Diffusion control of *n*-type impurities in Ge using co-doping technique for ultra-shallow and highly doped n^+/p junction in Ge nMOSFETs

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I. Introduction

Germanium is a promising channel material for MOSFETs of future generations, because of the higher mobilities of elec-tron and hole in Ge than in Si. Whereas the higher mobility has been realized in pMOSFETs, it has yet to be realized in nMOSFETs, mainly because of the high contact resistance at a metal/ n^+ Ge junction, originating from two factors: One is the high Schottky barrier formation at the interface, which is responsible for the Fermi-level pinning of metal at the charge neutrality level of Ge, close to the valence band.¹ The other one is poor electrical activation of n-type impurities in Ge due to the low solid solubility and the fast diffusion.² Among these issues, it is of great significance to suppress the fast diffusion resulting in the dose loss, since high chemical concentrations (C) of impurities at the surface region are needed to make electron concentrations (n) high. Although some annealing techniques for extremely short time, e.g., rapid thermal annealing and spike annealing, have been employed, they are insufficient for the formation of ultra-shallow n^+ Ge layers with sufficiently high n for Ge nMOSFETs.

In this work, the diffusions of n-type impurities in Ge codoped with n- and p-type impurities are investigated experimportantly and numerically. We find that the diffusion of n-type impurities in Ge can be dramatically suppressed by ptype ones. This can be understood in terms of the carrier compensation and the effective diffusion constant with n^2 dependence. Shallow n^+ Ge layers without p^+ Ge region are successfully formed using the co-doping technique.

II. Calculation and Experiment

We made a simulation program to calculate the profiles of the chemical concentrations (C-profiles) and the profiles of the electron concentrations (n-profiles) in Ge on the basis of the diffusion mechanism (Fig. 1). A dopant-vacancy pair model has previously been proposed for n-type dopants in Ge.³ The reaction of ionized P on substitutional sites with a singly positive charge, P_S^+ , and a vacancy with a doubly negative charge V^{2-} , generates singly negative dopant-vacancy pairs $(PV)^{-}$ [Eq. (1)]. The mechanism leads to a single diffusion equation [Eq. (2)] with an effective diffusion coefficient D_{eff} [Eq. (3)] dependent on n^2 . This dependence originates from the difference in the electric states between P_S^+ and $(PV)^-$.

$$\mathbf{P}_{S}^{+} + \mathbf{V}^{2-} \rightleftharpoons (\mathbf{PV})^{-}, \qquad (1)$$

$$\bigvee^{2^{-}} \qquad \qquad \frac{\partial C_{\mathrm{P}_{S}^{+}}}{\partial t} = \frac{\partial}{\partial x} \left[D_{\mathrm{eff}}(n) \frac{\partial C_{\mathrm{P}_{S}^{+}}}{\partial x} \right],$$
$$D_{\mathrm{eff}}(n) := D^{*}(n_{i}) \left(\frac{n}{n_{i}}\right)^{2},$$

FIG. 1: Schematic representation of indirect diffusion mechanism of n-type dopants in Ge. The mechanism is represented by Eqs. (1)-(4), where n(p) is free electron (hole) concentration, n_i is intrinsic carrier concentration, N_D (N_A) is donor (acceptor) concentration, and n_D (p_A) is the concentration of electrons (holes) in the donor (acceptor) level. $C_{\text{P}_S^+}$ is the same as N_D .

In light of this diffusion mechanism, we conceived the idea that the co-doping of p-type as well as n-type impurities could suppress the fast diffusion of n-type impurity: The coexistence of n- and p-type impurities causes carrier compensation. Then, the n would be reduced by the compensation, consequently leading to the slower diffusion of n-type impurity because of the n^2 dependence of D_{eff} . Therefore, we calculated

the diffusion of *n*-type impurities in Ge on the basis of the diffusion mechanism, taking the co-doping effect of n- and p-type impurities into account.

În our calculation, we set the conditions described below: The charge neutrality [Eq. (4)] is satisfied in this system. The effect of p-type impurities on the diffusion of n-type ones is reflected through the condition of the charge neutrality. P (B) is selected as n-type (p-type) impurity. The diffusion coefficient of P in Ge, obtained from the experimental profiles,² is applicable to the diffusion of P in the co-doped Ge. No diffusion of B in Ge occurs, which is a similar situation to that reported in the case of previous experiments.⁴ The initial profiles of P in Ge are sufficiently shallow (the P dose: $5 \times 10^{15} \text{ cm}^{-2}$, the projected range: 5 nm). The annealing condition is for 1 sec at 500°C.

Furthermore, the effect of the co-doping of P and B on the diffusion in Ge was investigated experimentally. The surfaces of substrates, Ga doped pGe(100) wafers, were first treated with 1% HF solution for 5 min, and then rinsed with deionized water for 10 min. After the treatments, B ions were first implanted into the substrates, followed by P. The substrates into which only P ions were implanted were also prepared. The implanted dose of P (B) was $5 \times 10^{15} (2 \times 10^{14} - 5 \times 10^{15}) \text{ cm}^{-2}$. The acceleration energies was 30 keV. For electrical activation, the substrates were annealed for 30 min at 400–600 $^{\circ}$ C in N₂. Secondary ion mass spectrometry (SIMS) was used to estimate C-profiles of the impurities in Ge. Spreading resistance probe (SRP) was employed to examine the profiles of the electrical concentrations at room temperature.

III. Results and Discussion

First, we investigated experimentally whether or not the co-doping of P and B into Ge is effective for the control of the diffusion of P in Ge. Figure 2(a) shows the SIMS profiles (C-profiles) of P in Ge without B after annealing at 600°C for 30 min in N₂. The SIMS profile before annealing is shown as well. The depth at $1 \times 10^{19} \text{ cm}^{-3}$ is ~100 nm before annealing whereas it exceeds 400 nm after annealing. This fast diffusion

is due to the n^2 dependence of D_{eff} as described above. The *C*-profiles of P and B in the co-doped Ge are shown in Fig. 2(b). Both doses are $5 \times 10^{15} \text{ cm}^{-2}$. We find that the co-doping effectively suppresses the diffusion of P in Ge. The depth at 1×10^{19} cm⁻³ is ~100 nm, which remains unchanged after annealing. Thus, it is clarified that the co-doping can dramatically suppress the diffusion of n-type impurities.



FIG. 2: The SIMS profiles of (a) P-implanted Ge, and (b) P- and B-implanted Ge. The dose of both \vec{P} and \vec{B} was $5 \times 10^{15} \text{ cm}^{-2}$ Each sample was annealed at 600° C for 30 min in N₂. Each SIMS profile of P before annealing is shown as well.

Although *n*-type impurity diffusion is suppressed, the region co-doped with both types in the Ge [Fig. 2(b)] is fully *p*-type, i.e., p^+ Ge. Therefore, we numerically examined the diffusion of P in Ge with various doses of B to find a way to control

(2)

(3)



FIG. 3: The simulated profiles of (a) the chemical concentrations and (b) the electron concentrations in Ge doped with P.

diffusion, assuming extreme conditions for the fabrication of ultra-shallow n^+ Ge layers without p^+ Ge region. Figure 3(a) shows the simulated C-profiles of P in Ge with no dose of B, where the time evolutions $(0, 0.1, \ldots, 1.0 \text{ sec})$ of the diffusions are depicted. As shown in Fig. 3(a), the diffusion causes the C-profiles to have a box-like shape, reproducing the typical experimental feature [Fig. 2(a)]. The *n*-profiles [Fig. 3(b)], on the other hand, are almost the same as the C-profiles in the range of $n > n_i$ because $n \simeq N_D$ when $N_A = 0$ according to Eq. (4).



FIG. 4: The simulated profiles of (a) the chemical concentrations and (b) the electron concentrations in Ge co-doped with P and B. There is a region with B of 2×10^{21} cm⁻³ in the range 7.3–18.7 nm.

Next, we examined the effect of the co-doping of P and B into Ge on the diffusion. Figure 4(a) shows the simulated C-profiles of P and B in Ge, the case where a constant C region of B is added to Ge in Fig. 3(a). The region with B is deeper than the region with P to avoid lowering n at surface. It is clear from Fig. 4(a) that the diffusion of P is blocked by B region. The n-profile [Fig. 4(b)] has a region where electrons are highly concentrated immediately below the surface, corresponding to the C-profile [Fig. 4(a)]. Thus, shallower n^+ Ge layers can be formed by the co-doping of P and B. Here, it should be noted that there is also a region deeper from the n^+ Ge layer where $n \ll n_i$. This is because there are a large number of holes. According to the law of mass action, p is then n_i^2/n , which is almost N_A . In this way, an extremely shallow n^+ Ge layer with



FIG. 5: The simulated profiles of (a) the chemical concentrations and (b) the electron concentrations in Ge co-doped with P and B. There is a region with B of 2.5×10^{20} cm⁻³ in the range 7.3–18.7 nm.

high n can be formed; however, p^+ Ge layer is also formed at once, reproducing a similar effect and a similar issue to those in the case of the experiment described above [Fig. 2(b)].

The formation of n^+ Ge layer without p^+ Ge region can be achieved by adjusting the C-profiles of p-type impurities: Figure 5(a) shows the C-profile of P and B in Ge. The concentration of B in Fig. 5(a) is lower than that in Fig. 4(a). Contrary to the case in Fig. 4(a), P diffuse in the region with B. Besides, the diffusion distances are shorter than those in Ge without B [Fig. 3(a)]. Here, it is worth noting that B region is over-whelmed by P region. We can deduce this behavior from the *n*-profile [Fig. $5(\mathbf{b})$]. At the first stage of the diffusion, n in the region with B is two orders of magnitude lower than n_i , leading to four orders of magnitude smaller D_{eff} . Therefore, P diffuse more slowly than that in Ge without B. After an optimum time of the diffusion, there are no regions of $n < n_i$, i.e., no p^+ Ge region [Fig. 5(b)]. Thus, the simulations prove that the co-doping of n- and p-type impurities into Ge is a possible way to form ultra-shallow n^+ Ge layers without p^+ Ge region if the concentrations of impurities and the time of the diffusion are appropriate.

Finally, we confirmed experimentally the theoretical prediction. Figures 6(a) and 6(b) show the SRP profiles of the electrical concentrations in Ge, where the doses of B are 2×10^{14} and 1×10^{15} cm⁻², respectively. The high electrical concentration regions around the surface are fully *n*-type, i.e., n^+ Ge layers alone. With the increase in annealing temperatures, the regions with electrons spread deep into the substrates. The profiles in Ge with B are shallower than those without B, the tendency of which more strongly depend on higher doses of B. Thus, the experiment as well as the simulation confirmed that shallow and highly doped n^+ Ge layers without *p*-type region could be formed by the co-doping of *n*- and *p*-type impurities.



FIG. 6: The SRP profiles of P- and B-implanted Ge (P with B) and of only P-implanted Ge (P w/o B). The doses of B were (a) 2×10^{14} and (b) 1×10^{15} cm⁻². Each dose of P was 5×10^{15} cm⁻². The samples were annealed at 400–600° C for 30 min in N₂.

Our experiments have not been optimized yet. Optimized further, this co-doping technique would be a possible way to form ultra-shallow and highly doped n^+/p junctions for Ge *n*MOSFETs.

IV. Conclusions

The co-doping of n- and p-type impurities, especially P and B, into Ge was investigated experimentally and numerically to form ultra-shallow and highly doped n^+ Ge layers for the development of Ge nMOSFETs. The diffusion of P in the co-doped Ge was controlled by adjusting the concentrations of B as well as the time of the diffusion. Shallow n^+ Ge layer without p^+ Ge region could be successfully formed by the co-doping technique.

Acknowledgments

The authors would like to thank T. Tezuka for making helpful suggestions. This work was supported by NEDO.

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