneal may be considered as an additional profile tuning approach. This paper represents an assessment of this concept by comparing junction depths and activation levels for various annealing ambient (pure N2, O2 rich, H2 rich). The role of the interstitials is further elucidated by considering the profile modifications for a B implant with or without an additional, shallow or deep, F coimplant. In the current experiment a relaxed thermal budget for dopant activation was applied in order to have a good processing control and reproducibility. This results in formation of deeper junctions than required for next generation technology node.14

Experiments were performed on 200 mm wafers and B profiles were formed by implantation of B (0.5 keV, 1×1015 atoms/cm², at incident angle of 7° to the surface normal). In some samples (prior to the B implant), an additional deep F profile was added by implantation with an energy of 10 keV with a dose of 2×1015 atoms/cm² also at an incident angle of 7°. Alternatively a BF2 implant (2.2 keV, 1×1015 atoms/cm²) was used, which leads to a F profile overlapping with the B profile. Pieces of wafers were annealed in a Heatpulse lamp oven at 950 °C for 30 s, with ramp-up rate around 100 °C/s and ramp-down rate around 70 °C/s. Three different gas ambient during anneal were used, i.e., N2 100%, H2 10%+N2 90% (stimulating the B desorption process),15 and O2 10%+N2 90% (stimulating I injection).15,16 After processing, B depth profiles were determined using secondary ion mass spectroscopy (SIMS) using an Atomika 4500 instrument, and the electrical activation was extracted from the sheet resistance measurements based on standard mobility data.17 In order to prevent any substrate contribution due to probe penetration, the sheet resistance was extracted from variable probe spacing measurements using spreading resistance probes with less than 5 nm penetration.18

The basic concept of this study is illustrated in Fig. 1. The anneal in a H2 rich ambient will stimulate B desorption, create an enhanced B flux toward the surface, and lower the total B content inside Si, thereby reducing the B indiffusion. The O2 rich anneal will promote the I injection and thus the B diffusion and deactivation. The incorporation of F will control the degree of the B-I interaction either overlapping

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with the B profile or extending much deeper. The positioning of F will impact the depth where the I trapping occurs, and thus vary the depth over which the B outdiffusion will be affected.

Figure 2(a) presents as-implanted and diffused chemical B profiles for the B-implant case after annealing in the three different ambients: pure N₂, H₂ rich, and O₂ rich. The junction depth as measured at concentration of $10^{19}$ atoms/cm³ equals 54 nm (H₂ rich), 73 nm (pure N₂), and 106 nm (O₂ rich), whereas the corresponding sheet resistance values are 389.5, 297, and 265 Ω/sq. Using the SIMS profiles and the corresponding sheet resistance values, we can extract the maximum electrically active B concentrations. Based on this analysis (and when disregarding the SIMS related surface peak in the first 2 nm), all B atoms appear to be electrically active for all conditions. Since the B concentration level for pure N₂ and H₂ rich profiles at the diffusion shoulder (depth of 10 nm) is identical, we can conclude of yet another effect suppressing B diffusion, i.e., vacancy injection from the surface³⁹ that recombines with interstitials and therefore suppress TED.

The O₂ rich anneal leads to a strong I injection, which dramatically enhances the B diffusion through the formation of mobile B-I clusters. The observed reduced concentration level in the SIMS profiles and the lower active B-concentration level ($4.5 \times 10^{19}$ atoms/cm³) are a result of the limited amount of B available for diffusion and not a characteristic of a reduced B activation. The enhanced diffusion is also responsible for the degradation of the junction abruptness.

Previous work on reducing B diffusion by coimplantation was focused on positioning of the trapping site (F or C) in between the source of the interstitials and the end-of-range damage (which is normally the source of the interstitials). In our oxidation experiments the interstitials originate from the surface and diffuse inward. Hence the effect of a deeper lying trapping site might be very different. To study this effect in more detail we have performed also a BF₂ and a B+deep F coimplant. SIMS B profiles after the different anneals are shown in Fig. 2(b), for the BF₂ implant and in Fig. 2(c), for the B +deep F coimplant. For the BF₂ case, the trends for diffusion with an O₂ or H₂ anneal ambient are similar to the case of the simple B implant [Fig. 2(a)], although some subtle differences can be seen as well. For instance, the observed reduction in junction depth after the H₂ rich anneal relative to the N₂ anneal is less than seen for the B case. This is probably related to the fact that B diffusion with the N₂ anneal is already reduced due to the presence of F (originating from the molecule BF₂ implant). The fact that the retained B dose is now reduced (Fig. 3) and that the B diffusion shoulder falls below the one seen for the pure N₂ anneal indicates that due to this reduced inward diffusion, the desorption process can act (longer) on a higher B concentration leading to a more severe B dose loss. Comparing the results for the O₂ rich anneals, it is clear that since the shallow F profile is positioned in between the source of the interstitials and the outdiffusing B tail; it can trap (partly) the interstitial flux and thus reduce the B outdiffusion. Unfortunately in all cases the observed sheet resistance values are high and indicate a smaller than 100% activation and/or a reduction in carrier mobility due to the presence of the F clusters.
Turning to the case of the deep F coimplant [Fig. 2(c)], similar observations can be made. The difference between N$_2$ and N$_2$+H$_2$ becomes even smaller in terms of junction depth, while the difference in the retained dose and the concentration of the diffusion shoulder is again present. However it is somewhat less pronounced as compared to the BF$_2$ case. In terms of junction depths an overlay of the BF$_2$ versus B+F case (not shown) indicates a slightly shallower junction depth for the B+F case for all anneal conditions (5 nm for N$_2$ and H$_2$, 10 nm for O$_2$). For the N$_2$ and H$_2$ cases this implies that the fact that the F profile extends deeper into the sample provides a continuous trapping region for the interstitials, thereby limiting the B diffusion to larger depths. The profile for O$_2$ ambient is very different compared to all other results and indicates a clear B trapping at the end-of-range region (formed after amorphization by F) at the depth of $\sim$35 nm. The BI clusters are not dissolved after activation anneal, suggesting $I$ supersaturation due to continuous interstitial injection from the surface. Note also the inverse B slope in the first 40 nm for this profile. F implantation induced amorphization and F retarded Si recrystallization enabled enhanced B diffusion during Si amorphous phase at a relatively high concentration level of $2 \times 10^{20}$ atoms/cm$^3$, producing boxlike profile. After complete recrystallization the injected $I$ flux pushed B deeper, forming retrograde profile. The enhanced B profile depth relative to the N$_2$ and N$_2$+H$_2$ anneals is again a result of the oxidation related interstitial injection. Compared to the B case, a reduced indiffusion is seen. When comparing the final B profile with the deep F profile, a close overlap is seen indicating that the B/I clusters will diffuse into the substrate and get dissolved whenever they reach a free fluorine-vacancy (FV) interstitial trapping pair. As such the B profile will mimic the F profile. The dopant profile in BF$_2$ case is deeper than that in F+B coimplantation scheme because whenever a BI cluster escapes from the F-rich region, it will be free to diffuse without any further interaction with any FV trapping pairs.

If we now cross compare all the junctions in Fig. 3 by looking at the trade off between $R_s$ and retained B dose, we may conclude that H$_2$ rich anneal always leads to the smallest B dose due to the impact of the desorption process. The latter is most pronounced in the BF$_2$ case due to the reduced B diffusivity. The O$_2$ rich anneal clearly promotes a rapid diffusion limiting the probability for B segregation at the surface. When using the $R_s$ and junction depth relation as figure of merit (Fig. 4), it is clear that the O$_2$ ambient always leads to the poorest performance due to the strong indiffusion by the interstitial injection. Vice versa, the H$_2$ rich ambient always leads to a reduced diffusion by the counteracting effect of the B desorption at the surface. The $K_F$-$X_F$ can be further mediated by adding trapping sites for the interstitials using F coimplantation. Obviously a BF$_2$ implant appears less appropriate, most likely due to B diffusion suppression resulting from excessive F concentration. A separate F implant extending beyond the B profile (and with less F in the B region) is more suited as it will significantly limit the diffusion in the tail region.

In summary we demonstrated the impact of the anneal ambient (N$_2$, O$_2$, or H$_2$ rich) on the B diffusion and activation, indicating a strong reduction in B in-diffusion for the H$_2$ rich anneals. Furthermore the reduced diffusion by adding F coimplant was demonstrated, whereby its positioning turns out to be an important parameter. The above findings are important in aiding in the regular B profile formation for the source/drain junctions. Moreover the understanding of the role of the H$_2$ anneal is important to grasp the effects of B dose loss when dealing with dopants in the thin body Si or other regions that get exposed to H$_2$ or O$_2$ outgassing liners and spacers.

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