

The Chemical Bonding Features of Fluorine and Boron in BF_2^+ Ion Implanted Si

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The chemical bonding configurations of fluorine and boron atoms in BF_2^+ ion implanted Si network have been studied by using x-ray photoelectron spectroscopy, infrared absorption and Raman scattering measurements. It is found that fluorine atoms in as implanted Si are mainly bonded to boron. By annealing at 900°C , BF bonds are thermally decomposed in the matrix and boron atoms are incorporated as four-fold coordinated acceptors, while fluorine atoms form thermodynamically stable SiF_x bonds ($x=2,3$) which appear to be located in the remaining defects. It is also shown that in the Raman spectra of recrystallized Si the full width at half maximum of the TO mode peak at 520 cm^{-1} and the intensity of the Si-B local mode at 620 cm^{-1} are well correlated with the BF_2^+ ion dose and can be used for determining the hole concentration.

1. INTRODUCTION

The implantation of BF_2^+ molecular ions has become an important doping technique for fabricating a shallow P^+ region because of the short projected range and the small ion channeling tail compared to the case of B^+ ion implantation. It is also known that a high density of fluorine remains in the implanted matrix even after 1000°C annealing^{1,2)} and the incorporated fluorine is responsible for secondary defect generation at high temperature annealing³⁾. Recently, it is reported that fluorine preimplantation followed by BF_2^+ implantation enables to form a very shallow (800 Å) p^+ -n junction with a sheet resistance of $400\ \Omega$ and can be used for deep subquarter micron p-channel MOSFETs⁴⁾.

Despite of the potential of a BF_2^+ implantation technique, the chemical bonding configurations of fluorine in the Si matrix and the detailed boron activation process are not well understood.

In this paper, the chemical states of fluorine and boron and the boron activation process in BF_2^+ implanted layers have been systematically studied by x-ray photoelectron spectra of F_{1s} and Si_{2p} core levels, Fourier

transformed infrared absorption (FT-IR) and Raman scattering.

2. EXPERIMENTAL PROCEDURE

Bare p-type Si(100) ($\rho=1\sim 3\ \Omega\text{cm}$) wafers or those covered with thermally grown SiO_2 (250 Å thick) were used as substrates. BF_2^+ ion implantation was carried out with a wafer configuration of 7 degrees off from the incident beam direction to minimize the channeling effect. The acceleration voltage and dose were 130 keV with $1\times 10^{15} \sim 1\times 10^{16}\text{ ions/cm}^2$ and 60 keV with $1\times 10^{16}\text{ ions/cm}^2$ at room temperature. The samples were isothermally annealed in dry nitrogen at a temperature of 800 or 900°C in a quartz tube furnace. The chemical bonding state and in-depth profile of fluorine in as-implanted and annealed wafers were examined by observing x-ray photoelectron spectra of F_{1s} and Si_{2p} core levels excited with an $\text{MgK}\alpha$ (1253.6 eV) soft x-ray at each step of sputter ion-etching with 2 keV Ar^+ ions. The binding energy was calibrated by the core level signals of Si_{2p} from an Si substrate at 99.3 eV and SiO_2 at 103.6 eV. The in-depth profiles of boron was measured by secondary ion mass spectroscopy (SIMS). The fluorine

distribution profile obtained from XPS was cross-checked also by SIMS. For the purpose of evaluating the crystallinity of a thin BF_2^+ ion implanted layer and the boron activation process by annealing, the Raman spectrum was taken at room temperature in the perpendicular scattering configuration with P polarized light incident at a glancing angle of 4 degrees along the $\langle 010 \rangle$ direction. A 514.5 nm line from an Ar^+ laser was used as an excitation source.

3. RESULTS AND DISCUSSION

The in-depth profiles of fluorine and boron in SiO_2 covered wafers implanted with 60 keV BF_2^+ to a dose of 1×10^{16} ions/cm² are examined by SIMS. For an as-implanted sample, the fluorine distribution exhibits a broad peak at a depth of about 350 Å from the SiO_2/Si interface (Fig. 1 (a)). The annealing at 800 °C causes redistribution of fluorine and its pile-up in SiO_2 . A subsidiary peak appears at about 500 Å deep from the SiO_2/Si interface and the fluorine concentration in Si is also reduced. The location of this subsidiary peak corresponds to the interface between the amorphized layer and underlying crystalline network¹⁾ because during the annealing fluorine is trapped by residual defects and secondary defects such as microvoids which mainly exist in the interface region³⁾. The boron distribution for the as-implanted wafer is slightly broader than that of fluorine and the peak position is almost the same as fluorine (Fig. 1(b)). Figure 2 represents the result of in-depth XPS analysis for fluorine. The B_{1s} signal is not detectable by XPS because the x-ray ionization cross section is small by a factor of 1/8.66 with respect to that of F_{1s} photoelectron. As shown in Fig. 2 (a) for an as-implanted sample, the F_{1s} signal at a binding energy of ~ 687.5 eV for a sputtering time of 2 min arises from fluorine in SiO_2 . Near the SiO_2/Si interface (sputtering time = 4 min) the additional signal at ~ 685.5 eV appears and becomes predominant in the Si substrate. Considering the fact that the F_{1s}

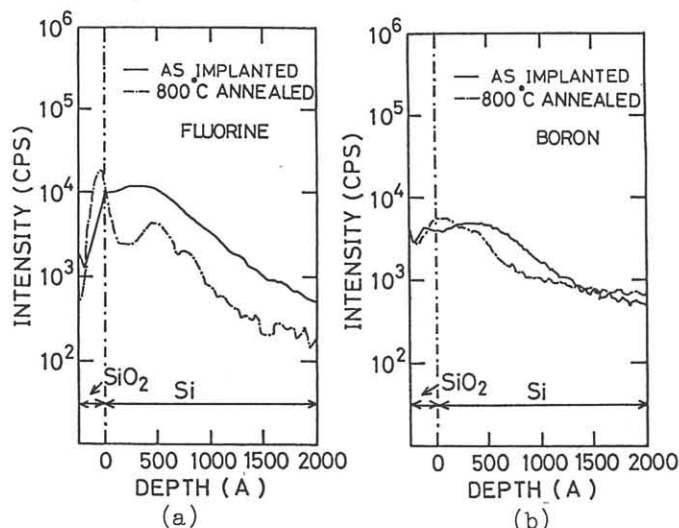


Fig. 1 In-depth SIMS profiles of fluorine (a) and boron (b) for as-implanted Si(100) with a dose of 1×10^{16} ions/cm² at 60 keV and an annealed wafer at 800°C for 5 min.

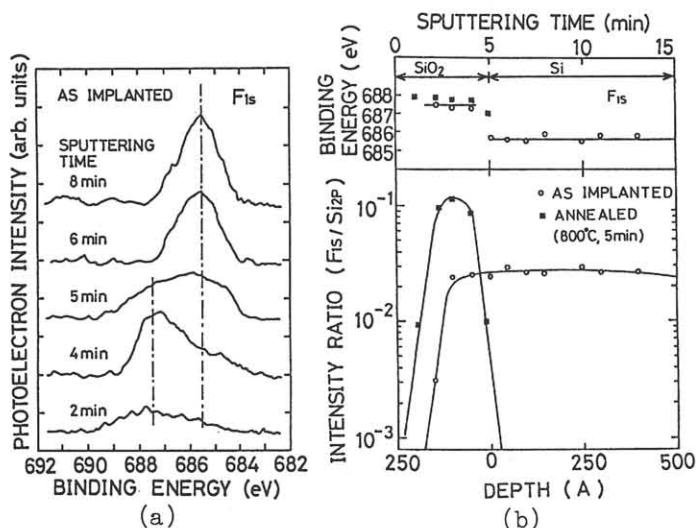


Fig. 2 F_{1s} XPS spectra at different sputtering times for an as-implanted sample (a) and in-depth profiles of integrated XPS intensity ratio of F_{1s} to Si_{2p} together with the F_{1s} binding energy in BF_2^+ implanted Si before and after annealing at 800°C for 5 min (b).

signal from fluorinated amorphous silicon (a-Si:F) in which fluorine atoms mostly form SiF bonds provides a 685.9 eV peak⁵⁾, the F_{1s} peak at ~ 685.5 eV observed in the as-implanted Si is apparently ascribable to SiF bonds. However, this might not be the case by the following reasons: The electronegativity of boron (2.04 in Pauling's scale) is close to that of silicon (1.90) and bond energy of BF (129 kcal/mol) is almost equal to that of SiF (132 kcal/mol)⁶⁾. Therefore,

the F_{1s} signal at ~ 685.5 eV could also be assigned as BF bonds. This is strongly supported by the result of FT-IR measurements as discussed later. The high energy shift of F_{1s} signal in SiO_2 (~ 687.5 eV) with respect to the F_{1s} signal in Si is explained by the presence of highly electronegative oxygen atoms at the second-nearest neighbor sites of fluorine atom in SiO_2 ⁷⁾. By annealing at 800°C for 5 min the fluorine content in Si becomes too small to detect, while in SiO_2 it is increased and the chemical shift remains unchanged (Fig. 2 (b)). The outdiffusion of fluorine by annealing and its pile-up in SiO_2 make it difficult to reveal the behavior of fluorine in Si by the use of XPS. In order to overcome this problem, BF_2^+ ions were deeply implanted to bare Si wafers by increasing the ion energy from 60 to 130 keV. The distribution of fluorine atoms in the implanted Si is rather broad and detectable even by annealing at 900°C for 30 min (Fig. 3). Note that in the region of 1400 Å deep from the surface only 40 % of the incorporated fluorine are lost by the 30 min annealing and the remaining fluorine density is still high (0.8 at. %). Fluorine pile-up at the surface is due to the presence of native oxide on the wafer. The F_{1s} binding energy is constant (~ 685.5 eV) in the direction of depth and exhibits a 2.0 eV chemical shift by annealing as shown in Fig. 3. This chemically shifted F_{1s} peak at ~ 687.5 eV could be assigned as SiF_2 and SiF_3 molecular units in Si because it is shown that the F_{2s} peak energy measured for fluorinated amorphous silicon⁵⁾ and the theoretical F_{2s} local density of states (LDOS) calculated by an orthogonalized linear combination of atomic orbitals (OLCAO) method⁸⁾ provide the F_{2s} binding energies for SiF_2 and SiF_3 bonds by respectively about 1.2 and 2.2 eV higher than that of SiF bonds. Since the energy difference between F_{1s} and F_{2s} signals is generally held constant, the observed 2.0 eV chemical shift of the F_{1s} signal by 900°C annealing indicates that fluorine atoms form thermodynamically stable SiF_2 and SiF_3

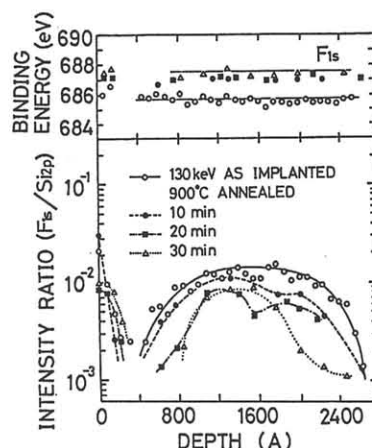


Fig. 3 In-depth profiles of integrated XPS intensity ratio of F_{1s} to Si_{2p} signal together with the F_{1s} binding energy in BF_2^+ implanted Si before and after annealing at 900°C .

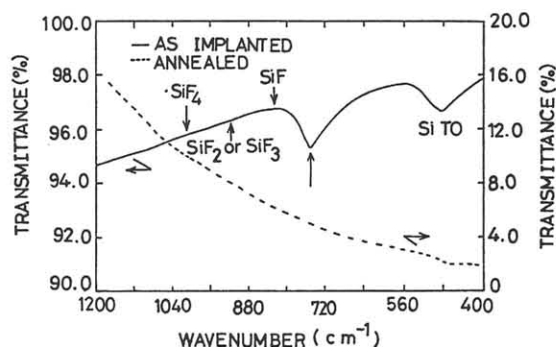


Fig. 4 Infrared absorption spectra for BF_2^+ implanted Si before and after annealing at 900°C for 10 min.

chemical bonds⁷⁾ through the thermal decomposition of BF bonds during annealing and they might be located in the residual lattice defects such as microvoids or dislocations existing in the amorphous/ crystalline network interface of as-implanted Si³⁾.

An FT-IR spectrum for as implanted Si shows no absorption bands due to SiF_x ($x = 1 \sim 4$)⁹⁾ which appear at $800 \sim 1100$ cm^{-1} as displayed in Fig. 4. This implies that as-implanted fluorine is bonded to boron probably through the recombination of B and F in the matrix. The absorption peak at 750 cm^{-1} is attributable to the stretching mode of BF molecular units partly connected to Si atoms. Also, in the figure the absorption observed at 480 cm^{-1} due to the TO phonon of Si network is forbidden in nonpolar Si, showing that a high density boron atoms and Si dangling bonds in the matrix induce the

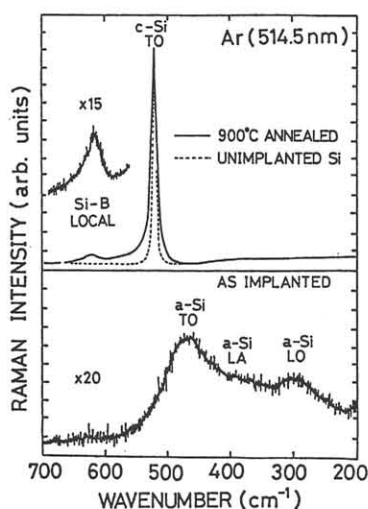


Fig. 5 Raman spectra for BF_2^+ implanted Si before and after annealing at 900°C for 10 min. The Raman spectrum of an unimplanted Si wafer is also indicated as a reference.

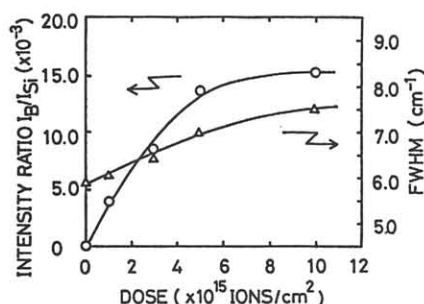


Fig. 6 Raman peak intensity ratio of Si-B local mode to c-Si TO mode and the full width at half maximum of c-Si TO mode for implanted samples after annealing at 900°C for 10 min as a function of the total dose in BF_2^+ implantation.

polar nature of Si-Si bonds¹⁰). The FT-IR spectrum after annealing at 900°C for 10 min exhibits strong free hole absorption and no observable features due to the vibrational mode.

The Raman spectra were used for the probe of crystallinity of the implanted Si layer. The amorphized silicon layer is completely recrystallized by annealing at 900°C for 10 min (Fig. 5). Also, implanted boron atoms are incorporated at the four-fold coordinated sites through recrystallization process, and hence the local mode due to four-fold coordinated boron¹¹) appears at 620 cm^{-1} . Note that the spectral width of the TO mode for the recrystallized Si becomes broader than that for an unimplanted p-Si(100) substrate ($N_A \approx 10^{16}\text{ cm}^{-3}$). This is not due

to the broadening by lattice defects, but due to the interference effect between high density excited holes and TO phonon¹¹), in consistence with the resistivity measurements. The intensity ratio of the Si-B local mode to the c-Si TO mode as well as the full width at half maximum of the c-Si TO mode monotonically increase with the total dose ranging from $1 \times 10^{15}\text{ BF}_2^+/\text{cm}^2$ to $1 \times 10^{16}\text{ BF}_2^+/\text{cm}^2$ (Fig. 6). The result of Fig. 6 is practically useful for the optical detection of the hole concentration without removing the protective oxide layer.

4. CONCLUSIONS

It is shown for the first time that fluorine atoms in as-implanted Si with a dose of $1 \times 10^{16}\text{ BF}_2^+ \text{ ions/cm}^2$ are mostly bonded to boron and changed to SiF_x ($x=2,3$) by annealing. Annealing of BF_2^+ implanted Si results in the broadening of the TO mode in the Raman spectra and the appearance of the Si-B local mode at 620 cm^{-1} , both of which can be used for a noncontacting measurement of activated hole concentration.

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