Fluorine-enhanced boron diffusion in amorphous silicon

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Silicon wafers were preamorphized with 70 keV Si^+ at a dose of 1×10^{15} atoms/cm^2, generating a deep amorphous layer of 1800 Å. Implants of 500 eV $^{11}B^+$, with and without 6 keV F^+, followed at doses of 1×10^{15} atoms/cm^2 and 2×10^{15} atoms/cm^2, respectively. After annealing at 550 °C, secondary ion mass spectroscopy determined that the diffusivity of boron in amorphous silicon is significantly enhanced in the presence of fluorine. Ellipsometry and cross-sectional transmission electron microscopy indicate the enhanced diffusion only occurs in the amorphous layer. Fluorine increases the boron diffusivity by approximately five orders of magnitude at 550 °C. It is proposed that the ability of fluorine to reduce the dangling bond concentration in amorphous silicon may reduce the formation energy for mobile boron, enhancing its diffusivity. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1576508]

As silicon based microelectronic devices continue to scale smaller, the drive to achieve shallower junction depths becomes more prevalent. Transient enhanced diffusion (TED) of dopant species is known to be a limiting factor in the formation of low resistivity, ultra shallow junctions within the source/drain extension regions of transistors.[1] Recently, there has been increasing interest within the coimplantation of fluorine and boron for ultra shallow junction formation. Previous studies have demonstrated the ability of fluorine to reduce boron TED and simultaneously increase boron solubility during high temperature rapid thermal annealing (RTA) and furnace annealing.[2–4] These effects are ascribed to the ability of fluorine to bind with excess silicon interstitials and therefore reduce boron interstitial cluster formation. However, these processes occur while silicon is in the crystalline state. During the initial processing stage, the implanted layer is amorphous. Thus, in order to gain a more complete understanding of dopant diffusion processes, it is of interest to study whether any boron diffusion occurs while silicon is in the amorphous state. Normally, the silicon recrystallizes at such a sufficiently low temperature that boron diffusion is not expected. However, recently it was reported that there appeared to be some anomalous redistribution of boron at low temperatures in the presence of fluorine.[5] This study attempts to determine if boron diffusivity is enhanced in amorphous silicon and to characterize any fluorine effects.

Several (100) *n*-type Czochralski silicon wafers were commercially implanted at room temperature. They were first preamorphized with 70 keV Si^+ at a dose of 1×10^{15} atoms/cm^2. A continuous amorphous layer 1800 Å deep was created, as confirmed by cross-sectional transmis-

sion electron microscopy (XTEM). The amorphized wafers were then implanted with 500 eV $^{11}B^+$ at a dose of 1×10^{15} atoms/cm^2 followed in some cases by a 6 keV F^+, 2×10^{15} atoms/cm^2 implant. Post-implant annealing was conducted within a tube furnace in a N_2 ambient at 550 °C for times ranging from 5 to 260 min. Amorphous layer thickness measurements were performed on a variable angle multiwavelength ellipsometer (VASE), at angles ranging from 65° to 75°. XTEM was used to verify the VASE measurements. Secondary ion mass spectroscopy profiles were obtained using an O_2^+ beam with a net impact energy of 600 eV and beam current of 180 nA.

The relatively thick (1800 Å) amorphous layer increased the time required for solid-phase epitaxial regrowth (SPER) to conclude, allowing a detailed analysis of the boron diffusion characteristics within amorphous silicon to be conducted. Two types of samples were studied. One sample was implanted with boron alone and the second with boron and fluorine. XTEM analysis revealed that the regrowth velocity increases when the amorphous-crystalline interface reaches the boron profile, at $10^{17}–10^{18}$ atoms/cm^3, for the sample containing boron alone. The interface is observed to slow down when it reaches the fluorine profile, at $10^{17}–10^{18}$ atoms/cm^3, for the sample containing both boron and fluorine. These data are consistent with previous studies where boron was shown to increase the silicon regrowth rate, while fluorine was shown to decrease it.[6–8] Based upon our results, it is clear that SPER at 550 °C ends shortly after the interface reaches the boron profile, after 30 min of annealing for the sample implanted with boron alone and after 130 min for fluorine coimplanted with boron. Thus, any boron motion exhibited within the first 30 min of annealing, in both the
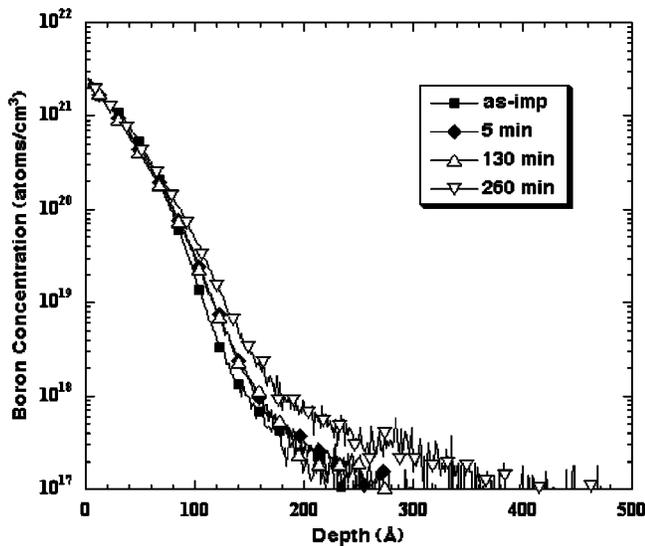
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FIG. 1. Boron concentration profile as a function of annealing time, in the absence of fluorine, at 550 °C.

FIG. 3. Fluorine concentration profiles as a function of annealing time at 550 °C.

presence and absence of fluorine, will be indicative of diffusion within amorphous silicon.

Boron concentration versus depth is shown within Fig. 1 for samples containing boron alone. It is evident that no significant boron diffusion occurs within the first 130 min of annealing, as the curves virtually superimpose. At a concentration of 2×10^{19} atoms/cm^3, the as-implanted and annealed boron depth is approximately 105 Å. Figure 2 shows the boron profiles when the boron-implanted sample is coimplanted with fluorine. As seen here, boron undergoes appreciable diffusion within the first 30 min of annealing in the presence of fluorine. These results indicate that the boron diffusivity is significantly enhanced in amorphous silicon in the presence of fluorine. At a concentration of 2×10^{19} atoms/cm^3, the boron junction depth increases by almost 40% after 30 min of annealing. The fluorine enhanced boron diffusion within amorphous silicon appears to have stopped after approximately 45 min of annealing. This corresponds to the time interval whereupon the dopants still
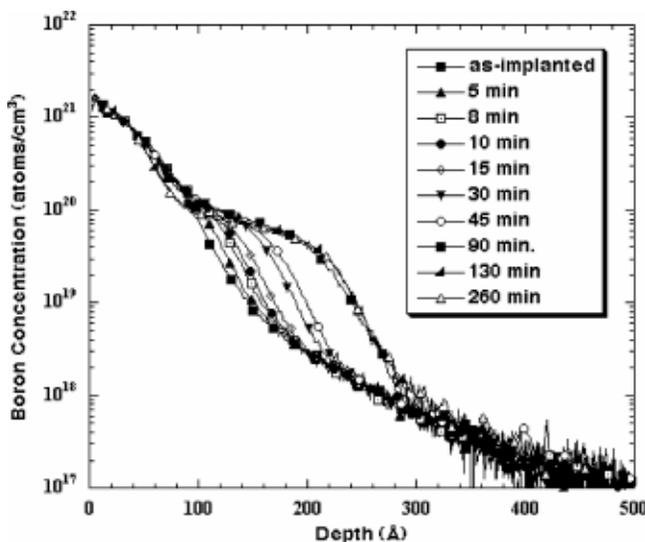
reside within amorphous silicon. Throughout the annealing process, the fluorine remains concentrated over the boron profile, as shown within Fig. 3. Thus, the fluorine induced diffusion enhancement occurs only in amorphous silicon and not crystalline silicon.

In Fig. 4, the boron junction shift versus annealing time at 550 °C is plotted for concentrations of 2×10^{18} atoms/cm^3 and 2×10^{19} atoms/cm^3. No appreciable motion was exhibited for the sample implanted with boron alone during SPER. However, the boron-implanted sample coimplanted with fluorine displayed significant dopant motion during SPER. Within the first 30 min of annealing, the boron junction shifted 50 Å at 2×10^{19} atoms/cm^3. Clearly, fluorine significantly enhances the diffusion of boron within amorphous silicon. This diffusion enhancement appears to subside once the amorphous-crystalline interface reaches the boron profile.

Over the years, the relationship between fluorine and silicon has been explored. It has been proposed that signifi-

FIG. 2. Boron concentration profile as a function of annealing time, in the presence of fluorine, at 550 °C.

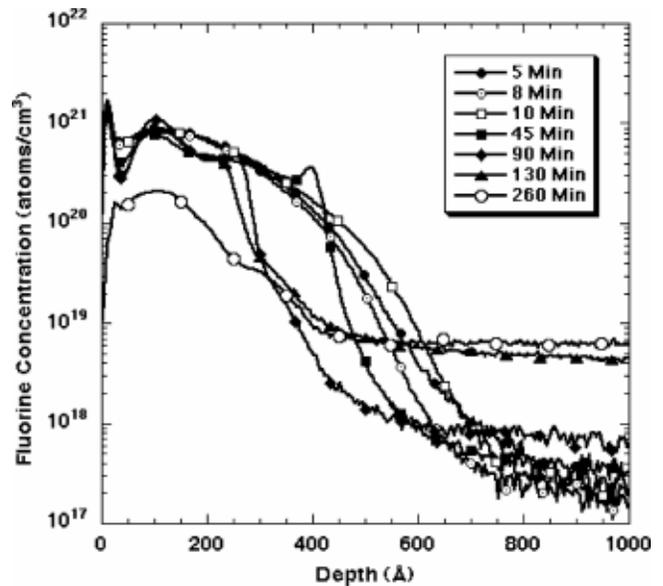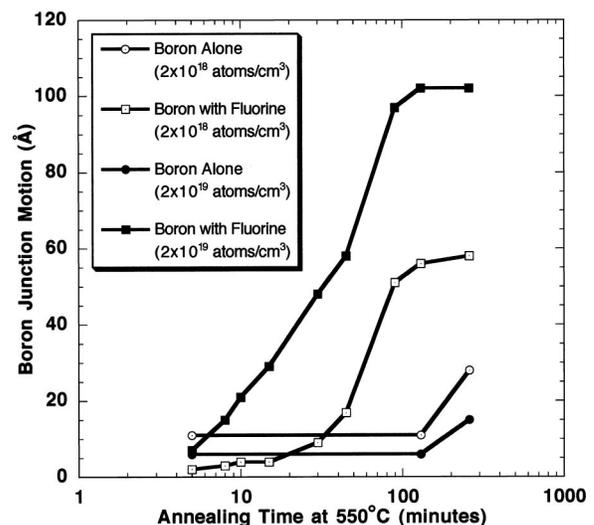FIG. 4. Boron dopant motion as a function of annealing time at 550 °C.

cant interaction occurs between dangling silicon bonds and fluorine atoms, whereby fluorine effectively ties up these dangling bonds.[9–11] The F–Si diatomic bond strength of 132 kcal/mol at 298 K is greater than the Si–Si (78.1 kcal/mol) or Si–B (68.9 kcal/mol) bonds.[12] The significant differences between these bond energies suggest that dangling bonds in amorphous silicon would preferentially bond with fluorine. It is proposed that by reducing the number of probable interactions between dangling silicon bonds and boron atoms, the fluorine can effectively increase the diffusivity of boron within amorphous silicon. This is accomplished as the fluorine decreases the dangling bond concentration, thereby greatly reducing the formation energy required for boron diffusion. Based upon a half Gaussian redistribution of boron at a concentration of 3×10^{19} atoms/cm^3, the boron diffusivity within amorphous silicon at 550 °C in the presence of fluorine is approximately 3×10^{-17} cm^2/s. This calculated diffusivity is more than five orders of magnitude larger than the extrapolated equilibrium diffusivity of boron in crystalline silicon of 2.7×10^{-22} cm^2/s.[13] These results imply that diffusion in the amorphous layer during SPER may contribute to a significant fraction of the total diffusion of the boron after RTA.

Based upon this study, we conclude that fluorine significantly increases boron diffusivity within amorphous silicon. It is proposed that fluorine enhances boron diffusion through the passivation of dangling bonds in amorphous silicon, thereby reducing the formation energy for mobile boron.

This inherent enhancement subsides once SPER is completed, whereupon fluorine has been previously shown to retard subsequent boron diffusion within crystalline silicon.[2–4] Fluorine drastically increases the boron diffusivity by five orders of magnitude at 550 °C, relative to expected boron diffusivity in crystalline silicon.

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