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Electrical properties of Ge crystals and effective Schottky barrier height of NiGe/Ge junctions modified by P and chalcogen (S, Se, or Te) co-doping

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The electrical properties of Ge crystals and the effective Schottky barrier height (SBH) of NiGe/Ge diodes fabricated by P and/or chalcogen (S, Se, or Te) doping were investigated for Ge *n*-channel metal–oxide–semiconductor field-effect transistors with a NiGe/*n*⁺Ge junction. The electron concentration in Ge was increased more by co-doping with chalcogen and P than by doping with P alone. Moreover, SBH values were decreased in NiGe/*n*Ge diodes and increased in NiGe/*p*Ge diodes compared with undoped NiGe/Ge by both P doping and P and chalcogen co-doping. Co-doping with Te and P was most effective in modifying the SBH. *Published by AIP Publishing.*
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For reducing the power consumption of complementary metal–oxide–semiconductor (CMOS) devices in the near future, Ge has attracted much attention as an alternative to Si for the channel material in field-effect transistors (FETs) because of the higher electron and hole mobilities in Ge (3900 and 1900 cm² V^{−1} s^{−1}, respectively¹) compared with Si (1500 and 450 cm² V^{−1} s^{−1} (Ref. 1)). Using a higher mobility material results in higher current drivability, leading to lower power consumption.

However, an issue in the fabrication of Ge *n*MOSFETs is the high contact resistivity (ρ_C) of metal contacts in *n*⁺Ge source/drain junctions, which results in high power consumption. The high ρ_C is due to the large Schottky barrier height (SBH) originating from Fermi level pinning.^{2,3} Because the charge neutrality level is near the valence band maximum (E_V) of Ge, the Fermi levels of various metals with different work functions tend to be strongly pinned near the E_V . In metal/*p*Ge junctions, Fermi level pinning causes a small SBH for holes (≈ 0.1 eV), leading to low ρ_C . In metal/*n*Ge junctions, however, it causes a large SBH for electrons (≈ 0.6 eV) that is almost the same as the bandgap of Ge, leading to high ρ_C .

One method for modifying the SBH of metal/Ge junctions, such as the NiGe/Ge junction, is segregation of dopants around the NiGe/Ge interface. Ohmic and rectifying characteristics have been reported in NiGe/*n*Ge and NiGe/*p*Ge junctions, respectively, fabricated by germanidation after P ion implantation (I/I).⁴ The modification of the current density–voltage (*J*–*V*) characteristics by P I/I has been explained by segregation of P at the NiGe/Ge interface. For NiGe/*n*Ge junctions fabricated by germanidation after S I/I, a low SBH of 0.15 eV has been reported, as estimated by the Arrhenius plot (temperature dependence of current).⁵

We previously investigated NiGe/Ge diodes doped with S or P or co-doped with both.^{6,7} In NiGe/Ge junctions, S

became segregated at the interface whereas P did not, for both co-doping with S and P and doping with S or P alone.^{6,7} Consistent with our results, a recent study found no segregation of P around the NiGe/Ge interface.⁸ NiGe/*n*Ge doped with S alone exhibited a higher reverse current than did undoped NiGe/*n*Ge. Doping with P alone or co-doping with S and P resulted in ohmic characteristics. The reverse current was higher in NiGe/*n*Ge and lower in the corresponding NiGe/*p*Ge for co-doping with S and P than for doping with P alone. According to the temperature dependence of current, the effective SBH was estimated to be ≈ 0.32 eV for doping with S alone, but < 0.01 eV for both doping with P alone and co-doping with S and P. The effective SBH value was defined as the value estimated by assuming the ideal Schottky current. Thus, co-doping with S and P could decrease the effective SBH for *n*Ge and increase it for *p*Ge.

Se is another chalcogen that, similarly to S, lowers the effective SBH of NiGe/*n*Ge junctions.^{9,10} However, no reports have investigated whether the chalcogen Te has an effect similar to that of S and Se on the SBH. Thus, more data are needed for comparing the effects of these chalcogens on the electrical characteristics of NiGe/Ge junctions. Furthermore, neither co-doping with Se and P nor co-doping with Te and P has been investigated.

Here, we fabricated P- and/or chalcogen-doped Ge substrates and NiGe/Ge diodes to examine their electrical properties and investigated the effects of different chalcogens on the SBH. We found that, compared with doping with P alone, co-doping with P and chalcogen increased electron concentrations in the Ge substrates, even at low temperatures, and also modified the effective SBH of NiGe/Ge junctions to a greater extent.

P- and/or chalcogen-doped Ge substrates and NiGe/Ge diodes were fabricated as previously reported.^{6,7} Briefly, after SiO₂ deposition and contact hole formation on Sb (Ga)-doped *n* (*p*)-type Ge(100) substrates (0.05–0.25 Ω cm), the substrates were implanted with chalcogen (5×10^{14} cm^{−2}) or

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P ($1 \times 10^{15} \text{ cm}^{-2}$) ions or both ($5 \times 10^{14} \text{ cm}^{-2}$ of chalcogen and $1 \times 10^{15} \text{ cm}^{-2}$ of P). The acceleration energies of P, S, Se, and Te were set to 10, 10, 17, and 20 keV, respectively, to achieve the same projected range values. Ni films ($\approx 15 \text{ nm}$ thickness) were deposited on the substrates by sputtering. Rapid thermal annealing was performed for Ni germanidation at 250, 350, or 450 °C in N_2 for 1 min. Unreacted Ni on NiGe was removed using HCl solution. On the back side of each diode, an Al layer was formed by thermal evaporation to reduce the back contact resistance. NiGe/Ge diodes without doping were also fabricated as references. Impurity concentration (N) and electron concentration (n) profiles were examined by secondary ion mass spectrometry (SIMS) and spreading resistance profiling, respectively. The NiGe/Ge interface positions were defined as corresponding to the half-maximum intensities of the Ni peaks in the SIMS profiles. The J - V characteristics of the NiGe/Ge diodes were measured at 223–413 K.

The SBH (Φ) was estimated in two ways. The first was by theoretical fitting with an equation for Schottky current at 300 K, taking into account the series resistance (R_S) and parallel resistance (R_P) based on the following:¹¹

$$J := A^* T^2 \exp \left[-\frac{q\Phi}{k_B T} \right] \left\{ \exp \left[\frac{q(V - JR_S)}{k_B T} \right] - 1 \right\} + \frac{V - JR_S}{R_P}, \quad (1)$$

where the Richardson constant A^* for n -type Ge(100) (resp., p -type Ge) is ≈ 143 (≈ 41) $\text{A cm}^{-2} \text{ K}^{-2}$.¹² The second way was from the temperature dependence of Eq. (1)

$$\Phi = -(k_B/q) \Delta \log(|J|/T^2) / \Delta(1/T). \quad (2)$$

If the measured current can be treated as an ideal Schottky current, then the two SBHs should have almost the same value. This evaluation enables confirmation of whether the current satisfies the Schottky current conduction mechanism.

First, we investigated the profiles in P- and chalcogen-doped Ge before NiGe formation. In the P-doped Ge (Ge:P) and S-doped Ge (Ge:S) [Figs. 1(a) and 1(b), respectively], the N profiles remained unchanged after annealing at 250 to 450 °C, while the n profiles in Ge:P revealed that n increased with temperature. Electron generation ($n \approx 2 \times 10^{16} \text{ cm}^{-3}$) was also observed in Ge:S after annealing at 450 °C [Fig. 1(b)].

The electron generation in chalcogen-doped Ge (Ge:chalcogen) can be explained by the behavior of the chalcogen as a double donor in Ge. Chalcogens in Ge form two different donor levels, E_1 and E_2 , which are occupied by one and two electrons, respectively, and are related to the respective ionization energies: $E(0/+) = 2E_2 - E_1$ and $E(+/++) = E_1$. From the micro- or grand-canonical ensemble in statistical mechanics (e.g., Ref. 13), we can derive the occupation probabilities (f_1 and f_2) of double donors

$$f_1 = 2 \exp [(E_1 + \mu)/k_B T] / \Xi, \quad (3)$$

$$f_2 = \exp [2(E_2 + \mu)/k_B T] / \Xi, \quad (4)$$

where $\Xi := 1 + 2 \exp [(E_1 + \mu)/k_B T] + \exp [2(E_2 + \mu)/k_B T]$ and μ is the Fermi level (chemical potential). Note that the occupation probabilities for double donors are different from

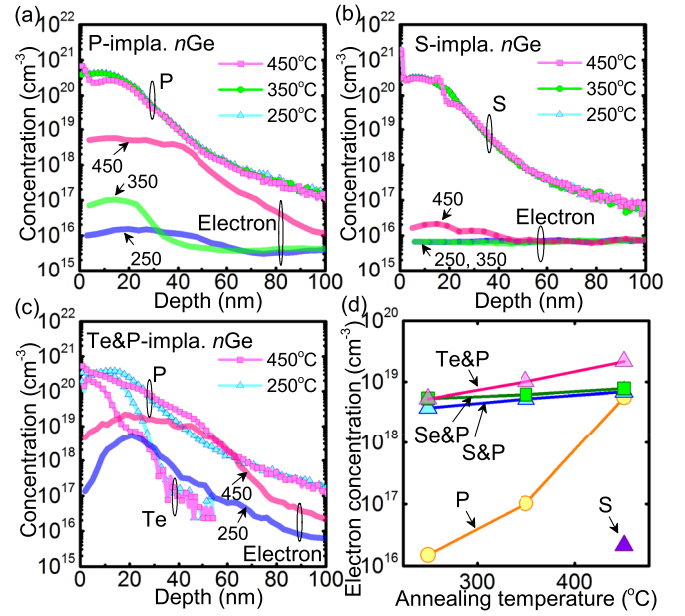


FIG. 1. Profiles of impurity and electron concentrations in Ge. The impurities are (a) P, (b) S, and (c) both Te and P. Annealing temperatures after ion implantation were 250, 350, and 450 °C with an annealing time of 1 min. (d) Relationship between annealing temperature and maximum electron concentration in Ge.

the Fermi–Dirac occupation probability for single donors, such as for P in Ge. For example, in the case of $N_D = 1 \times 10^{18} \text{ cm}^{-3}$ for S, Se, and Te, the calculation based on Eqs. (3) and (4) under the charge-neutrality constraint gives $n/N_D \approx 0.02, 0.03, 0.52$ and $n \approx 2.0 \times 10^{16}, 2.5 \times 10^{16}, 5.2 \times 10^{17} \text{ cm}^{-3}$ where N_D is the donor concentration and n/N_D is the electrical activation ratio at 300 K [$E(+/++) = 0.590, 0.512, \text{ and } 0.332, E(0/+) = 0.280, 0.268, \text{ and } 0.093 \text{ eV}$ for S, Se, and Te in Ge, respectively¹⁴]. Note that for double donors, the maximum activation ratio n/N_D under our definition is 2. The calculation indicates that Ge:Te brings about the highest activation ratio, followed by Ge:Se and then Ge:S.

According to the calculation described above, Ge:S acts as a double donor with a low electrical activation ratio on the order of 10^{-2} at around 300 K and $N_D = 1 \times 10^{18} \text{ cm}^{-3}$. However, the value of $n \approx 2 \times 10^{16} \text{ cm}^{-3}$ in the experiments is lower than expected for $N \approx 10^{20} \text{ cm}^{-3}$ [Fig. 1(b)]. We attributed the low n in Ge:S to the low solid solubility of S in Ge, not to low electrical activation. In Ge:Se and Ge:Te, no increase in n was observed. This was probably due to the lower solubility of Se and Te in Ge compared with that of S in Ge.

Although no increase in n was observed in Ge:Te, a higher increase in n was observed in Ge co-doped with Te and P (Ge:Te&P) than in Ge:P, particularly at 250 °C [Fig. 1(c)]. Figure 1(d) summarizes the relationship between annealing temperature and maximum n in P- and/or chalcogen-doped Ge and reveals that n in Ge co-doped with P and chalcogen (Ge:P&chalcogen) increases with annealing temperature. Among the chalcogens, Te most effectively increased n at higher temperatures.

The increased n in Ge:P&chalcogen was probably due to the chalcogen decreasing the defect density in Ge. Defects occur in Ge due to I/I damage. Because defects such as vacancies¹⁵ and divacancies^{16,17} act as acceptor-like defects,

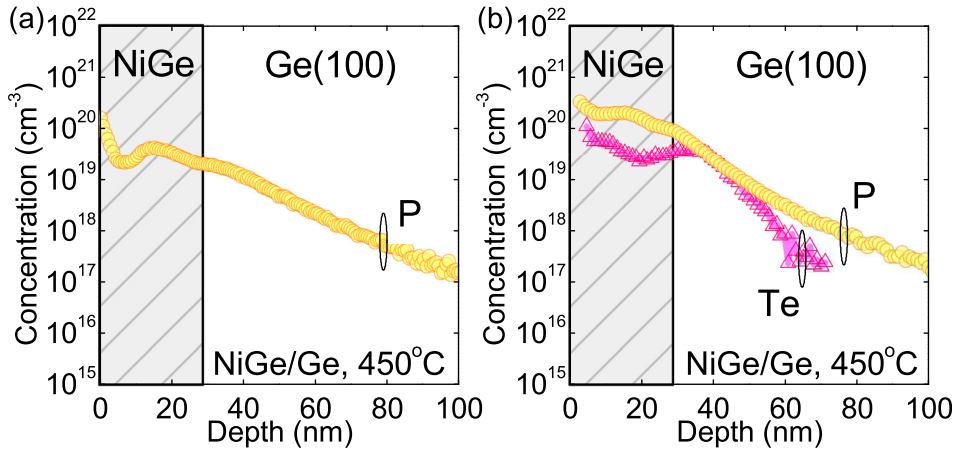


FIG. 2. Profiles of (a) P-doped NiGe/Ge and (b) Te- and P-co-doped NiGe/Ge fabricated by germanidation at 450 °C for 1 min.

they generate holes, which compensate for the electrons from P in Ge and the decrease in n , if the density of defects and the concentration of substitutional P in Ge are comparable. Furthermore, vacancies and P tend to form electrically neutral donor-vacancy (P_2V)⁰ complexes,¹⁸ leading to electrical deactivation of P in Ge. In the case of doping with P alone, high-temperature annealing is necessary to repair I/I damage. In the case of co-doping with P and chalcogen, on the other hand, chalcogens substitute for vacancies, thereby changing defect-related acceptor levels into occupied (donor) levels.¹⁷ Because the electrical activation of chalcogens in Ge is low, the concentration of substitutional chalcogen is greater than n . Therefore, it seems that the chalcogen reduced the number of defects ($\sim 10^{18} \text{ cm}^{-3}$), even though a low n ($\sim 10^{16} \text{ cm}^{-3}$) was generated by doping with chalcogen alone. Furthermore, chalcogen could substitute for the vacancy in (P_2V)⁰, leading to the activation of P in Ge. Thus, co-doping with P and chalcogen increased n more than did doping with P alone, and the difference in n between the two is larger at lower activation temperatures.

Next, we fabricated NiGe/Ge under the same annealing conditions applied to Ge to obtain the profiles in Fig. 1. Figure 2 shows N profiles in Te- and P-co-doped NiGe/Ge (Te&P-NiGe/Ge) and P-doped NiGe/Ge (P-NiGe/Ge) diodes. A region with the same N for Te as for P exists around the NiGe/Ge interface outside the NiGe, although N is lower for Te than for P in the diode without NiGe [Fig. 1(c)]. This tendency also occurred in the cases of co-doping with Se and P and co-doping with S and P, reproducing our previous results showing that S but not P segregated around the NiGe/Ge interface.⁶ This shows that Se and Te segregate similarly to S around the interface.

We investigated the J - V characteristics of the NiGe/Ge diodes that were analyzed to obtain the profiles in Fig. 2. We found that J increased more for the chalcogen-doped NiGe/ n Ge diodes (chalcogen-NiGe/ n Ge) than for the reference diode [Fig. 3(a)]. However, the J - V characteristics still exhibited ohmic behavior for the corresponding chalcogen-NiGe/ p Ge diodes [Fig. 3(b)]. We estimated the SBH values using the two methods described above [Fig. 3(c)], and the results are shown in Fig. 3(d). We can reasonably expect that the SBH estimated from the temperature dependence would be higher than that estimated by theoretical fitting to Eq. (1). That is, we expect the plots to lie below the solid line in

Fig. 3(d), because the temperature dependence of SBH should be similar to that for the bandgap energy (E_G) and E_G decreases with increasing temperature.¹ This tends to lead to slight overestimation of the SBH, but several SBH values exhibited the opposite tendency and were distributed above the solid line in Fig. 3(d). Although the difference was at most 0.2 eV, this value is significant because even a small decrease in the SBH dramatically increases J . For instance, a 0.06 eV decrease in the SBH increases J by an order of magnitude, according to Schottky theory [Eq. (1)]. The difference between the two SBH values indicates that the J - V characteristics of the chalcogen-NiGe/Ge diodes cannot be explained by Schottky theory.

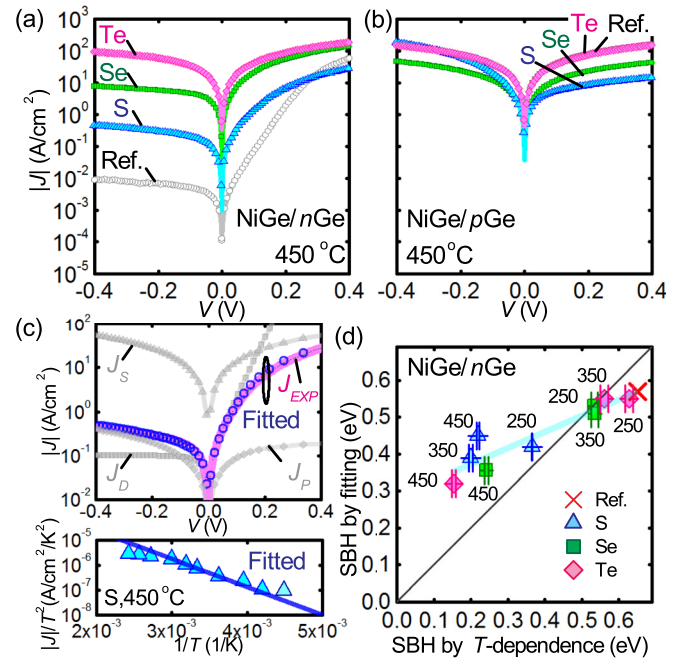


FIG. 3. J - V characteristics of chalcogen (S, Se, or Te)-doped (a) NiGe/ n Ge and (b) NiGe/ p Ge diodes. Results for an undoped NiGe/Ge diode are shown for reference. (c) J - V characteristics fitted using Eq. (1) and Schottky plot of current at 300 K using Eq. (2). J_{EXP} (experimental current) fitted with $J = J_D + J_P$ [Eq. (1)], where J_D is the ideal Schottky current, $J_P [= (V - IR_S)/R_P]$ is the parallel current due to R_P , and $J_S (= V/R_S)$ is the current due to R_S without a diode. Plots for S-doped NiGe/ n Ge fabricated at 450 °C are shown as a representative example. (d) Relationship between SBH values of NiGe/ n Ge estimated from Fig. 1(a) by two methods: theoretical fitting at 300 K using Eq. (1) and Schottky plot of current using Eq. (2).

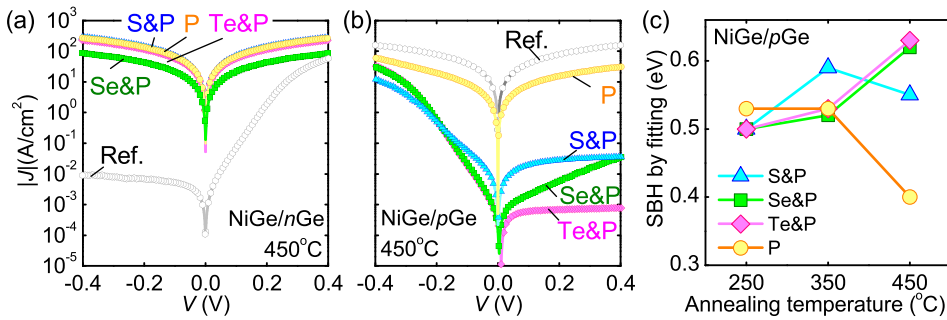


FIG. 4. J - V characteristics of P- and chalcogen (S, Se, or Te)-co-doped (a) NiGe/ n Ge and (b) NiGe/ p Ge diodes. Results for an undoped NiGe/Ge diode are shown for reference. (c) Relationship between annealing temperature for germanium and SBH values of NiGe/ p Ge estimated by theoretical fitting at 300 K using Eq. (1).

Several mechanisms have been proposed for the reduction in the SBH of chalcogen-NiGe/ n Ge junctions. Two possible mechanisms are the formation of a S-Ge dipole layer and a decrease in the interface trap density.⁵ However, neither mechanism can satisfactorily explain the difference between the two SBH values that were estimated in different ways [Fig. 3(d)]. Although this is the case for Si, it has been proposed that S reduces the ρ value of NiSi/ n Si through a doping effect, rather than by reducing the SBH.¹⁹ Since S is an n -type dopant, the band bends with an increase in the concentration of electrically active S, reducing the depletion width. Thermionic field emission, which flows at an energy level between the SBH and the Fermi level of NiSi, is then more dominant than the Schottky current. This mechanism may also be possible for Ge and other chalcogens (i.e., Se and Te) if the solid solubility limit of chalcogens in Ge is larger near the NiGe/Ge interface than in bulk Ge. If chalcogens are present in Ge around the interface, the currents through the chalcogen donor levels may be dominant, which act as assist levels for electrons,^{7,9,10} for example, by trap-assisted tunneling (TAT)²⁰ or the Poole-Frenkel effect (field-assisted thermal ionization).²¹

These models, together with our previously reported model for S-NiGe/Ge,⁷ suggest the following mechanism for SBH modification in chalcogen-NiGe/Ge. In n -type diodes, chalcogen doping reduces the effective SBH through TAT or the Poole-Frenkel effect at low n and through thermionic field emission at high n . Chalcogen-doped NiGe/ n Ge diodes exhibited higher currents in the order of Te, Se, and S, probably because Ge:Te creates high activation ratios in the same order as predicted by the above-mentioned calculation. It has been proposed that the activation temperature of impurities is lower in NiGe/Ge than in bulk Ge because of the effect of metal (Ni)-induced crystallization,⁴ but they could have the same order of the activation ratio. In p -type diodes, chalcogen doping forms an n Ge layer around the NiGe/Ge interface resulting in an n/p junction. This junction acts as a hole barrier, thereby reducing hole current, when the width and height of the barrier are sufficiently large. In contrast with n -type diodes, the donor level of chalcogens in p -type diodes does not cause the current to increase because it does not act as an assist level for holes. The effective SBH of holes thus increases. Here, only a slight decrease in current was observed for chalcogen-NiGe/ p Ge, likely because the increase in the effective SBH of holes was insufficient.

For P- and chalcogen-co-doped NiGe/ n Ge (P&chalcogen-NiGe/ n Ge) diodes, the J - V characteristics exhibited ohmic behavior similar to that of P-NiGe/ n Ge diodes [Fig. 4(a)]. For

the corresponding NiGe/ p Ge diodes, in contrast, the J - V characteristics exhibited rectifying behavior [Fig. 4(b)]. In these NiGe/ p Ge diodes, J decreased more than in the reference diode, and co-doping with Te and P was the most effective for decreasing J . Figure 4(c) shows the relationship between the NiGe formation temperature and SBH value of the NiGe/ p Ge diodes. The chalcogen-NiGe/ p Ge and reference diodes exhibited almost ohmic characteristics [Fig. 3(b)], because the series (substrate) resistance R_s was dominant, limiting the estimated SBH to approximately ≤ 0.3 eV. Therefore, the effective SBH values of only the chalcogen-NiGe/ p Ge and reference diodes were expected to be around 0.3 eV at most. In contrast, for the P-NiGe/ p Ge and P&chalcogen-NiGe/ p Ge diodes, the SBH values were > 0.3 eV. This tendency is explained by the mechanism of effective SBH modification of chalcogen-NiGe/Ge described above. Compared with doping with P or chalcogen alone, co-doping with P and chalcogen was more effective for increasing the SBH. Although the activation temperature level of impurities may differ between NiGe/Ge and bulk Ge, the effect is more likely related to the increase in n from doping Ge:P with chalcogens (Fig. 1).

In summary, doping with P and/or chalcogen (S, Se, or Te) in Ge substrates and NiGe/Ge diodes was investigated to examine the electrical properties of Ge crystals and to modify the effective SBH of NiGe/Ge junctions. We found that electrons were generated in Ge:chalcogen substrates. Despite the low n in Ge:chalcogen, a higher n was observed in Ge:P&chalcogen than in Ge:P. The difference in n between Ge:P&chalcogen and Ge:P was larger, particularly at lower temperature (250 °C). This is probably because chalcogens substitute for defects, such as vacancies or divacancies, eliminating the defect levels in the bandgap. NiGe/Ge diodes were fabricated under the same annealing conditions as for Ge. In NiGe/ n Ge diodes, chalcogen and P co-doping and P doping resulted in ohmic characteristics. In NiGe/ p Ge diodes, chalcogen and P co-doping resulted in rectifying characteristics. This suggests that the chalcogen increased the activation ratio of P around the NiGe/Ge interface. The high-to-low and low-to-high order of Te, Se, and then S for currents in chalcogen-NiGe/ n Ge and P&chalcogen-NiGe/ p Ge junctions, respectively, can be explained by the same order for increasing activation ratios in Ge:chalcogen.

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