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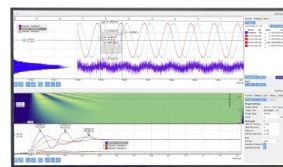
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ABSTRACT

Self-compensation in Ge- and Si-doped Al_{0.3}Ga_{0.7}N has been investigated in terms of the formation of III vacancy and donor-vacancy complexes. Both Ge- and Si-doped AlGa_{0.3}N layers showed a compensation knee behavior with impurity compensation (low doping regime), compensation plateau (medium doping regime), and self-compensation (high doping regime). A maximum free carrier concentration of $4\text{--}5 \times 10^{19} \text{ cm}^{-3}$ was obtained by Ge doping, whereas Si doping resulted in only half of that value, $\sim 2 \times 10^{19} \text{ cm}^{-3}$. A DFT calculation with the grand canonical thermodynamics model was developed to support the hypothesis that the difference in self-compensation arises from the difference in the formation energies of the V_{III}-n•donor complexes relative to their onsite configurations. The model suggested that the V_{III}-2•donor and V_{III}-3•donor complexes were responsible for self-compensation for both Ge- and Si-doped AlGa_{0.3}N. However, a lower free carrier concentration in Si-doped samples was due to a high V_{III}-3•Si concentration, resulting from a lower energy of formation of V_{III}-3•Si.

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Germanium (Ge) is known as a shallow donor in GaN that allows for free carrier concentrations exceeding 10^{20} cm^{-3} .^{1–5} Kirste *et al.* proposed the possibility of plasmonic applications using heavily Ge-doped GaN with a carrier concentration of up to $2.4 \times 10^{20} \text{ cm}^{-3}$.⁵ They observed bandgap renormalization and band filling with the corresponding Moss–Burstein shift in Ge-doped GaN at low temperatures. This allowed for the observation of a bulk and surface plasma resonances, as confirmed by infrared ellipsometry, at 2.8 μm and 5 μm , respectively. Ajay *et al.* demonstrated the highest carrier concentration reported to date in Ge-doped GaN as $6.7 \times 10^{20} \text{ cm}^{-3}$.¹ Unlike Si, which is the most commonly employed dopant for the III-nitrides, heavy Ge doping does not induce tensile stress and surface roughening.³ Gordon *et al.* have proposed by hybrid functional calculations that high carrier concentrations may also be possible in AlGa_{0.3}N by Ge doping.⁶ When the Al mole fraction is higher than 0.52, however, some models predict that Ge undergoes a DX transition where Ge is slightly displaced from the substitutional III-site. As Ge in the DX configuration no longer behaves as a shallow donor, the carrier concentration is expected to be significantly lower than the Ge concentration. This expected decrease in carrier concentration has been experimentally observed at Al mole fractions above 0.5 in Ge-doped AlGa_{0.3}N.^{7–9}

In addition, conductivity in Si-doped AlGa_{0.3}N is reduced when the Si concentration exceeds a certain maximum carrier concentration, i.e., Si doping shows “knee” behavior, arising from self-compensation. Harris *et al.* have identified V_{Al}-n•Si complexes as the primary compensators in highly Si-doped AlN by density functional theory (DFT) calculations using hybrid exchange-correlation functionals.¹⁰ Their calculations indicated that the formation of V_{III}-n•Si with n = 2, 3 became more favorable in the self-compensation regime; thus, the Fermi level decreased with Si concentration, resulting in lower carrier concentrations. We have reported that the onset of self-compensation in Si-doped AlGa_{0.3}N depended on the chemical potentials in the growth environment.¹¹ The formation energy of the compensating point defects was modified through chemical potential control (CPC), which in turn depended on the vapor supersaturation of the growth species. The supersaturation was varied by growth temperature and NH₃ partial pressure. The highest conductivity reported in Si-doped Al_{0.7}Ga_{0.3}N of 160 S/cm with a carrier concentration of $3 \times 10^{19} \text{ cm}^{-3}$ was achieved under metal-rich conditions, which increased the formation energy of V_{III}-related point defects.¹¹ Therefore, a better understanding of compensating point defects is necessary to achieve highly conductive AlGa_{0.3}N layers.

Although a decrease in carrier concentration with increasing Al mole fraction in Ge-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x < 0.5$) has been observed experimentally,^{7–9} i.e., below the composition leading to the DX transition, little is known about the nature of the compensation mechanism. In this study, self-compensation in heavily Ge-doped AlGaIn is investigated. The electronic properties of Ge-doped AlGaIn are compared with Si-doped samples as a way to contrast possible compensation mechanisms. Based on the Hall effect measurement and DFT calculations, we propose that electrically neutral $\text{V}_{\text{III}}\text{-3}\cdot\text{donor}$ and acceptor-type $\text{V}_{\text{III}}\text{-2}\cdot\text{donor}$ complexes are responsible for the observed self-compensation and that Ge is a better choice for highly conductive $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers ($x < 0.5$) due to a lower probability for $\text{V}_{\text{III}}\text{-3}\cdot\text{Ge}$ formation as compared to $\text{V}_{\text{III}}\text{-3}\cdot\text{Si}$ formation.

AlGaIn layers were grown on AlN templates on c-plane sapphire substrates in a vertical, rf-heated, low-pressure MOCVD reactor equipped with an open showerhead. A sapphire substrate surface was exposed to H_2 at 1100 °C for 7 min and annealed in NH_3 ambient at 950 °C for 4 min. A 20-nm-thick AlN nucleation layer was deposited at 650 °C and annealed at 1050 °C for 15 min to obtain Al-polarity.¹² A 300-nm-thick AlN template was grown on the nucleation layer at temperatures ranging from 1150 °C to 1250 °C. The reactor total pressure was kept constant at 20 Torr for all growth runs. Trimethylaluminum (TMA), triethylgallium (TEG), and NH_3 were used as Al, Ga, and N precursors, respectively. GeH_4 (1000 ppm in N_2) and SiH_4 (10 ppm in N_2) were used as the Ge and Si dopant source, respectively. Subsequently, the 500-nm-thick n-type AlGaIn layers were grown on top of 500-nm-thick unintentionally doped AlGaIn layers at 1000 °C in H_2 diluent gas with 1 slm NH_3 flow rate for both dopant types and concentrations. X-ray diffraction measurements were carried out using a Philips X'Pert materials research diffractometer to determine the Al mole fraction in the AlGaIn layers.¹³ Indium metal was employed as Ohmic contact for the Hall effect measurement in the Van der Pauw geometry. Room temperature photoluminescence (PL) was measured to characterize the optical properties of the AlGaIn layers. Si and C concentrations were obtained from secondary ion mass spectroscopy (SIMS), while the Ge concentration was determined by comparing the electrical properties of Ge-doped AlGaIn with ones of Si-doped AlGaIn.

Since all of the AlGaIn samples in this study were grown under the same growth conditions, except Ge and Si precursor flow rates, the difference in the V_{III} -donor induced compensation in Ge-doped and Si-doped AlGaIn layers arose from the dopant type, i.e., formation energy of $\text{V}_{\text{III}}\text{-n}\cdot\text{donor}$ complex. A relatively high growth rate of $\sim 1.5 \mu\text{m/h}$ with high metalorganic flow rates and low growth temperature of 1000 °C enhances the formation of carbon impurities on nitrogen sites (C_{N}),¹¹ which are main acceptor-type compensators.¹⁴ However, these high supersaturation conditions were necessary to suppress the formation of $\text{V}_{\text{III}}\text{-n}\cdot\text{donor}$ complexes to obtain a high free carrier concentration, which was the purpose of this study.

The Al mole fraction targeted in this study was determined based on the following requirements: (1) Ge does not undergo the DX transition. Blasco *et al.* and Bagheri *et al.* have shown a steep increase in the Ge donor activation energy with increasing Al mole fraction above 0.5, resulting in an abrupt drop in the carrier concentration.^{8,9} Since the free carrier concentration is significantly reduced by the DX center formation in Ge-doped AlGaIn in the above-mentioned studies,^{8,9} the Al mole fraction above 0.5 is undesirable to investigate the self-

compensation. (2) When the Al mole fraction is lower than 0.24, the observed carrier concentration was similar to the Ge concentration in GaN.⁸ This observation suggests that self-compensation is not significant at low Al mole fractions. In contrast, more than one order of magnitude lower carrier concentration than Ge concentration in AlGaIn at an Al mole fraction of 0.36 has been observed. Taking into account the Al mole fraction below the DX transition, the reduction of the free carrier concentration is considered to be a consequence of compensation. From these criteria, an Al mole fraction between 0.3 and 0.4 was employed in this study.

The electronic properties of Ge- and Si-doped AlGaIn layers as a function of donor concentration are displayed in Fig. 1. Three different doping regimes were clearly observed in Ge-doped AlGaIn in Fig. 1(a): low, middle, and high doping regimes. In the low doping regime ($[\text{Ge}] < 4 \times 10^{19} \text{ cm}^{-3}$), impurity compensation plays the main role and the electronic properties are determined by the acceptor-type impurities. From the SIMS measurement, the C_{N} concentration was estimated to be $\sim 1 \times 10^{19} \text{ cm}^{-3}$. Due to the C_{N} defects, the mobility collapse was also confirmed in this low doping regime in Fig. 1(a).¹⁵ For both Ge-doped and Si-doped samples, the mobility collapse is seen in Figs. 1(a) and 1(b) at $\sim 1 \times 10^{19} \text{ cm}^{-3}$, which corresponds to the C concentration. As the C concentration was identical in Ge-doped and Si-doped samples, the mobility collapse (or sharp decrease in carrier concentration) occurred at the same donor concentration, $\sim 1\text{--}2 \times 10^{19} \text{ cm}^{-3}$. As the Si concentration was known from the SIMS measurements, the Ge concentration was estimated by observing the mobility collapse in the low doping regime. In addition, threading dislocations also act as carrier compensators in this regime. As suggested by Kyle *et al.*, threading dislocations introduce acceptor-type charge trap states in n-type GaN.¹⁶ The threading dislocations can be compensators with one acceptor charge per c-lattice constant. This translates into acceptor-type trap density of low 10^{17} cm^{-3} in our AlGaIn layers.¹¹ By comparing the compensation levels between C_{N} ($\sim 1 \times 10^{19} \text{ cm}^{-3}$) and threading dislocations (low 10^{17} cm^{-3}), the main compensator in the low doping regime is attributed to the C_{N} defect.

In the middle doping regime, a linear increase in the carrier concentration was observed as a function of Ge concentration. As the Ge concentration increased from $1 \times 10^{20} \text{ cm}^{-3}$ to $2 \times 10^{20} \text{ cm}^{-3}$, the carrier concentration remained relatively constant at $4\text{--}5 \times 10^{19} \text{ cm}^{-3}$, indicating the onset of self-compensation. With a further increase in the Ge concentration in the high doping regime, the carrier concentration exhibited an abrupt drop due to self-compensation ($[\text{Ge}] > 2 \times 10^{20} \text{ cm}^{-3}$). The carrier concentration sharply decreased from $4 \times 10^{19} \text{ cm}^{-3}$ to $3 \times 10^{18} \text{ cm}^{-3}$, while the Ge concentration increased from $2 \times 10^{20} \text{ cm}^{-3}$ to $4 \times 10^{20} \text{ cm}^{-3}$. As seen in Fig. 1(a), Hall mobility also decreased in this regime, indicating a high concentration of carrier scattering centers. Si-doped AlGaIn samples in Fig. 1(b) also exhibited a similar behavior in different doping regimes. Here, complexes between the cation vacancy (V_{III}) and donor were found responsible for compensation.¹¹

One may claim that the secondary phase such as Ge_xN_y layer could be formed due to the heavy Ge doping when exceeding the solubility limit of Ge.^{4,17} However, Ge-doped samples used in this study did not exhibit any significant change in their properties with increasing Ge doping concentration. Although Ge-doped samples showed a high density of hexagonal pits, the surface morphology (not shown)

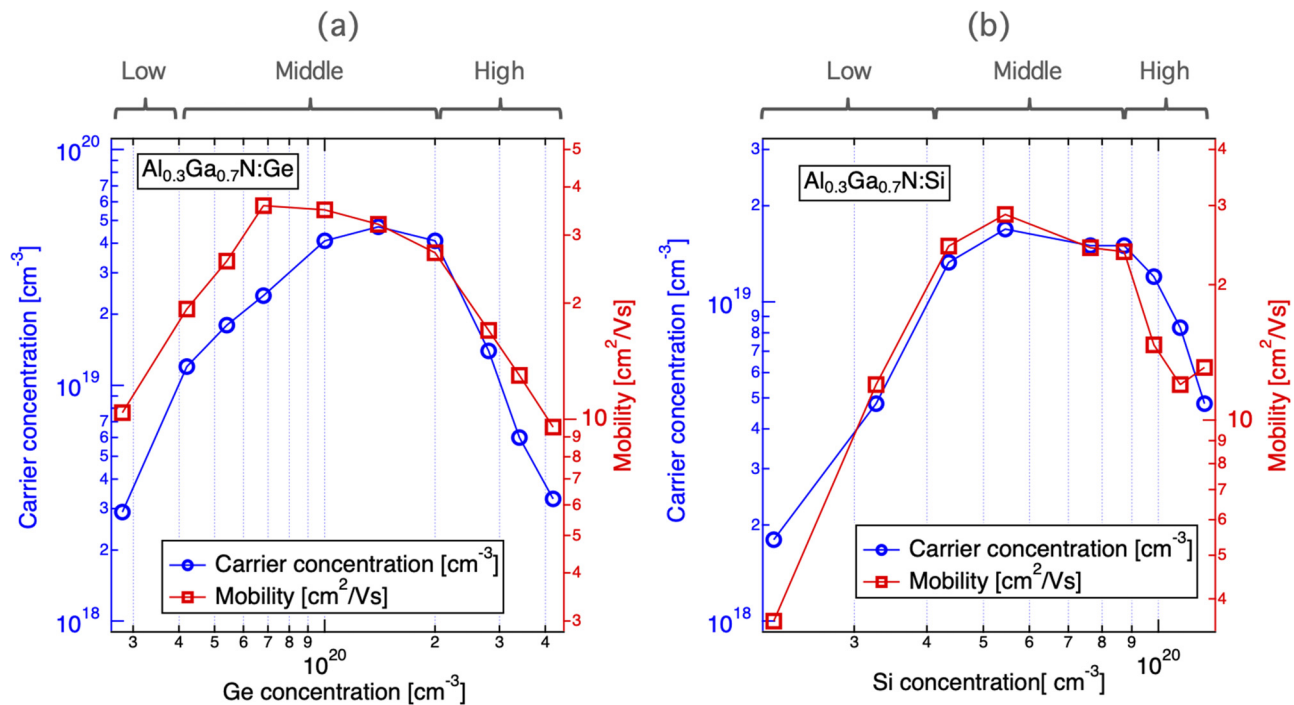


FIG. 1. Free carrier concentration and Hall mobility in (a) Ge-doped and (b) Si-doped AlGaIn as a function of donor (Ge and Si) concentration. Both Ge-doped and Si-doped AlGaIn layers exhibit a decrease in carrier concentration with increasing donor concentration (self-compensation) in the high doping regime.

did not change at a Ge concentration from $\sim 7 \times 10^{19} \text{ cm}^{-3}$ (maximum carrier concentration) to $\sim 2 \times 10^{20} \text{ cm}^{-3}$ (highest Ge concentration in this work), suggesting that the crystallographic symmetry maintained in this Ge concentration range. PL spectra also confirmed no abrupt change in the optical properties by high Ge doping. Furthermore, electrical properties in Fig. 1 were continuously changed with the Ge concentration, as observed in Si-doped samples. The results indicate that the Ge concentration up to $\sim 2 \times 10^{20} \text{ cm}^{-3}$ did not result in the secondary phase formation in our AlGaIn samples.

Compensation mechanisms due to the C_N and threading dislocations in the low doping regime depend on growth parameters and can be assumed to be the same for both dopants under the same growth conditions. The behavior of the two dopant in AlGaIn is displayed in Fig. 2. For Ge-doped AlGaIn, the maximum achieved carrier concentration was $4\text{--}5 \times 10^{19} \text{ cm}^{-3}$, which was more than twice as high as for Si-doped samples ($2 \times 10^{19} \text{ cm}^{-3}$). For both dopants, the carrier concentrations strongly decreased beyond the maximum carrier concentration. The beginning of the self-compensation in Si-doped samples corresponded to the carrier concentration of $\sim 2 \times 10^{19} \text{ cm}^{-3}$ at [Si] $\sim 6 \times 10^{19} \text{ cm}^{-3}$, while the carrier concentration in Ge-doped AlGaIn increased up to $\sim 5 \times 10^{19} \text{ cm}^{-3}$ at [Ge] $\sim 1.4 \times 10^{20} \text{ cm}^{-3}$. In addition, a high pit density of $\sim 10^{10} \text{ cm}^{-2}$ was observed on Si-doped AlGaIn surface with the Si concentration for the maximum carrier concentration ($\sim 2 \times 10^{19} \text{ cm}^{-3}$), while the pit density was relatively low at low 10^9 cm^{-2} in Ge-doped samples at a carrier concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$.

Since the $[C_N]$ and dislocation density were the same for both sets of samples, there must be a difference in the formation of the

related $V_{\text{III}}\text{--}n\cdot\text{donor}$ complexes between the two different donors. As such, the following hypothesis can be formulated: the difference in self-compensation arises from the difference in the formation energies of the $V_{\text{III}}\text{--}n\cdot\text{donor}$ complexes relative to their onsite configurations,

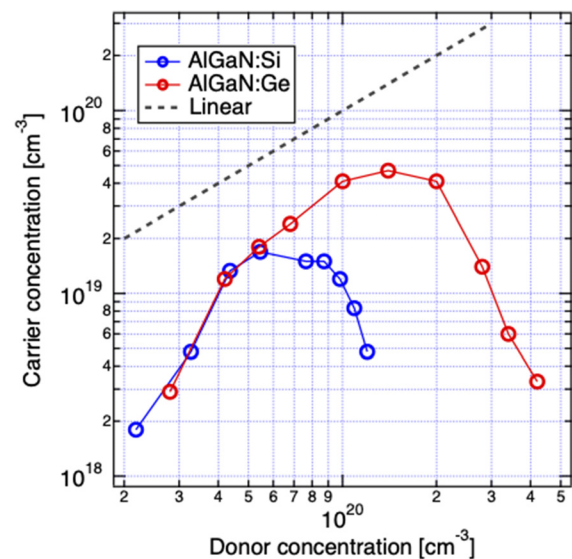


FIG. 2. Carrier concentration in Al_{0.3}Ga_{0.7}N as a function of donor concentration ([Ge] or [Si]). The black dashed line indicates a linear relationship between donor and carrier concentrations.

i.e., $V_{\text{III}}\text{-n}\cdot\text{Ge}$ or $V_{\text{III}}\text{-n}\cdot\text{Si}$ vs substitutional Ge_{III} or Si_{III} . Such differences have been predicted for Si- and Ge-doped GaN,¹⁸ and the differences in efficacy between silicon and germanium in AlN are well known.⁶ To further elaborate on this hypothesis, we developed a computational model based on density functional theory and supported by the asphalt point defect simulation informatics suite (supplementary material).¹⁹ Developing an accurate model that considers the alloy explicitly presents significant computational challenges due to the number of unique configurations of multimember complexes as well as inherently random occupation of Al and Ga atoms on cation sites in $\text{Al}_x\text{Ga}_{1-x}\text{N}$. To circumvent this challenge, we have developed a scheme for projecting computationally obtained defect thermodynamics and the electronic density of states from the endmembers (AlN and GaN) into the alloy, as a first approximation.

Point defects including on-site, DX, vacancies, and multi-donor complexes with up to three donors were simulated in AlN and GaN. Harris *et al.* describe the set of unique configurations for multimember-vacancy complexes $V_{\text{III}}\text{-n}\cdot\text{Si}$ ($n = 1, 2, 3$) in the wurtzite structure.¹⁰ From that set, we consider only those that have been shown to have a considerable effect on compensation, as described in much more depth by Baker *et al.*¹⁸ This set includes unique configurations of the following for both Ge and Si: three single-donor vacancy complexes, seven two-donor vacancy complexes, and six three-donor vacancy complexes. Even with results interpolated from explicit point defect simulations in AlN and GaN, still a significant number of simulations was needed to take into account the different charge states of $V_{\text{III}}\text{-n}\cdot\text{Si}$ and $V_{\text{III}}\text{-n}\cdot\text{Ge}$ complexes and other defects needed to complete the charge balance model.

For the interpolation, the finite-size-corrected DFT, total energies of every charge state of every defect and bulk supercell were linearly interpolated as

$$E_{\text{alloy}}^{\text{tot}} = (n)E_{\text{AlN}}^{\text{tot}} + (1 - n)E_{\text{GaN}}^{\text{tot}},$$

where n is the fraction of aluminum. Chemical potentials were similarly interpolated. The densities of states presented unique challenges in this respect. They were decomposed into valence and conduction bands, and the number of states per unit energy was linearly interpolated. Lastly, the interpolated bands were re-assembled with the band edges set to the linearly interpolated valence band and a band-bowing-corrected interpolated conduction band edge.²⁰

These interpolated data were then used to calculate the concentrations of on-site donors and multi-donor-vacancy complexes in Ge- and Si-doped $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ layers as a function of dopant concentration. Percentages of donors forming multi-donor-vacancy complexes relative to remaining on-site defects are shown in Fig. 3. Solid lines represent the percentages of Ge (red) and Si (blue) remaining on-site as a function of increasing donor concentration and dashed lines represent the percentages of Ge and Si, which form multi-donor-vacancy complexes. These complexes, labeled $V_{\text{III}}\text{-n}\cdot\text{Ge}$ and $V_{\text{III}}\text{-n}\cdot\text{Si}$, contain the single-, two-, and three-donor-vacancy complexes described previously. In the low doping limit, both impurities predominantly incorporate as on-site donors. As the impurity concentration increases, the on-site donors begin to be compensated by multi-donor-vacancy complexes. Comparing the two impurities in Fig. 3, it is found that the percentage of on-site Si drops off faster than on-site Ge, and in the high doping regime, multi-Si-vacancy complexes increase at a faster rate than multi-Ge-vacancy complexes. Further model analysis of

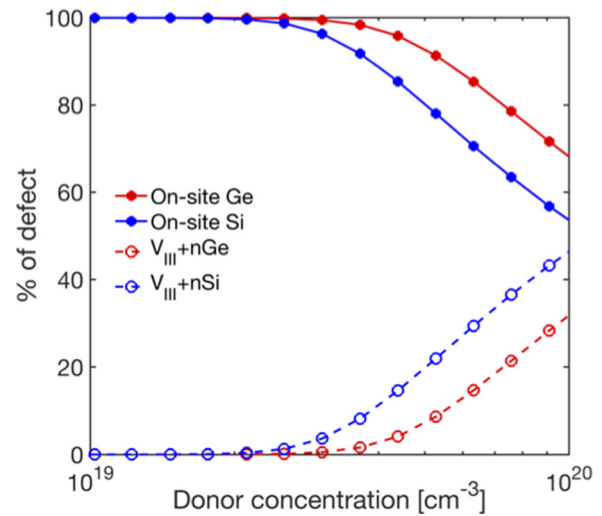


FIG. 3. Percentages of defects that form multi-donor vacancy complexes relative to remaining on-site. Solid lines represent percentages of on-site defects and dashed lines represent the total of multi-donor vacancy complexes $V_{\text{III}}\text{-n}\cdot\text{Ge}$ and $V_{\text{III}}\text{-n}\cdot\text{Si}$, where $n = 1, 2$, and 3 .

multi-donor-vacancy complexes reveals that these percentages are highly sensitive to the donor concentration. As the donor concentration increases to high doping regimes, $V_{\text{III}}\text{-2}\cdot\text{donor}$ and $V_{\text{III}}\text{-3}\cdot\text{donor}$ complexes dominate the total multi-donor-vacancy complex concentration, while single-donor-vacancy complex concentration remains relatively low. These multi-donor-vacancy complexes have previously been shown to contribute to self-compensation.¹⁰ As seen in Fig. 3, the concentration of the $V_{\text{III}}\text{-3}\cdot\text{donor}$ is higher in Si-doped samples in comparison to Ge-doped ones. Due to the rapid increase in the $V_{\text{III}}\text{-3}\cdot\text{Si}$ concentration with the increasing Si doping level, the on-site Si concentration is lower than that of on-site Ge for all doping concentrations. This indicates that a higher % of Si atoms is consumed to form $V_{\text{III}}\text{-3}\cdot\text{Si}$ in the high Si-doped regime. The model offers three basic predictions based on the $V_{\text{III}}\text{-n}\cdot\text{donor}$ complex formation hypothesis: (1) the onset of self-compensation occurs at lower doping levels for Si-doped AlGa_{0.7}N; (2) Ge doping leads to a higher peak carrier concentration (under the same growth conditions), and (3) as the nature of the donor complexes is similar, a qualitative similar optical emission transition (deep luminescence peak) is expected.¹⁰

The first two predictions are consistent with the Hall measurements presented in Figs. 1 and 2. To validate the third prediction, room temperature PL measurements were carried out using a series of Ge- and Si-doped $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$ layers grown with reduced C concentration, i.e., lower metalorganic flow rates. Figure 4 displays the PL spectra from the Ge- and Si-doped AlGa_{0.7}N samples. As expected from our previous study of Si-doped AlGa_{0.7}N,¹¹ the defect luminescence regarding V_{III} and donor complex appears with increasing donor concentration, while the C_N peak was observed in the low doping condition. As seen in Fig. 4(a), when the [Ge] is relatively low, the dominant defect luminescence originates from the C_N defect, whereas the $V_{\text{III}}\text{-n}\cdot\text{Si}$ peak appears in the self-compensation regime. The same trend is also observed in Si-doped AlGa_{0.7}N layers shown in Fig. 4(b). In order to characterize the difference in concentrations of $V_{\text{III}}\text{-n}\cdot\text{Si}$ and

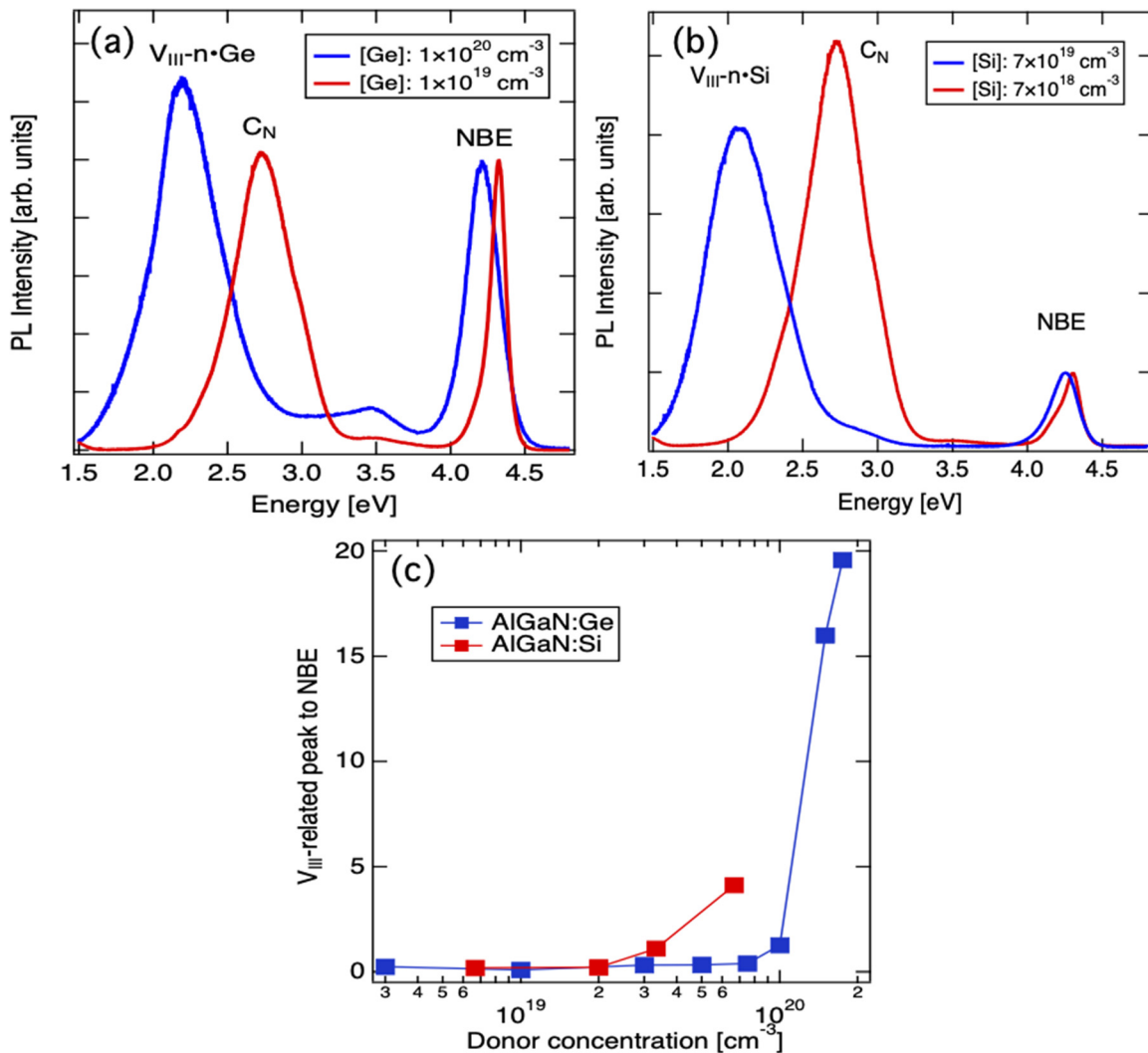


FIG. 4. Room temperature PL spectra from (a) Ge-doped and (b) Si-doped AlGa_{0.3}Ga_{0.7}N. Defect peaks due to C_N at ~2.7 eV and V_{III}-n•D at ~2.1 eV are observed in both Ge- and Si-doped AlGa_{0.3}Ga_{0.7}N. V_{III}-related defect peak intensity as a function of donor concentration is summarized in (c).

V_{III}-n•Ge, the relative intensities to the near band edge peak are plotted in Fig. 4(c). In the low doping regime, there is no clear difference between Ge- and Si-doped samples. A sharp increase in the V_{III}-n•Si peak was observed in Si-doped samples at [Si] ~ 3 × 10¹⁹ cm⁻³, whereas a higher Ge concentration (~1 × 10²⁰ cm⁻³) was needed for the increase in the V_{III}-n•Ge peak. This result suggests that the V_{III}-n•Ge concentration is lower than the V_{III}-n•Si concentration at the same donor concentration, which agrees with predictions (1) and (3) and leads to the observed higher carrier concentrations in Ge-doped AlGa_{0.3}Ga_{0.7}N. As such, Ge offers a technological advantage as a shallow donor over Si for highly conductive Al_xGa_{1-x}N layers (x < 0.5) based on the nature of the self-compensation. This realization is an example of dopant engineering in ultra-wide bandgap semiconductors, where dopant selection is not only based on (1) being a shallow “hydrogenic” donor but (2) also dependent on the compensating

complexes that form with the dopant and (3) their corresponding formation energies.

In summary, self-compensation in Ge- and Si-doped Al_{0.3}Ga_{0.7}N layers has been investigated in terms of III vacancy and donor-vacancy complex (V_{III}-n•Ge and V_{III}-n•Si) formation. Both Ge- and Si-doped AlGa_{0.3}Ga_{0.7}N exhibited a compensation knee behavior composed of impurity compensation, compensation plateau, and self-compensation. A maximum free carrier concentration of 4–5 × 10¹⁹ cm⁻³ was obtained by Ge doping, whereas the carrier concentration achieved in Si-doped samples was only half of that value, ~2 × 10¹⁹ cm⁻³. DFT calculations with the grand canonical thermodynamics computational model supported the hypothesis that the difference in self-compensation arose from the difference in the formation energies of the V_{III}-n•donor complexes relative to their onsite configurations. The model predicted that the major point defects contributing to self-compensation were

V_{III-2} -donor and V_{III-3} -donor complexes for both Ge- and Si-doped AlGaIn. The increase in the on-site Si concentration with doping was not as significant as that of Ge due to the more rapidly increasing V_{III-3} -Si concentration, resulting from the lower formation energy of V_{III-3} -Si. These predictions are consistent with the observed difference in carrier concentration and photoluminescence spectra. This is a good example of dopant engineering in ultra-wide bandgap semiconductors beyond the common rules for traditional semiconductors.

See the [supplementary material](#) for the DFT calculations.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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