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 annealing$^{3}$. Recently, it is reported that fluorine pre-implantation followed by BF$_2^+$ implantation enables to form a very shallow (800 Å) p$^+$-n junction with a sheet resistance of 400 Ω and can be used for deep subquarter micron p-channel MOSFETs$^4$.

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) (ρ=1~3×10$^{15}$) 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 1×10$^{15}$ ~ 1×10$^{16}$ ions/cm$^2$ and 60 keV with 1×10$^{16}$ 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 MgKα (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$_{2p}$ form 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 (010) 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 $1 \times 10^{16}$ ions/cm$^2$ are examined by SIMS. For an as-implanted sample, the fluorine distribution exhibits a broad peak at a depth of about 350 A 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 A 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 network$^1$ because during the annealing fluorine is trapped by residual defects and secondary defects such as microvoids which mainly exist in the interface region$^2$. 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 $F_{1s}$ signal from fluorinated amorphous silicon (a-SiF) in which fluorine atoms mostly form SiF bonds provides a 685.9 eV peak$^5$, 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 (1.9) and bond energy of BF (129 kcal/mol) is almost equal to that of SiF (132 kcal/mol)$^6$. Therefore,
the F\textsubscript{18} signal at \( \approx 685.5 \text{ eV} \) 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\textsubscript{18} signal in SiO\textsubscript{2} (\( \approx 687.5 \text{ eV} \)) with respect to the F\textsubscript{18} signal in Si is explained by the presence of highly electronegative oxygen atoms at the second-nearest neighbor sites of fluorine atom in SiO\textsubscript{2}\textsuperscript{(7)}. By annealing at 800°C for 5 min the fluorine content in Si becomes too small to detect, while in SiO\textsubscript{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\textsubscript{2} make it difficult to reveal the behavior of fluorine in Si by the use of XPS. In order to overcome this problem, BF\textsubscript{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 only 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\textsubscript{18} binding energy is constant (\( \approx 685.5 \text{ eV} \)) in the direction of depth and exhibits a 2.0 eV chemical shift by annealing as shown in Fig. 3. This chemically shifted F\textsubscript{18} peak at \( \approx 687.5 \text{ eV} \) could be assigned as SiF\textsubscript{2} and SiF\textsubscript{3} molecular units in Si because it is shown that the F\textsubscript{28} peak energy measured for fluorinated amorphous silicon\textsuperscript{(5)} and the theoretical F\textsubscript{28} local density of states (LDOS) calculated by an orthogonalized linear combination of atomic orbitals (OLCAO) method\textsuperscript{(8)} provide the F\textsubscript{28} binding energies for SiF\textsubscript{2} and SiF\textsubscript{3} bonds by respectively about 1.2 and 2.2 eV higher than that of SiF bonds. Since the energy difference between F\textsubscript{18} and F\textsubscript{28} signals is generally held constant, the observed 2.0 eV chemical shift of the F\textsubscript{18} signal by 900 °C annealing indicates that fluorine atoms form thermodynamically stable SiF\textsubscript{2} and SiF\textsubscript{3} chemical bonds\textsuperscript{(7)} 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 Si\textsuperscript{(3)}.

An FT-IR spectrum for as implanted Si shows no absorption bands due to SiF\textsubscript{x} (\( x = 1 \sim 4 \))\textsuperscript{(9)} which appear at 800\textsuperscript{-1}1000 cm\textsuperscript{-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\textsuperscript{-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\textsuperscript{-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
polar nature of Si–Si bonds). 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 boron appears at 620 cm⁻¹. Note that the spectral width of the T0 mode for the recrystallized Si becomes broader than that for an unimplanted p-Si(100) substrate (N_A = 10¹⁶ cm⁻²). This is not due to the broadening by lattice defects, but due to the interference effect between high density excited holes and T0 phonon, in consistence with the resistivity measurements. The intensity ratio of the Si–B local mode to the c-Si T0 mode as well as the full width at half maximum of the c-Si T0 mode monotonically increase with the total dose ranging from 1x10¹⁵ BF²⁺/cm² to 1x10¹⁶ BF²⁺/cm² (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 1x10¹⁶ BF²⁺ ions/cm² are mostly bonded to boron and changed to SiFₓ (x=2,3) by annealing. Annealing of BF²⁺ implanted Si results in the broadening of the T0 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.

REFERENCES