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Hole Generation without Annealing in High Dose Boron Implanted Silicon: Heavy Doping by B_{12} Icosahedron as a Double Acceptor

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A high hole concentration region about $1x10^{21}cm^{-3}$ was generated without any post-annealing by high dose boron ion implantation into silicon. XPS measurement and FTIR absorption spectra revealed that B_{12} icosahedron was created in as-implanted samples. Generation of holes can be explained by the model that B_{12} icosahedron acts as a double acceptor.

1. INTRODUCTION

Post-annealing was always considered essential for the activation of the implanted dopants into silicon substrates, because the implanted atom is regarded as being located at interstitial site and not acting as a dopant. Boron is the most popular impurity as a p-type dopant in silicon, and various studies have been reported on the thermal behavior of boron with high dose.[1,2] However, the authors have found out that a high concentration of holes were generated in boron implanted silicon substrates without post-annealing in the high dose region of more than $1x10^{16}cm^{-2}$. Such an activation process of boron cannot be explained by a usual substitution of boron atoms into silicon sites. In this paper, the structural properties of boron-as-implanted silicon substrates, as well as the electrical characteristics are reported.

2. EXPERIMENT

Boron was implanted at 35 keV into a (001) silicon substrate with the dose between $5x10^{14}$ and $1x10^{17}cm^{-2}$ at room temperature. The samples were annealed for 1 hour in nitrogen ambient. Sheet resistance was measured by Van der Pauw methods. Stripping Hall method was used to measure the depth profile of carriers generated by boron ion implantation. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical state of implanted boron. Fourier transform infrared spectroscopy (FTIR) spectra were also measured in order to investigate the atomic position of boron in silicon. The absorption spectra were compared to those of elemental boron.

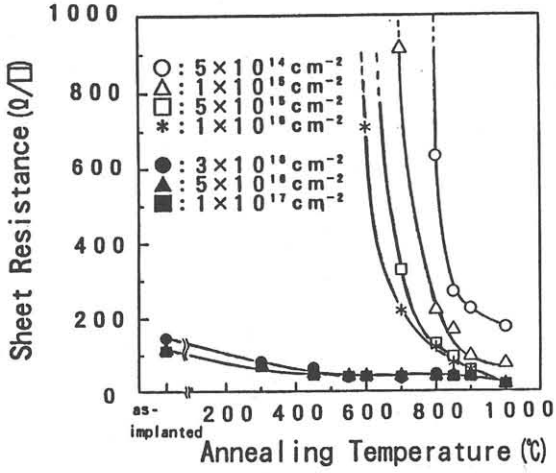

Fig.1 Annealing temperature dependence of the sheet resistance

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3. ELECTRICAL CHARACTERISTICS OF BORON IMPLANTED SILICON SUBSTRATE

Figure 1 shows the annealing temperature dependence of the sheet resistivity for various boron dose. It should be noted that the low sheet resistivity was obtained for the samples with the dose more than $1x10^{16}cm^{-2}$, regardless of the annealing temperature. Even the samples without any post-annealing, which is uaually essential to activate the implanted dopants, have low sheet resistivity. The same results were obtained regardless of the temperature of the wafer or the beam current, which means that such an activation of boron is not due to the self-annealing during implantation.

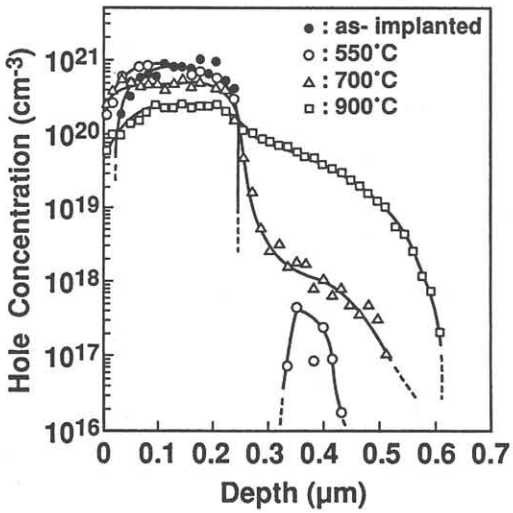

Fig.2 Depth profile of hole concentration. Boron dose was $1x10^{17}cm^{-2}$.

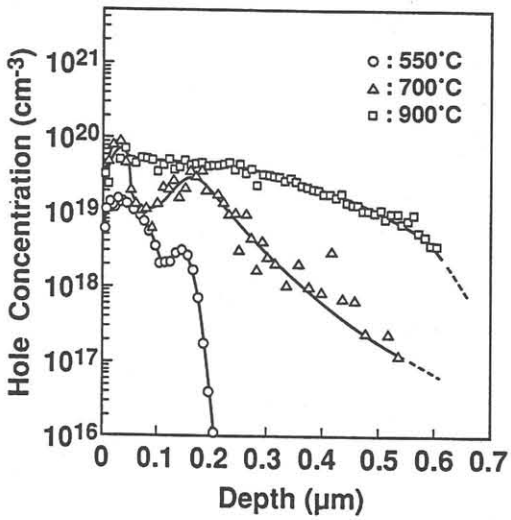

Fig.3 Depth profile of hole concentration. Boron dose was $1x10^{16}cm^{-2}$.

Figure 2 shows the depth profile of hole concentration of the samples with boron dose of $1x10^{17}cm^{-2}$, measured by Stripping Hall method. It was shown that high hole concentration region about $1x10^{21}cm^{-3}$ can be generated at the richest boron depth even in the as-implanted sample. Higher annealing temperature causes lower hole concentration. Figure 3 shows the depth profile of hole concentration of the samples with boron dose of $1x10^{16}cm^{-2}$, as a comparison. High temperature annealing more than $900^{o}C$ is essential in order to obtain high concentration hole region of about $1x10^{20}cm^{-3}$.

4. SPECTROSCOPIC INVESTIGATION AND A NEW MODEL FOR IMPLANTED BORON

Chemical state of boron in high dose boron implanted sample was investigated by XPS. Figure 4 shows the XPS spectrum for boron implanted sample with the dose of $1x10^{17}cm^{-2}$. A surface layer with about 1100Å thick was removed by the repetition of anodic oxidation and diluted HF etching in order to measure the region where the boron concentration was the highest. Boron peaks at 186.8eV and 187.5eV are due to the 3-folded and 4-folded boron in silicon.[3] Boron peak at the energy of 188.1 eV, which was the strongest and has not been reported for boron doped silicon, is attributed to elemental boron or borides which consist of icosahedral boron, B_{12}.

Figure 5 shows the FTIR spectra of a boron implanted substrates with various boron dose at wave numbers between 650 and 1050 cm^{-1}. Some absorption peaks were observed at about the wave numbers of 680, 800 and 930 cm^{-1}. It is clearly shown that the heights of these peaks depend on

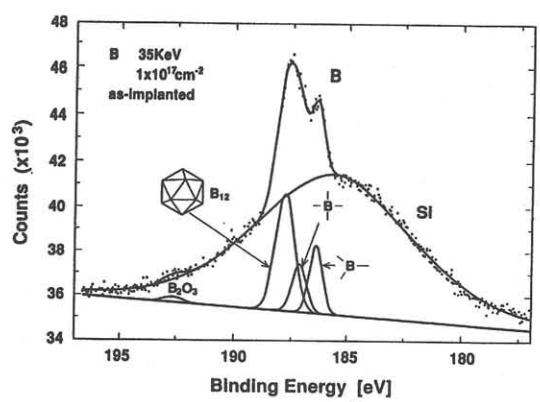

Fig.4 XPS spectrum.

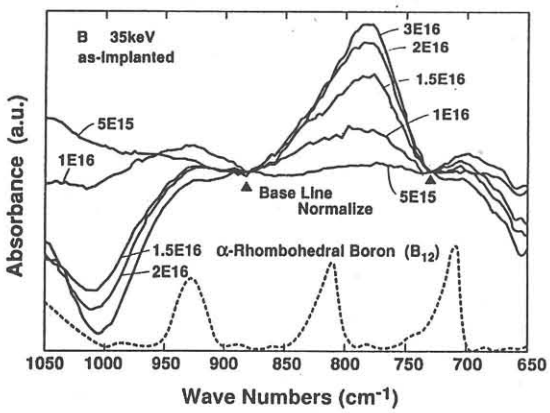

Fig.5 FTIR spectra.

the boron dose. This suggests that these peaks are originated by the implantation of boron. The absorption spectrum of metallic boron with the structure of α-rhombohedral is also shown in Fig.5, and absorbance at the wave numbers of 680 and 800 cm^{-1} are due to icosahedral boron, B_{12}.[4] It is clearly observable that the absorption spectrum for α-rhombohedral boron has peaks at almost the same wave numbers as boron implanted samples. This confirms the formation of B_{12} in boron implanted silicon.

Formation of B_{12} can explain the hole generation with the model that B_{12} acts as a double acceptor. In order to form the icosahedral structure, B_{12} usually requires 2 extra electrons.[5] 38 electrons are required for an icosahedron bonded to the outward 12 silicon atoms, while 36 electrons are available for bonding, because each 12 boron atoms supply 3 valence electrons. If 2 electrons are taken from silicon lattice, hole concentration is expected to be 2/12 of the number of boron atoms constituting B_{12}. The experimentally obtained sheet hole concentration was also about 2/12 of the boron dose in high dose boron implanted samples. However, it was shown by comparing each separated peak for boron in the XPS spectrum in Fig. 4 that not all of implanted boron atoms had icosahedral structure and that the rest of boron atoms are 3-folded or 4-folded. This means that a part of the generated holes is not due to B_{12} structure but 4-folded boron.

In order to satisfy the model, B_{12} has to make covalent bonds to the surrounding silicon lattice. This is possible by substituting tetragonal 5 silicon atoms, because B_{12} and tetragonal silicon atoms have similar volume and

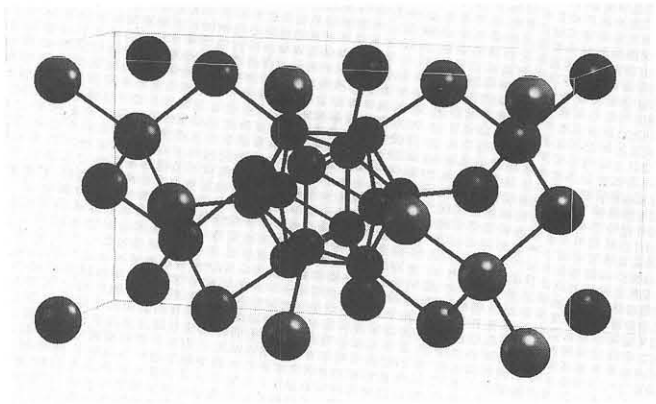

Fig.6 Atomic configuration based on the model that B_{12} makes covalent bonds to the silicon lattice.

both of them have 12 outward bonding electrons. So, B_{12} can bond to the surrounding silicon atoms without any dangling bonds and any high stress. Figure 6 shows 2 unit cells of silicon lattice, in which tetragonal 5 silicon atoms are substituted by B_{12}, based on the above model. The boron-silicon distance is similar to that otained in SiB_6,[6] and this suggests that B_{12} can exist in silicon lattice.

5. CONCLUSION

A high hole concentration region about $1x10^{21}cm^{-3}$ was generated without any post-annealing by high dose boron ion implantation into silicon. Such generation of holes can be explained by a new model that B_{12} icosahedron acts as a double acceptor.

6. ACKNOWLEDGEMENT

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7. REFERENCES

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