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Atomic configuration study of implanted F in Si based on experimental evidences and ab initio calculations

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Abstract

The effects of F on B diffusion and activation in Si were investigated through experiments and ab initio calculations. It was found that F atoms captured by vacancy type defects originating from ion implantation form two stable F–V configurations, while the F atoms remaining in Si affect B activation by forming stable F–B complex. During the initial stage of annealing, B diffusion in highly F-doped regions is suppressed significantly due to the recombination of generated self-interstitials with F atoms, resulting in a decrease in self-interstitial concentration.

Keywords: Diffusion; Ion implantation; Secondary ion mass spectrometry; Boron; Silicon; Doping and impurity implantation

1. Introduction

BF_2^+ ion implantation yields shallower junction depth than B^+ ion implantation when implanted into single-crystal Si at the same effective energy [1–3]. There are, however, serious concerns that F, when split from BF_2^+ ions, influences electronic characteristics and dopant diffusion.

In this work, the microscopic physical mechanisms responsible for the experimentally observed phenomena are elucidated by investigating the kinetics of F in Si through experiments and ab initio calculations.

This paper is organized as follows: the experimental and calculation methods are described in Sections 2 and 3, respectively; the results and discussion are presented in Section 4, and we conclude the paper in Section 5.

2. Experimental method

Flow charts of the experimental procedures employed in this study are schematically illustrated in Fig. 1.

2.1. F diffusion in crystalline and re-crystallized Si

Amorphous Si wafers formed by Si^+ ion implantation at 150 keV and 1×10^{15} cm^{-2} were annealed at 820 °C for 3 min to form re-crystallized Si wafers, followed by F atom implantation into both crystalline and re-crystallized Si.

2.2. Effect of F on B diffusion and activation

B^+ ions were implanted at 2 keV and 1×10^{15} cm^{-2} into an amorphous Si layer formed by Si^+ ion implantation at 150 keV and 1×10^{15} cm^{-2}. F^+ ions were

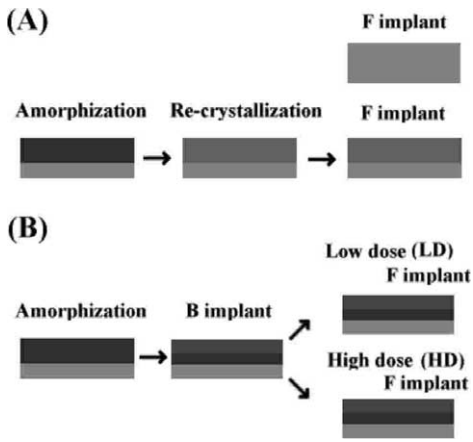

Fig. 1. Schematic illustration of the experimental flow chart.

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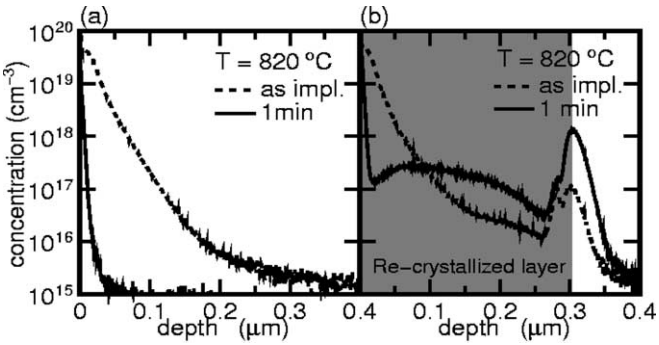

Fig. 2. Effect of F on implantation damage. SIMS profiles of (a) single-crystal Si and (b) recrystallized Si (shaded region) implanted with F^+ at 5 keV and 1×10^{15} cm^{-2} and annealed at 820 °C for 1 min in N_2.

then implanted at 5 keV and 2×10^{13} cm^{-2} (low dose: LD) or 2×10^{15} cm^{-2} (high dose: HD).

2.3. F–B model verification

F^+ ions were implanted into B-doped superlattice (BDSL) at 100keV and 1×10^{14} cm^{-2}.

After ion implantation, these samples were annealed in dry N_2 ambient in a furnace at 720–820 °C for 1–30 min. Depth profiles of the implanted ions were measured using secondary ion mass spectrometry (SIMS). B activation profiles were measured by the spreading resistance (SR) technique.

3. Calculation method

We investigated the kinetics of F atoms in Si by ab initio calculation based on a generalized gradient approximation [4,5]. We used an efficient plane-wave ultrasoft pseudopotential code for Si lattice constant of 0.54 nm. Cutoff of the calculated kinetic-energy of electron wave functions in 64-atom supercells was 150 eV. $2 \times 2 \times 2$ Monkhorst–Pack k-point sampling was used.

Total energy calculations reveal that interstitial F is more stable than substitutional F by about 0.94 eV, indicating that F atoms occupy interstitial sites.

4. Results and discussion

4.1. F–V experiment and calculation

Fig. 2 shows the depth profiles of the as-implanted F before and after annealing for 1 min at 820 °C for experiment (A). Most of the F atoms implanted into crystalline Si rapidly diffuse out of the lattice during annealing (Fig. 2(a)). However, those F atoms implanted into the re-crystallized region remain in the end-of-range (EOR) defects [6,7] and in the re-crystallized region as well (Fig. 2(b)).

A previous positron annihilation experiment [8,9] revealed that vacancy type defects exist in the re-crystallized Si layer. These vacancy type defects in the re-crystallized layer capture implanted F atoms and suppress F diffusion, as shown in Fig. 2(b).

To verify the above assumption, we carried out the following ab initio calculations. An F atom was placed near point V in the center of the supercell for several initial configurations. The F atom moving around V is negatively charged as shown in the charge density distribution (Fig. 3(a)), and then is eventually captured by a Si dangling bond at a distance of 0.15 nm.

F and V converge into 2 stable configurations (Fig. 3(b) and (c)); a planar structure (b) and a three-dimensional structure (c). Note that the total energy of configuration (b) is 0.012 eV lower than that of (c), but this energy difference is negligibly small in the high temperature annealing process. The difference between these configurations originates from the initial atomic configurations of F and Si atoms around V. Starting F

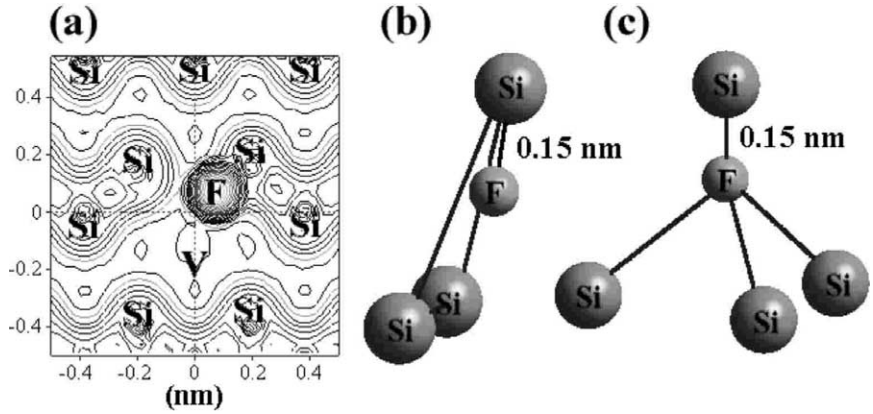

Fig. 3. (a) Charge density distribution near F–V complex and F–V structure in (b) stable planar F structure or (c) stable three-dimensional F structure.

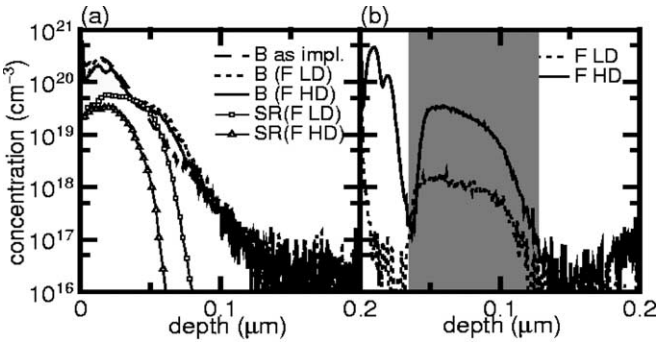

Fig. 4. Effect of F on B diffusion and activation. SIMS and SR profiles of (a) B at 2 keV and 1×10^{15} cm^{-2} and (b) F at 5 keV and 2×10^{13}–10^{15} cm^{-2} co-implanted into amorphous Si annealed at 820 °C for 30 min in N_2.

at a significant distance from V results in configuration (b), whereas initiating F in the vicinity of V results in configuration (c).

These calculation results support the idea that vacancy type defects in the re-crystallized region capture implanted F.

The interaction of F with larger vacancy clusters [10–12] was also investigated through ab-initio calculations in order to identify additional microscopic mechanisms.

4.2. F–B experiment and calculation

Fig. 4 shows the results for the experiment (B). Fig. 4(a) depicts the depth profile of the as-implanted B before annealing and the diffusion and activation profiles of B after annealing at 820 °C for 30 min. Fig. 4(b) shows the diffusion profile of co-implanted F. It should be noted that B diffusion and activation were suppressed significantly in the tail region with increasing F dose. The number of F atoms captured in the shaded region in Fig. 4(b) also increased with the F implantation doses. This result suggests that F remaining in the shaded region interacts with B, resulting in electrical deactivation of B. Based on these experimental results, it is plausible that the formation of either F–V or F–B suppresses B activation and diffusion as well.

In order to clarify this proposal, we calculated the total energy in the system of F and B atoms incorporated into Si lattice. In the calculation, a B atom was placed at the center of the supercell, and F was initiated near the B in several initial configurations. The calculations revealed that the F atom enters into a Si–B bond and pushes the substitutional B and Si out of the initial position, as shown in Fig. 5(b). In this configuration, F combines with a Si atom via a 0.15 nm bond and the three remaining Si–B bonds become 0.21 nm. The charge density distribution in Fig. 5(a) suggests that in the F–B structure, substitutional B is inactive because the F atom terminates a Si chemical bond.

4.3. Additional experiments and results

We performed a further experiment (C) to verify the validity of the model based on the above F–B experiments and calculation results.

Fig. 6 shows the results for experiment (C). Fig. 6(a) shows the depth profiles of B and F before annealing, and Fig. 6(b) shows those after annealing. During ion implantation F atoms migrate into the Si substrate and are captured at the 4th–6th B-doped layers, suggesting that the F–B structure shown in Fig. 5(b) is formed in the B-doped layers. However, after annealing, F atoms diffuse from all the B-doped layers and accumulate in the inter-layers (Fig. 6(b)). This result suggests that F atoms form pairs with I (self-intersititals) rather than with B during the transient stage in post-annealing, in which the substrate becomes supersaturated with self-interstitials.

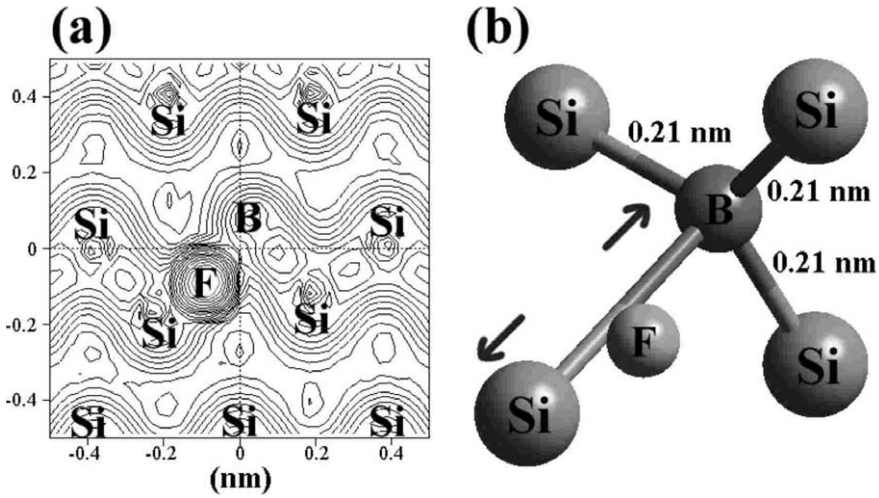

Fig. 5. (a) Charge density distribution near F–B complex and (b) stable F–B structure configuration.

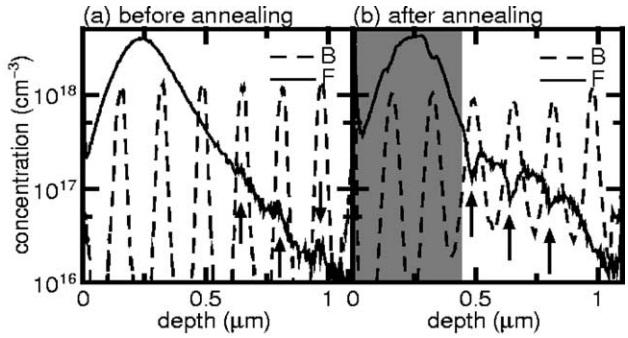

Fig. 6. F and B profiles of BDSL samples. F implanted at 100 keV and 3×10^{13} cm^{-2} (a) prior to annealing, and (b) after annealing at 820 °C for 1 min in N_2. B diffusion is strongly suppressed in the shaded region.

The experimental results show that the 1st and 2nd B-doped layers diffuse less than the other one as shown in Fig. 6(b). This can be explained by assuming that the diffusion constant of F is proportional to the free self-interstitial concentration and that there is a critical F concentration that suppresses B diffusion (1×10^{18} cm^{-2}), above which self-interstitials generated in ion implantation are consumed by F atoms. The experimental results also demonstrated that F diffuses out of the B delta-doped region with I in the transient phase. This is attributed to the increase in the abundance of positively charged I^+ at the B-doped layers, resulting in the formation of FI^+ pairs according to the reaction

$$F + I^+ \leftrightarrow FI^+$$

The FI^+ pairs then diffuse out of the B-doped layers and decompose into F and I.

5. Conclusion

The kinetics of implanted F atoms in Si was studied in detail through experiments and ab initio calculations. The ab initio calculations revealed that implanted F atoms are captured by vacancy type defects resulting in F-vacancy pairs in two stable configurations of either two- or three-dimensional structures. It was also found that F atoms remaining in Si after thermal annealing affect the activation of B by forming the B–F complex. In the transient phase F was found to combine with self-interstitials, significantly suppressing B diffusion.

Acknowledgements

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