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Contribution of Carbon to Growth of Boron-Containing Cluster in Heavily B-doped Silicon

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Introduction

Carbon (C) incorporation into silicon (Si) has become essential in current high-performance complementary metal-oxide-semiconductor field-effect transistors (CMOSFETs) technology. The reason is that C atoms are markedly useful in controlling diffusion of dopant atoms in Si. Substitutional C atoms can capture excess self-interstitial Si atoms and suppress the diffusion of ion-implanted intersitial-type dopants such as Boron (B) in Si.[1,2] Recently, it was reported that the B activation ratio varies depending on incorporated C content in B^+ implanted Si:C layers.[3] In the B concentrations higher than ~$1x10^{21}cm^{-3}$, the B activation ratio in Si is decreased with C incorporation. Thus, many studies on stable B-containing clusters and precipitates in heavily doped Si with C additive have so far been conducted. However, the impact of the C incorporation on activation and clustering of B atoms in Si is still a matter of research.

In this work, we focused on chemical bonding features of B and C atoms in heavily B-doped Si with different C contents after high-temperature annealing by using high-resolution x-ray photoelectron spectroscopy (XPS).

Experimental Procedure

A blanket $Si_{1-y}:C_y$ (y: 0-0.0063) film with a thickness of 100nm was grown epitaxially on a n-type Si (100) substrate with a resistivity of 1~2ohm-cm using residual pressure chemical vapor deposition below 600 ˚C in a gas mixture of silane and dilute methylsilane diluted with hydrogen. To study the diffusion and activation of B in the $Si_{1-y}:C_y$ film, B ions were implanted at an acceleration energy of 2.5keV with a fluence of $3x10^{15}cm^{-2}$ into the $Si_{1-y}:C_y$ layer. Then, conventional spike annealing was performed at 1050˚C for 1.5s residence time at a preheating temperature below 650˚C in nitrogen.

The B profiles of $Si_{1-y}:C_y$ were measured by secondary-ion mass spectroscopy (SIMS) with Cs^+ as the primary ion. The electrical properties of B^+ implanted $Si_{1-y}:C_y$ layer were evaluated by Hall measurement with a Van der Pauw method. To characterize the chemical bonding features of B in heavily B-doped $Si_{1-y}:C_y$ layer, the photoemission spectra from B1s and Si2p were measured by utilizing monochromatized AlKα radiation (1486.6eV: XPS). The chemical bonding features of C in heavily B-doped $Si_{1-y}:C_y$ layer was characterized by measuring core-line C1s spectrum excited by synchrotron radiation (7939eV: HA-XPS) at a beam line of BL47XU in SPring-8.

Results and Discussion

The depth profiles of B in the $Si_{1-y}:C_y$ layers with a B-fluence of $3x10^{15}cm^{-2}$ after spike annealing at 1050˚C are shown in Fig. 1. Obviously, the B diffusion was suppressed with increasing C content in Si. This suppression of the B diffusion suggests that C atoms interact with Si interstitials. Notice that no marked change in the B profile near B peak concentration was observable. Considering the fact that stable B-containing clusters and precipitates are easily formed at higher B concentrations by high-temperature annealing[4] such as spike annealing at 1050˚C, it is likely that the suppression of intrinsic B diffusion and an increase in B peak concentration are not simply interpreted in terms of C incorporation into Si.

In addition, the C incorporation shows a marked impact on the B activation as seen in Fig. 2, where the dependences of the sheet carrier concentration (N_s) measured by Hall measurements, and of the total B dose measured by SIMS on the C content are represented. The total B dose was decreased as compared with the implanted B dose, due to outward diffusion. With an increase in C content, the N_s of the B activated region in $Si_{1-y}:C_y$ decreased slightly, while the total B dose was independent on the C content. An approximately 24% N_s decrease was observed in the B activation layer in $Si_{0.9937}:C_{0.0063}$ in comparison to heavy B-doping in Si. This implies that the formation of electrically inactive B-containing clusters is enhanced by C incorporation.

To investigate the impact of C atoms on the formation of B-containing clusters, the chemical bonding features of B atoms in C-incorporated Si layer, where the B concentration has its maximum, were characterized by XPS. Figure 3 shows B1s spectrum for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layer with a B-fluence of $3x10^{15}cm^{-2}$ after 1050˚C spike annealing, which was taken at a photoelectron take-off angle of 90˚ after removal of the surface layer with a thickness of about 10 nm by a repetition of wet-chemical oxidation and diluted HF etching in order to characterize the region with a B concentration over ~$1x10^{21}cm^{-3}$. From the spectral deconvolution after subtracting a broad Si plasmon spectrum from the measured spectrum, 4 different B-bonding states were resolved. The components peaked at 187.3, 188.0, and 192.0eV are due to the three-folded, four-folded, and oxidized B in Si, respectively.[4-6] The strongest component peaked at 188.6 eV is attributed to clustered B.[4-6] For B^+ implanted samples with various C contents the B1s signals were deconvoluted, as shown in Figs. 4(a) and (b). Each spectrum was normalized with $Si2p^{0+}3/2$ peak at 99.04eV. The amount of the clustered B markedly increased with increasing C content. An increase in the clustered B amount by approximately 84% was observed in the heavily B-doped layer in $Si_{0.9937}:C_{0.0063}$ compared with that in pure Si. At the same time, the amount of the three-folded B slightly decreased with increasing C content. In the heavily B-doped layer of $Si_{0.9937}:C_{0.0063}$, the three-folded B was decreased by ~46% in comparison to the heavy B-doping in Si. It is also found that C incorporation enhances the formation of B-containing clusters in the region with a B concentration higher than ~$1x10^{21}$ cm^{-3} in 1050˚C spike annealing, resulting in a decrease in the B activation ratio as shown in Fig. 2.

To examine the chemical bonding features of C atoms in B^+ implanted layer, C1s spectra excited by synchrotron radiation were measured. Figure 5 shows the HA-XPS C1s spectrum taken at a take-off angle of 80˚ for $Si_{0.9937}:C_{0.0063}$ layers implanted with a B-fluence of $3x10^{15}cm^{-2}$ after 1050˚C spike annealing. The observed C1s spectrum consists of three components, in which the major component peaked at ~286.4 eV is attributed to C-C and C-H bonds, and subsidiary components peaked at ~287.5 eV and ~284.0eV are assigned to be C=C bonds and C-B bonds, respectively.[7] No signals due to C-B bonds were observed in B^+ implanted Si without C incorporation after 1050˚C spike annealing. Furthermore, C1s HA-XPS spectrum taken at a take-off angle of 30˚ for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layers shows that a decrease in the signals due to C-B bonds as represent in Fig. 6. The result confirms that the direct bonding of C with B atoms becomes significant in the region with a B concentration over ~$1x10^{21}cm^{-3}$. From the analysis of the channeling RBS spectra,[3] we also found that the crystalline quality of a B^+ implanted Si layer is much worse than that of the B^+ implanted $Si_{0.9937}:C_{0.0063}$ layer with a fluence of $3x10^{15}cm^{-2}$ after 1050˚C spike annealing. Considering that, in the heavily B-doped layer in Si, the precipitation of clustering during annealing induce and accumulate a strain in the Si lattice, the incorporation of C atoms with a covalent radius smaller than Si atoms is likely to play a role on the relaxation of such strain caused by progressive clustering. Thus, it is suggested that the C-B bonds are responsible for the direct bonding of C with B atoms in the stable B containing clusters.

To examine the thermal stability of B-containing clusters in Si, for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layers with a fluence of $3x10^{15}cm^{-2}$, the change in B1s spectrum with additional furnace annealing at 900 or 1000˚C for 1800 s in N_2 was also measured at a take-off angle of 90˚, as shown in Figs. 7(a) and (b). In the heavy B-doping in Si without C incorporation, the formation of the B-containing clusters and precipitates were promoted with additional annealing at 900˚C, which can be interpreted in terms of a limitation on solid solubility of B atoms in Si under thermodynamic equilibrium annealing at 900˚C as high as ~$6x10^{19}cm^{-3}$.[8] But in contrast, with additional annealing as high as 1000˚C, the signals due to clustered B become hardly observed (Fig. 7(a)), indicating that the thermal decomposition of B-containing clusters and precipitates and resultant diffusion of B atoms proceed during annealing at 1000˚C. Such precipitation and decomposition of B-containing clusters in Si are affected by C incorporation as shown in Fig. 7(b). With a C incorporation of 0.63at.%, the B-containing

clusters and precipitates were no longer increased by 900˚C anneal, but markedly promoted by 1000˚C anneal as seen in Fig. 7(b). The mechanism on the precipitation and decomposition of B-containing clusters depending on the C incorporation is not clear yet. This can be interpreted in terms that a covalent bond of B-C is stronger than that of Si-B since C is a more electronegative element than Si.

Conclusions

It is found that C atoms accelerate the formation of B-containing clusters in the region with a B concentration over ~$1x10^{21}cm^{-3}$ after 1050˚C spike annealing, resulting in decrease in B activation. It is likely that the promotion of C-B bonds in such heavily B-doped region as confirmed by HA-XPS involves in the relaxation of lattice strain caused by the precipitation of stable B-containing clusters. Also, the intrinsic B-diffusion and decomposition of B-containing clusters are markedly suppressed by C incorporation under thermodynamic equilibrium annealing at 1000˚C, which is attributable to gaining the covalent bond strength with the formation of C-B bonds.

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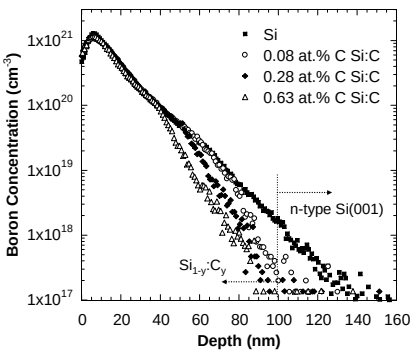

Fig.1 B profiles in pure Si and $Si_{1-y}:C_y$ layers with three different C content after 1050˚C spike annealing. The B fluence was fixed at 3 x 10^{15} cm^{-2}.

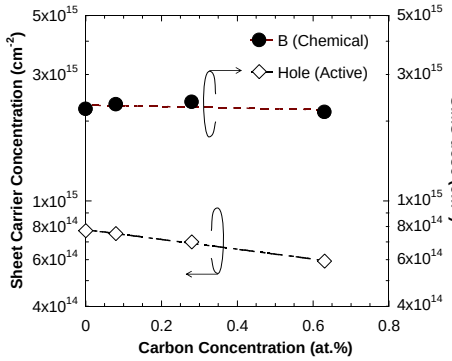

Fig.2 N_s and chemical B dose of B^+ implanted $Si_{1-y}:C_y$ layer after 1050˚C spike annealing as functions of C content, which were determined by Hall and SIMS measurements, respectively.

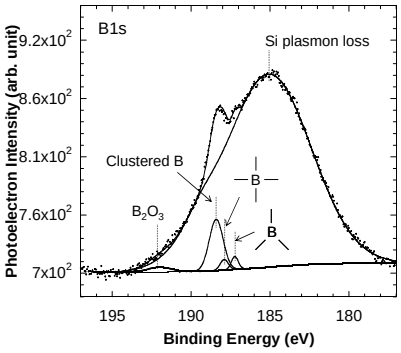

Fig.3 XPS spectrum including B1s signals for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layer after 1050˚C spike annealing. The photoelectron take-off angle was set at 90˚.

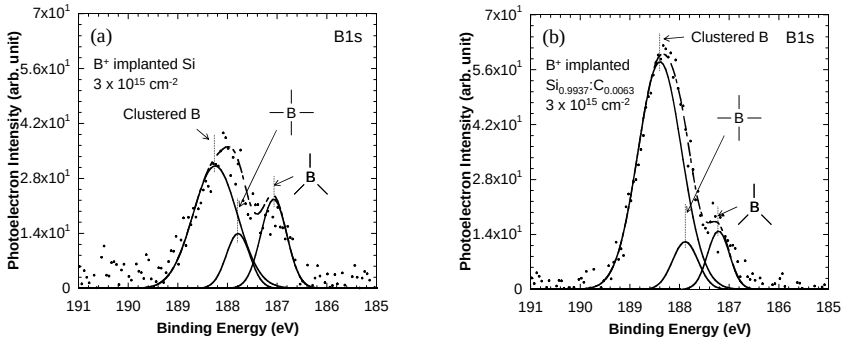

Fig.4 B1s XPS spectra for B^+ implanted **(a)** Si and **(b)** $Si_{0.9937}:C_{0.0063}$ layers after 1050˚C spike annealing, in which Si plasmon signals were subtracted from each of measured spectra. In each case, the surface layer was etched back to characterize the region near B concentration peaks as high as ~$1x10^{21}$ cm^{-3} as seen in Fig. 3. The B-implantation fluence and the photoelectron take-off angle were fixed at $3x10^{15}$ cm^{-2} and 90˚, respectively.

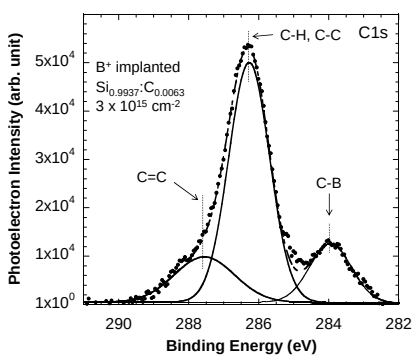

Fig. 5 HA-XPS spectrum of C1s signals for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layer after 1050 ˚C spike annealing, which was taken at a photoelectron take-off angle of 80˚. The B-implantation fluence was fixed at 3 x 10^{15} cm^{-2}.

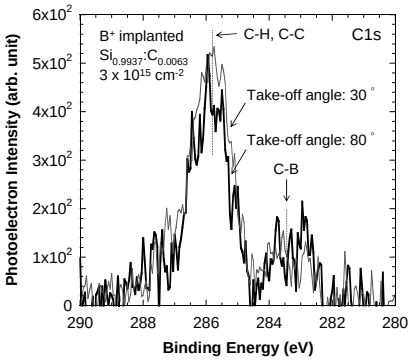

Fig. 6 HA-XPS spectra of C1s signals for B^+ implanted $Si_{0.9937}:C_{0.0063}$ layer after 1050˚C spike annealing, which were taken at take-off angles of 30 and 80˚. The B-implantation fluence was fixed at $3x10^{15}cm^{-2}$.

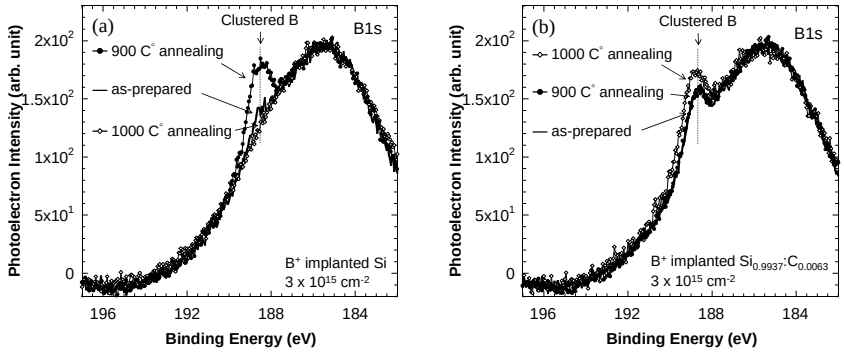

Fig. 7 XPS spectra including B1s signals for B^+ implanted **(a)** pure Si and **(b)** $Si_{0.9937}:C_{0.0063}$ layers after additional annealing at 900 and 1000˚C for 1800s in N_2. In each case, the spectrum was taken from the region near the B concentration peak at a photoelectron take-off angle of 90˚ and normalized with $Si2p^{0+}3/2$ peak at 99.04 eV.