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# Hole generation in B-implanted Ge without annealing: Formation of $B_{12}$ cluster acting as a double acceptor

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## I. Introduction

The formation of ultra-shallow and highly doped layer in semiconductor substrate has been studied for higher-performance LSIs of future generations. In the conventional process, impurities are usually introduced by ion implantation, and then annealing is performed to electrically activate the impurities; however, annealing causes the diffusion of impurities that makes it difficult to form shallow and highly doped layers.

Surprisingly, Mizushima *et al.* have found [1,2] that high-hole-concentration layers are generated in high-dose ($\geq 3 \times 10^{16}\,\mathrm{cm}^{-2}$) B-implanted Si(100) substrates without any annealing process. They proposed the formation of icosahedral $B_{12}$ cluster [Fig. 1(a)] acting as a double acceptor in $Si_5$ substitutional sites in the as-implanted Si.

The structure of $B_{12}$ cluster in Si has been studied theoretically on the basis of the first-principles local density functional approach. Okamoto *et al.* proposed[3] that cubo-octahedron [Fig. 1(b)] is more stable than icosahedron. In contrast, Yamauchi *et al.* proposed[4] that icosahedron is more stable than cubo-octahedron.

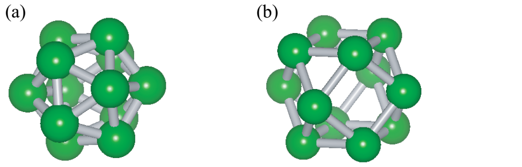


FIG. 1: Schematic illustrations of (a) icosahedral and (b) cubo-octahedral $B_{12}$ clusters.

Our concern is whether the hole generation without annealing appears in Ge because of the similarities to Si, e.g., the same group IV and the same diamond structure. It is of technological as well as scientific importance to investigate the electrical properties of B in Ge. Ge has recently attracted much attention as a new channel material for LSIs, because of the higher mobilities of electron and hole in Ge than in Si. For its realization, the dopant properties, e.g., solubility, diffusivity, and activation ratio, have to be fully examined. To our knowledge, however, little is known about B-implanted Ge in detail.

In this study, profiles of impurity concentrations and hole concentrations in B-implanted Ge are investigated under various conditions. We present, for the first time, hole generation in B-implanted Ge without annealing.

## II. Experiment

The surface of substrates, 3 in. $n$Ge(100) wafers with Sb, were first treated with 1% HF solution for 5 min, and then rinsed with purified water for 10 min. After the treatments, B ions were implanted into the substrates. The implantation doses of B were $1 \times 10^{13-17}\,\mathrm{cm}^{-2}$. The acceleration energy in each case was 30 keV. The ion beams were tilted by 7°with respect to the normal to the surface. Using thermo-tape that changes color on reaching a specific temperature, we have confirmed that the temperature during implantation is less than 82°C, which is too low to cause re-growth and to electrically activate dopant in Ge. The Ge substrates annealed for 30 min at 400-600°C in $N_2$ were also prepared. The profiles of the impurity concentrations and the carrier concentrations were examined by secondary ion mass spectrometry (SIMS) and spreading resistance profiling (SRP), respectively. The crystallinity was checked by Rutherford backscattering spectrometry (RBS). The bonding state was confirmed by x-ray photoelectron spectroscopy (XPS) with Ar sputtering.

## III. Results and Discussion

First, we investigated the profiles of impurity concentrations and hole concentrations of $n$Ge(100), into which various doses B ($1 \times 10^{13-17}\,\mathrm{cm}^{-2}$) were implanted. Figure 2(a) shows the profiles of impurity concentrations. The implanted B exist around the surface, nearly symmetrically with the projected range $R_P$ (broken line). The profiles of hole concentrations, corresponding to the impurity ones, are shown in Fig. 2(b). Interestingly, high-hole-concentration layers (max: $\sim 8 \times 10^{20}\mathrm{cm}^{-3}$) are observed in Ge without annealing, similar to the case in Si. It should be noted that there is a specific difference in the B dose starting to generate holes without annealing between Si and Ge: for Si, it is $3 \times 10^{16}\,\mathrm{cm}^{-2}$ whereas for Ge, $1 \times 10^{13}\,\mathrm{cm}^{-2}$, which is the lowest dose investigated in this experiment. Unlike the impurity-concentration profiles, the hole-concentration profiles at the dose of $> 1 \times 10^{15}\,\mathrm{cm}^{-2}$ are apparently asymmetrical with around $R_P$. The hole concentrations in the surface side (left side of broken line) are lower than those in the deeper side (right side of broken line).

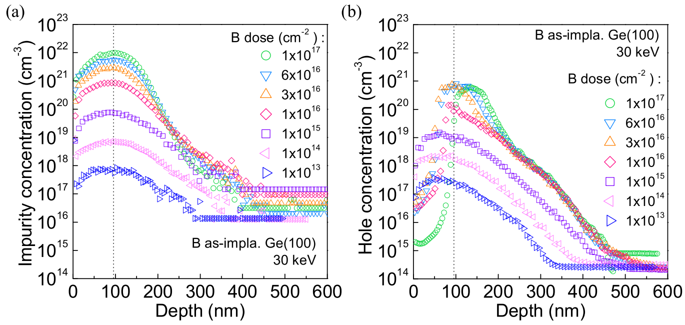


FIG. 2: Profiles of (a) impurity concentration and (b) hole concentration of B-implanted Ge(100) substrates. No samples were annealed. The doses were $1 \times 10^{13-17}\,\mathrm{cm}^{-2}$. Each broken line indicates $R_P$.

The asymmetry of the hole-concentration profiles can be explained by the crystallinity: Figure 3 shows RBS spectra for aligned and random directions. The minimum yield $\chi_{min}$ is estimated to be 0.74, indicating poor crystallinity. It is worth noting that this value is not local but the average one for Ge. The profiles of the crystallinity can be reproduced from the RBS spectra, revealing that the crystallinity rate of the surface side is lower than unity, indicating noncrystalline (Fig. 4). It is clear from the profiles of the crystallinity, the impurity concentration, and hole concentration that the low hole concentration in the surface side originates from the poor crystallinity, probably due to the implantation damage. Likewise, the tendency for the hole concentration to decrease with B dose can be understood in terms of the ion implantation damage. We note here that the profiles of hole concentration are asymmetrical at the hole concentrations of $>10^{20}\,\mathrm{cm}^{-3}$ probably because of the ion implantation damage. If such a

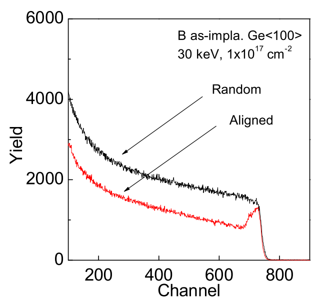


FIG. 3: RBS spectra of B-implanted Ge(100). The dose was $1 \times 10^{17}\,\mathrm{cm}^{-2}$. The sample was as-implanted. The minimum yield $\chi_{min}$ is estimated to be 0.74.

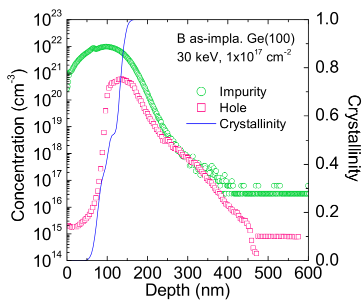


FIG. 4: Crystallinity of B-implanted Ge reproduced from the RBS spectra (Fig. 3). Profiles of impurity concentration and hole concentration are also shown.

high-hole-concentration is required, lower acceleration energy than 30 keV might be effective to suppress the damage. On the other hand, the crystallinity rate of the deeper side is nearly unity. Thus, it is obvious that high-hole-concentration layer was formed in the nearly crystalline deeper region even though high-dose B was implanted.

Combining the SIMS and SRP data allows us to examine the electrical activation behavior of B in Ge. Figure 5 shows the relationship between the impurity concentrations $N_A$ and the hole concentrations $p$. $N_A$ at the depth where SRP was performed were interpolated from the SIMS data to enable comparison of the measurement results of the two methods at the same depth. The relationship distributes almost on the same line of $p/N_A < 1$, suggesting the same activation ratio of less than unity in the wide range of impurity concentrations ($10^{16-22}\,\mathrm{cm}^{-3}$).

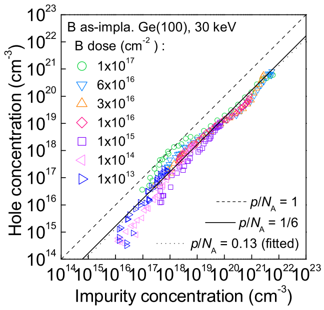


FIG. 5: Relationship between the impurity concentration $N_A$ and the hole concentration $p$ of B-implanted Ge substrates. The doses were $1\times10^{13-17}\,\mathrm{cm}^{-2}$. The broken line ($p/N_A$=1) corresponds to an activation ratio for fully activated B. The solid line ($p/N_A$=1/6) indicates an effective activation ratio for fully activated $B_{12}$ double acceptor.

By analogy with the case of Si, the formation of $B_{12}$ cluster in Ge is a possible model for the hole generation in B-implanted Ge without annealing. According to theoretical prediction,[3,4] $B_{12}$ cluster in Si acts as a double acceptor. If the $B_{12}$ clusters are fully electrically activated, then the activation ratio $p/N_A$ is effectively regarded as 1/6 (=2/12). The data for each activation ratio fall on close to the solid line corresponding to the activation ratio of 1/6. This suggests that $B_{12}$ clusters acting as double acceptor are formed without annealing in Ge as well as in Si.

Next, we investigated the annealing effect on the profiles of the B-implanted Ge. The profiles of the impurity concentrations [Fig. 6(a)] reveal that no diffusion of B occurred after annealing at 400-600°C, which is in complete contrast to P that easily diffuses in Ge.[5] The corresponding hole-concentration profiles [Fig. 6(b)] show the different behaviors: The hole-concentration around the surface (left side of broken line) increases with annealing temperature. On the other hand, in the deeper region (right side of broken line), the hole-concentration profile shows no change. We consider that the annealing causes re-growth around the surface, thereby increasing hole concentration with temperature. On the other hand, the deeper region is nearly crystalline according to RBS (Fig. 4). Almost the same hole concentration in the deeper region implies the existence of thermally stable acceptors.

Here, we examine the influence of the implantation damage on the hole generation. Figure 7 shows the profiles of impurity concentration and carrier concentration of C-implanted $n$Ge(100) without annealing, whose condition is the similar to

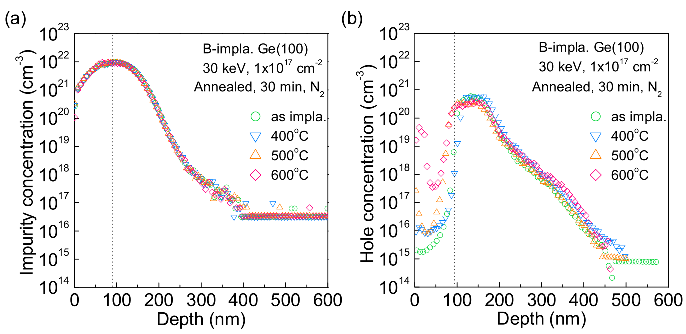


FIG. 6: Profiles of (a) impurity concentration and (b) hole concentration of B-implanted Ge(100) substrates. The dose in each case was $1\times10^{17}\mathrm{cm}^{-2}$. The annealing temperatures were 400, 500, and 600°C. The profiles of as-implanted samples are also depicted.

that of B implantation ($1\times10^{16}\,\mathrm{cm}^{-2}$, 30 keV). Since C has almost the same mass as B, C would cause almost the same damage as B. The profile of carrier concentration revealed that the holes were generated even in the C-implanted regions in Ge without annealing, though C is not dopant. This suggests that the defects in Ge behave as acceptors.[6] However, the maximum hole concentration in C-implanted Ge without annealing is $3\times10^{15}\,\mathrm{cm}^{-3}$, which is about five orders of magnitude lower than that of B-implanted Ge. This supports the view that B ions implanted into Ge behave as acceptors without annealing.

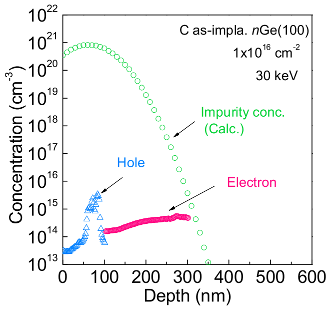


FIG. 7: Profiles of impurity concentration and hole concentration of C-implanted $n$Ge(100). The sample was as-implanted. The dose was $1\times10^{16}\,\mathrm{cm}^{-2}$. The calculated profile of the impurity concentration is also shown.

Finally, we confirmed the bonding states of B in Ge. Figure 8 shows the XPS spectra. The sputtering time of "w/o B" is longer than that of "with B". Whereas no B 1s peak appeared in the case " w/o B ", B 1$s$ was observed in the case "with B". The B 1$s$ peak seems to consist of two peaks at least (Inset in Fig. 8): a peak for three- and/or four-coordinate B (∼187 eV) and a peak for $B_{12}$ (∼188 eV), by analogy with $B_{12}$ cluster in Si.[1,2]

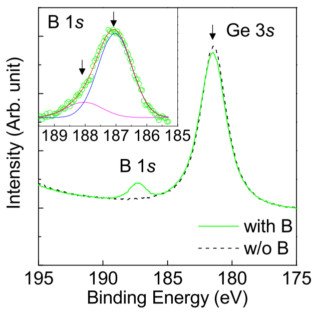


FIG. 8: XPS spectra for B-implanted Ge, which were sputtered by Ar. The case "w/o B" was sputtered for longer time than the case "with B". The sample was the same as that in Fig. 4. The B 1$s$ separated into two peaks is also shown.

Thus, it is reasonable to suppose the formation of $B_{12}$ cluster as a double acceptor in high-dose B as-implanted Ge. On the other hand, the states of B in the case of low dose have not yet been clarified. Further work is needed to resolve this issue.

## IV. Summary

Hole generation (max: $\sim8\times10^{20}\,\mathrm{cm}^{-3}$) in B-implanted Ge without annealing was observed. The activation ratio in the wide range of impurity concentrations ($10^{16-22}\,\mathrm{cm}^{-3}$) is almost the same value of 1/6. These results can be explained by assuming $B_{12}$ cluster formation as a double acceptor in the as-implanted Ge.


## Acknowledgments

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