Anomalous diffusion of fluorine in silicon

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The diffusion of ion implanted F in Si has been studied by the use of secondary ion mass spectroscopy and thermal desorption spectroscopy. In the dose range studied (below amorphization threshold), F exhibits an anomalous out-diffusion behavior which is characterized by the depletion of F in Si substrate at temperatures \( \geq 550 \, ^\circ \text{C} \) with complete suppression of diffusion deeper into the bulk of Si. F species which migrate to the surface react with native oxide and Si to form volatile Si oxyfluoride and Si fluoride, which then evaporate from the surface. There is clear evidence that the formation of Si oxyfluoride correlates strongly with the thermally activated anomalous migration of F. While the driving force for the anomalous F migration has not yet been identified, it appears that the electric field is not a dominant mechanism.

It is known that the incorporation of fluorine in a metal-oxide-semiconductor (MOS) structure improves its radiation hardness and lowers its interface degradation due to hot electron effects. On the other hand, the incorporation of F into polycrystalline Si gate during chemical vapor deposition of W using WF₆ may be undesirable. In order to better understand and control the location and amount of F, the diffusion of F in Si is investigated in this work. While a theoretical calculation suggests that F atom may diffuse as \( \text{F}^- \) through interstitial channels in a perfect Si crystal, experimental studies involving ion implantation with high doses of F indicate that the redistribution of F in Si is strongly influenced by the magnitude and distribution of damage that remains after annealing; F tends to be gettered in regions of residual damage. In the case where high doses of F cause the formation of an amorphous layer, it has been reported that F can be depleted from Si at high temperatures, which has been attributed to the recrystallization of the amorphous layer rejecting F atom from the Si lattice. In this work we investigated the diffusion of F in Si using low energy and low dose F implantation (below amorphization threshold, \( \sim 10^{15} / \text{cm}^2 \)) so as not to introduce too much damage. In addition to secondary ion mass spectroscopy (SIMS), we also used thermal desorption spectroscopy (TDS) to study the volatile surface species during annealing.

Single-crystal \( p \)-type (boron-doped) Si (100) wafers with a resistivity of 0.8–2 \( \Omega \cdot \text{cm} \) were mainly used in this study, although additional \( n \)-type (phosphorous-doped, 0.8–2 \( \Omega \cdot \text{cm} \)) and \( n^- \)-type (arsenic-doped, \( \leq 0.002 \) \( \Omega \cdot \text{cm} \)) Si (100) wafers were also used to evaluate the dopant effect. Wafers were cleaned by the standard RCA process, and a thin oxide layer (10–20 \( \text{Å} \)) exists on the surface after cleaning. Subsequent F⁺ implantation was carried out at an energy of 30 keV and a dose of either \( 1 \times 10^{12} \) or \( 1 \times 10^{13} / \text{cm}^2 \). After implantation, isochronal annealing was performed in pure He ambient at temperatures between 300 and 1050 \( ^\circ \text{C} \) for 30 min. Helium gas was purified in a titanium getter furnace at 850 \( ^\circ \text{C} \) before entering the annealing furnace. The SIMS measurement was carried out with a CAMECA IMS-4f ion microanalyzer using a cesium primary beam; the depth calibration was done by measuring the sputtered crater with a profilometer. The desorption experiment was carried out in an ultrahigh vacuum chamber (base pressure of \( 2 \times 10^{-10} \) Torr) with a Dycor quadrupole mass spectrometer.

Figure 1 shows the redistribution of fluorine atom after isochronal annealing at elevated temperatures in Si implanted with \( 1 \times 10^{13} / \text{cm}^2 \) of F⁺. Unlike previous studies involving high doses of F, no multiple peaks are observed in the SIMS profiles, indicating that F atoms are not trapped at any specific defect sites. Strikingly, however, in contrast to normal diffusion, F atoms migrate preferentially towards the surface of Si, and the diffusion of F into bulk silicon is completely suppressed. Such an anomalous diffusion phenomenon has never been observed for other impurities in Si. Moreover, there appears to be a critical temperature for the redistribution of F to occur. At temperatures below (or equal to) 500 \( ^\circ \text{C} \), virtually no movement of F is detected by SIMS profiling, but the migration of F starts abruptly at a temperature \( \sim 550 \, ^\circ \text{C} \). This critical temperature can be seen more clearly in Fig. 2, where the amounts of F retained inside Si are displayed for two different doses of F⁺ (\( 1 \times 10^{12} \) and \( 1 \times 10^{13} / \text{cm}^2 \)). The F content, as obtained by integrating the area under SIMS profiles, decreases rapidly at higher temperatures. The fact that the migration of F only occurs at a temperature above 550 \( ^\circ \text{C} \) suggests a strongly temperature-dependent thermally activated process. Since the out-diffusion of F may involve several steps, and the time required to reach steady state may be varied at different temperatures, the straight
FIG. 1. SIMS concentration profile of F in Si(100) implanted with $1 \times 10^{13}$/cm$^2$ of F$^+$ and annealed for 30 min at the temperatures shown.

lines in Fig. 2 are merely a guide to the eyes. However, the steeper slope for the sample with a higher dose suggests that the out-diffusion process occurs faster in Si with a higher F concentration.

In order to elucidate the associated chemical reactions, the volatile species are measured in situ during annealing by the use of thermal desorption spectroscopy (TDS). A typical desorption spectrum is shown in Fig. 3(a). Based upon mass-charge ratio and isotopic finger prints, two peaks at 63 and 85 (amu) in TDS are identified as SiF$_3^+$ and SiOF$^+$, respectively. The SiF$_3^+$ peak is probably due to the desorption of SiF$_4$ as commonly found in the etching reaction between atomic F and Si$^*$. Although there is no reported cracking pattern from a parent molecule which includes SiOF$^+$, it is likely to be a fragment of SiOF$_2$ moiety after electron impact. The detection of SiOF$^+$ peak is indicative of chemical reactions between the surface SiO$_2$ layer and F atoms which migrate from the bulk. The formation of SiF$_4$ may be either due to direct reaction of F with Si or through replacing bridging oxygen in SiO$_2$ by F.

The intensities of SiF$_3^+$ and SiOF$^+$ signals from a sample implanted with $1 \times 10^{13}$/cm$^2$ of F$^+$ are shown as a function of time at several elevated temperatures in Fig. 3(b). At temperatures below 500 °C, no SiOF$^+$ and SiF$_3^+$ signals can be detected, suggesting a negligible amount of F leaving the surface. The intensity of SiOF$^+$ begins to increase at 550 °C, in agreement with the critical temperature for the onset of F migration. The gradual increase in the intensity of SiOF$^+$ is also consistent with the time required for the diffusion of F to the surface. When the temperature is raised further to 600 °C, the intensity of SiOF$^+$ increases drastically, and finally reaches a steady state after ~40 min of annealing. Such a correlation between the SiOF$^+$ signal and the amount of F retained in Si strongly suggests that the volatile Si oxyfluoride is the dominant pathway for the desorption of F. In contrast to the drastic change in the SiOF$^+$ signal with temperature, the change in the SiF$_3^+$ intensity is relatively small, suggesting its weaker connection with the thermally activated anomalous migration of F.

The eventual desorption of fluorine may involve five steps: (1) bulk transportation of F to the near-surface re-
region, (2) adsorption of F at available surface (or interface) sites, (3) surface (or interface) migration of F, (4) reaction of F with SiO₂ and/or Si to form SiOF₂ and SiF₄, and (5) desorption of F containing moieties from the surface. For a dilute system as in this case (1 X 10¹² and 1 X 10¹³/cm² of F are equivalent to total coverages of ~0.001 and 0.01 monolayers), the probability for a Si atom to attract one F atom is roughly proportional to the concentration of F containing moieties in the vicinity. Since the formation of SiOF₂ requires two F atoms while SiF₄ requires four, the former should have a substantially higher rate of formation, if one considers the reaction probability alone. This may explain why we observe stronger Si oxyfluoride signals, even though SiF₄ has a larger heat of formation than SiOF₂. By the same token, the out-diffusion process is expected to occur faster in Si with a higher F concentration as shown in Fig. 2, because of the increased reaction probability due to a larger amount of available F. The nature of the adsorption sites may also play an important role in the formation of volatile species. The interface between SiO₂ and Si is known to act as a favorable sink for F;¹² the concentration of F may accumulate in that region and enhance the reactions. Because of its large electronegativity, F tends to exist as F⁻ in Si.³ It is known that the etching reaction between Si and F depends strongly upon the concentration and type of dopant, which has been attributed to electric field effects.⁴ To investigate the possibility whether a similar mechanism might be responsible for the directionality of F diffusion, we studied a number of Si substrates with different dopant types (i.e., n, n⁺, and p). Despite their wide range of Debye lengths, SIMS measurements on all three substrates yield exactly the same F concentration profile after annealing, indicating that dopant in Si has no influence on the migration of F. The high concentration of intrinsic carriers at temperatures above 550 °C should quite effectively screen the Coulombic interactions between the surface and the F⁺ atoms inside Si. While the driving force for the anomalous migration of F in Si remains elusive, the possibility due to electric field effect can probably be ruled out.

In summary, although theoretical studies indicate that F diffusion involves normal interstitial motion in the perfect Si crystal, we find anomalous diffusion which results in depletion of F from Si at >550 °C with complete suppression of diffusion deeper into the bulk of Si substrate. Since the migration of F only occurs at temperatures above 550 °C, it suggests a strongly temperature dependent thermally activated process. Direct observation of volatile Si oxyfluoride and Si fluoride moieties shows clearly for the first time that the chemical reactions between F and SiO₂ (and/or Si) precede the desorption of F from Si. While the driving force for the observed anomalous F migration remains unknown, it appears that the possibility of electric field effect can be ruled out.

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⁶Since the SIMS detection limit for F is about 1 X 10¹⁰ atoms/cm³, the concentration depth profiles are terminated at 0.25 μm. In addition, the F⁺ surface signal depends on the surface oxide and contamination levels, thereby providing little useful information, so this region is omitted from Fig. 1. As demonstrated later (Fig. 3), F which migrates to the surface in fact leaves the sample as a volatile product.
⁷Silicon has three isotopes: 28 (92.3%), 29 (4.7%), and 30 (3%). Oxygen also has three isotopes, but ¹⁶O dominates (99.8%). Fluorine has only one isotope ¹⁹F.