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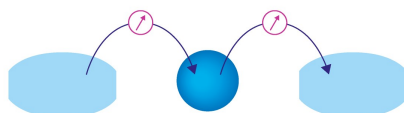
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ABSTRACT

Contrary to the arsenides where donors undergo stable DX transition, we find that Ge in AlGa_N does not suffer from the DX transition; instead, it undergoes a shallow donor (30 meV) to deep donor (150 meV) transition at ~50% Al content in the alloy. This finding is of profound technological importance as it removes fundamental doping limitations in AlGa_N and AlN imposed by the presumed DX⁻¹ acceptor state. The charge state of Ge below and above the transition was determined by co-doping with Si, which remains a shallow donor in AlGa_N for up to 80% Al. It was found that Ge occupied a donor state with a (0/+) thermodynamic transition for AlGa_N alloys below and above the transition. Ge as a shallow donor was completely ionized at room temperature; however, the ionization of the deep donor required elevated temperatures, commensurate with its higher ionization energy. This behavior is not unique to Ge; preliminary findings show that Si and O in AlGa_N may behave similarly.

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INTRODUCTION

Achieving controllable n-type doping in ultra-wide-bandgap Al-rich AlGa_N and AlN will lead to significant breakthroughs in optoelectronics, plasmonics, and high-voltage and high-power electronics.^{1–4} Si and recently Ge have been utilized as shallow donors with low ionization energies (<30 meV) in GaN and AlGa_N. Si remains a shallow donor in Al_xGa_{1-x}N for $x < 0.8$ and Ge for $x < 0.5$,^{5–9} with challenges primarily related to compensation due to impurities and vacancies.^{10–15} Among the solutions to reduce compensation, simple optimizations of the growth conditions via temperature, gas flow, and pressure have been studied.^{10,16–22} Further improvements have been achieved by more advanced approaches involving defect formation energy manipulation via chemical potential and defect quasi-Fermi level control methods.^{12,23–25} However, when Al content exceeds 80% for Si (or equivalently 50% for Ge), an abrupt increase in the ionization energy of the donors is observed, associated with orders of magnitude lower carrier concentrations at room temperature.^{5–9} The abrupt increase in the ionization energy has been attributed to the DX formation as a result of relaxation of

the donor to an off-site configuration.^{5,7,26,27} The DX formation has been understood as a form of self-compensation that results in the coexistence of d⁺ shallow donor and DX⁻ acceptor, where the latter “pins” the bulk Fermi level deeper in the bandgap, resulting in a constant, low carrier concentration that is independent of doping. Consequently, within this model, the DX represents a fundamental upper limit to the free carrier concentration and conductivity in AlN and Al-rich AlGa_N.

DX associated with a shallow to deep center transition with an increase in ionization energy was originally observed in the arsenide system in Te doped Al_xGa_{1-x}As ($x > 0.22$) and later for Si, Ge, and Sn doped AlGaAs. In those cases, the DX was observed to stabilize with increased Al composition or applied hydrostatic pressure.^{28–35} Similar to AlGa_N, DX⁻¹ in AlGaAs resulted in a reduction in carrier concentration and an increase in the ionization energy. To further understand the DX formation, the band structure of AlGaAs was examined. For the zincblende AlGaAs, either increasing the Al content or applying hydrostatic pressure²⁸ shifted all conduction band minima at Γ , L, and X points in the Brillouin zone to higher

energies, albeit at different rates, with the highest change observed at Γ .²⁸ Consequently, above a certain Al composition ($x \sim 0.4$) or an equivalent hydrostatic pressure, AlGaAs was no longer a direct bandgap semiconductor with the Γ subband rising above the L and X subbands. Interestingly, the shallow donor configuration followed the Γ subband, resulting in a low ionization energy in Ga-rich, direct bandgap AlGaAs. However, the DX followed the average energy of the subbands and became more stable than the shallow donor state at higher Al-content or when hydrostatic pressure was applied.^{28,30,36,37} Therefore, the DX formation appeared to be a shallow to deep level transformation of the substitutional donors induced by the relative changes in the conduction subband structure depending on the crystal structure of the host.³⁸ The Chadi and Chang model (CCM) was further employed to explain DX⁻¹ formation of some donors in GaAs and AlGaAs.³⁹ Within this model, DX⁻¹ is a localized deep state occupied by two electrons that repel each other and can be stabilized only by a large lattice relaxation resulting in the strong electron-phonon coupling and bond rupturing, resulting in local trigonal symmetry (C_{3v}).

In contrast to the arsenide system, shallow to deep transition for Si, Ge, or O donors in AlGaN and AlN is not well understood. The nitrides exhibit a wurtzite crystal structure, and their band structure shows the conduction band minimum at Γ point for the entire compositional range (i.e., they retain the direct bandgap even at 100% Al content). However, a shallow to deep transition of the donors in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ was observed along with a sudden increase in the ionization energy (beyond that expected from the influence of the effective mass) from a few tens of meV to a few hundreds of meV when x exceeded 0.8, 0.5, and 0.4 for Si, Ge, and O, respectively.^{5,7,40} Mehnke *et al.* attributed the increased ionization energy of Si:AlGaN for compositions above 80% to the DX formation and identified the DX as an acceptor state via EPR (electron paramagnetic resonance) studies.⁴¹ Similarly, Zeisel *et al.* observed persistent photoconductivity (PPC) and an EPR signal in Si-doped AlN when illuminated by 1.3 eV light and concluded that the Si shallow donor was transitioning into a DX acceptor.⁴² Son *et al.* employed temperature-dependent EPR studies in unintentionally Si-doped AlN and found a DX⁻ configuration with an ionization energy of ~ 150 meV coexisting with on-site Si, which was behaving as a shallow donor.^{43,44} Extending the DX studies to AlGaN, Trinh *et al.* and Nilsson *et al.* concluded the beginning of the negative-U behavior for Si in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (when $x > 0.77$) by measuring temperature-dependent EPR, where the DX⁻ was concluded to form, but was very close to the shallow donor.^{45,46} Gordon *et al.* have predicted the stable DX⁻¹ state for Si, Ge, and O in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ when $x > 0.94$, $x > 0.52$, and $x > 0.61$, respectively. The DX⁻ was expected to shift away from the shallow donor with an increase in the Al composition.²⁶

However, EPR identifies the DX⁻ once it is excited into the neutral shallow donor state with unpaired spin. In fact, Orlinskii *et al.* extended the EPR studies with ENDOR (electron-nuclear double resonance) spectra and identified singlet and triplet states of the shallow donor.⁴⁷ Hence, so far, the DX⁻¹ identification has been indirect. In addition, the lack of the EPR signal at higher temperatures was attributed to either the diamagnetic character of the DX center or broadening of the EPR signal for highly localized

defect centers and could not be used directly as a proof of DX⁻¹ formation.^{33,35} Moreover, elevated temperatures could change the electron occupancy and correspondingly the charge states of other point defects present in AlN whose effect could be recorded as a vanishing EPR signal. Based on EPR and C-V studies, Irmscher *et al.* proposed an alternate explanation of the high resistivity in Si-doped AlN. The coexistence of a shallow impurity band and an acceptor-type electron traps at < 1 eV from the conduction band was modeled to be responsible for the high ionization energy of Si in AlN and the low n-type conductivity.⁴⁸ Furthermore, Skierbiszewski *et al.* performed pressure-dependent conductivity studies in Si-doped $\text{Al}_{0.58}\text{Ga}_{0.42}\text{N}$ and observed a DX-like behavior induced by pressure but attributed a donor characteristic to it, which was contrary to the conventional acceptor DX configuration.⁴⁹ While DX study in nitrides is mainly based on Si doping, only recently Bagheri *et al.* investigated the DX nature by utilizing Ge.⁷ Ge seems to transition to the deep level at lower Al content and provide a better platform for studying DX where other challenges such as ohmic contacts and compensating point defects are not crucial in AlGaN. A sudden increase in the ionization energy of Ge in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ was observed when x exceeds 0.5. Nevertheless, at the transition Al content, two-slope behavior for electron concentration vs temperature was witnessed. It was hypothesized that only the distribution of Ge as shallow and deep donors can lead to the observed behavior and Ge as DX⁻¹ cannot explain the two ionization energies.⁷ However, there exists no direct proof for electron occupancy of Ge and other donors in their deep states in AlGaN.

Therefore, for donors in AlGaN and AlN, mainly the increase in the ionization energy along with the observation of PPC and disappearance of the EPR signal by increasing temperatures were used in the literature to allude to the formation of a donor-related DX⁻¹ state. However, the latter two observations are necessary conditions but not sufficient as evidence for the formation of the DX⁻¹ state. PPC could arise due to macroscopic effects, such as interfaces and surfaces, or due to doping or compositional inhomogeneities, or due to microscopic effects, such as deep point defects acting as traps.^{33,50,51} In addition, PPC has also been observed in GaN and low Al-content AlGa_N, where DX⁻¹ is not expected to be stable.^{52,53}

Consequently, a more direct investigation of the charge state of the "DX" is necessary in III-nitrides. A more direct approach in determining the negative charge state (double electron occupancy) of the DX and its compensating nature can be achieved by co-doping. In this method, one of the dopants is a non-DX-forming shallow donor and the other is the donor whose transition into DX is to be studied. Measuring the concentration of dopants relative to the carrier concentration, the charge state of the DX may be determined.^{31,38,54,55} Employing this method, Baj *et al.* confirmed the negative charge state of the DX related to Ge in GaAs under hydrostatic pressure, where Ge was known to have a transition from a shallow donor to a deep state, hypothesized to be DX as determined by co-doping with Te, which remained a shallow donor under similar conditions.⁵⁴ Therefore, in the zincblende arsenide system, donors were confirmed to undergo DX⁻¹ (with two electron occupancy) transition above a certain Al composition (or a corresponding hydrostatic pressure).⁵⁵ Since Ge and Si in AlGa_N undergo deep level

transition at vastly different compositions (0.5 and 0.8, respectively), they are ideal to study the DX formation in AlGa_N.⁷ Hence, in this work, we used Si and Ge co-doped AlGa_N of various compositions to track the electron occupancy of the Ge deep state.

EXPERIMENTAL

All AlGa_N films were grown on c-oriented sapphire wafers in a vertical, low pressure (20 Torr), RF-heated MOCVD reactor with triethylgallium (TEG), trimethylaluminum (TMA), and ammonia as gallium, aluminum, and nitrogen precursors, respectively.¹³ Prior to the low temperature AlN nucleation layer (20 nm) at 650 °C, the sapphire substrate surface was exposed to H₂ at 1100 °C for 7 min and in NH₃ ambient for nitridation at 950 °C for 4 min. Then the nucleation layer was annealed at 1050 °C for 15 min to obtain Al-polarity prior to the growth of a 100 nm thick high temperature AlN layer at 1200 °C that served as an Al-polar AlN template. The AlN templates were annealed at the atmospheric pressure under N₂ for 1 h at 1700 °C to obtain low dislocation density ($\sim 10^9$ cm⁻²), as described elsewhere.⁵⁶ Subsequently, a 500 nm unintentionally doped AlN layer, followed by a 400 nm thick Ge doped or Ge and Si co-doped AlGa_N layer, were grown. Germane and silane were used as the Ge and Si precursors, respectively. For Ge and Si co-doped samples, Si concentration was maintained constant at 1×10^{19} cm⁻³, while Ge concentration varied from undoped to 5×10^{19} cm⁻³. The AlGa_N layers were grown under a H₂ diluent at 1100 °C under 0.3 slm of NH₃. An ION-TOF time-of-flight secondary ion mass spectrometer (TOF-SIMS) was used to determine the Ge and Si concentrations in AlGa_N films. The acquisition conditions for the non-interlaced sputtering mode used for the measurement are described elsewhere.⁵⁷ Silicon and germanium concentrations were determined under a negative ion detection mode and calibrated against an ion-implanted Al_{0.3}Ga_{0.7}N standard. Accordingly, the doping level variation for each AlGa_N film was less than 20%. The aluminum/gallium ratio was also extracted from the SIMS data following the procedure explained elsewhere⁵⁸ and it agreed with the x-ray diffraction (XRD) measurements of the composition. The dislocation density in AlN template and AlGa_N layers ($\sim 10^9$ cm⁻²), as well as AlGa_N composition, was determined by x-ray diffraction (XRD) using a Philips X'Pert materials research diffractometer with a Cu anode and using methods described elsewhere.⁵⁹ The uncertainty in the Al composition of AlGa_N films was less than 1%. Ohmic contacts were realized on all AlGa_N films by evaporation and rapid thermal annealing of V/Al/Ni/Au metal stacks at 850 °C for 60 s.⁶⁰ Electrical characterization was performed using an 8400 series LakeShore AC/DC Hall measurement system. Room temperature and temperature-dependent carrier concentration measurements were obtained under Van der Pauw configuration in a temperature range of 300–900 K.

RESULTS AND DISCUSSION

The AlGa_N compositions for this study were chosen to address three different scenarios for dopant configurations: (1) Al_{0.4}Ga_{0.6}N, where both Si and Ge behave as shallow donors that are almost fully ionized¹³ at room temperature and the impurities assume the d⁺ state; (2) Al_{0.65}Ga_{0.35}N, where Si behaves as a shallow donor (d⁺) but Ge assumes a deep state (~ 150 meV),^{6,7} which can be either the presumed DX⁻¹ acceptor or a deep donor

with negligible ionization at room temperature, i.e., D⁰, as indicated by our previous work;⁷ and (3) a transitional composition, Al_{0.5}Ga_{0.5}N, where Si behaves as a shallow donor but Ge transitions from the shallow state to a deep state and coexists in both configurations. As such, the Ge transitioning from the shallow state in Al_{0.4}Ga_{0.6}N to a deep state in Al_{0.65}Ga_{0.35}N, while Si remaining a shallow donor, allows for a direct identification of the Ge charge state. To minimize the influence of compensation, primarily C_N and V_{III} complexes, all AlGa_N layers were grown with active compensation control using previously established techniques.^{10,24}

In the first case, we study Al_{0.4}Ga_{0.6}N, where both Si and Ge are shallow donors.

Figure 1(a) shows the measured carrier concentration in Al_{0.4}Ga_{0.6}N as a function of Ge concentration in the absence and presence of Si doping at 10^{19} cm⁻³. Both Ge and Si act as shallow donors and the measured free electron concentration is approximately the sum of Si and Ge concentrations. Both dopants are fully ionized, and the compensation is negligible up to a Ge concentration of 2×10^{19} cm⁻³ (total dopant concentration of 3×10^{19} cm⁻³). At higher Ge concentrations, self-compensation by the formation of V_{III}-nGe_{III} complexes suppresses further increase in the carrier concentration.¹⁵ Figure 1(b) shows the corresponding temperature-dependent carrier concentration for Si (1×10^{19} cm⁻³) doped Al_{0.4}Ga_{0.6}N co-doped with Ge. As expected, a low ionization energy (less than 30 meV) is observed across the entire temperature range with no evidence of any deep states. The shallow donors are hydrogenic-like and their ionization energy depends only on the properties of the host lattice and is independent of the dopant. Therefore, both Ge and Si are in the d⁺ state in Al_{0.4}Ga_{0.6}N.

In the second case, we study Al_{0.65}Ga_{0.35}N, where Si remains a shallow donor and Ge transitions to the deep state that is the subject of this study.⁷

Figure 2(a) shows the room temperature carrier concentration as a function of Ge concentration in the presence and absence of Si (1×10^{19} cm⁻³). In the absence of Si, Ge shows a typical “knee” behavior with carrier concentrations below 10^{17} cm⁻³ and ionization on the order of $\sim 1\%$ for all doping levels. This corresponds to Ge occupying a deep state with an ionization energy of ~ 150 meV.⁷ In order to identify the charge occupancy of this deep state, the samples were co-doped with a verified shallow donor, Si. As expected, a Si-doped sample without Ge showed a carrier concentration corresponding to the Si concentration of $\sim 10^{19}$ cm⁻³. Practically full ionization of Si shifts the Fermi level in AlGa_N close to the conduction band where Ge is predicted to be stable in the deep state.²⁶

When Ge is added to this n-type system, one expects two different outcomes corresponding to Ge being in the neutral D⁰ or DX⁻¹ acceptor state. If Ge behaves as a neutral deep donor, it will not attract electrons from the conduction band and, thus, adding Ge to a Si-doped sample is not expected to change free carrier concentration. In contrast, if Ge forms a negatively charged DX⁻¹ acceptor state, the carrier concentration of the Si-doped samples should decrease as each Ge captures a free electron to form a negative acceptor state. Therefore, a compensation of the free electrons by Ge as the acceptor is expected, which leads to a sudden drop in the carrier concentration as the Ge concentration reaches the Si concentration. As shown in Fig. 2(b), if Ge forms DX⁻¹, the free

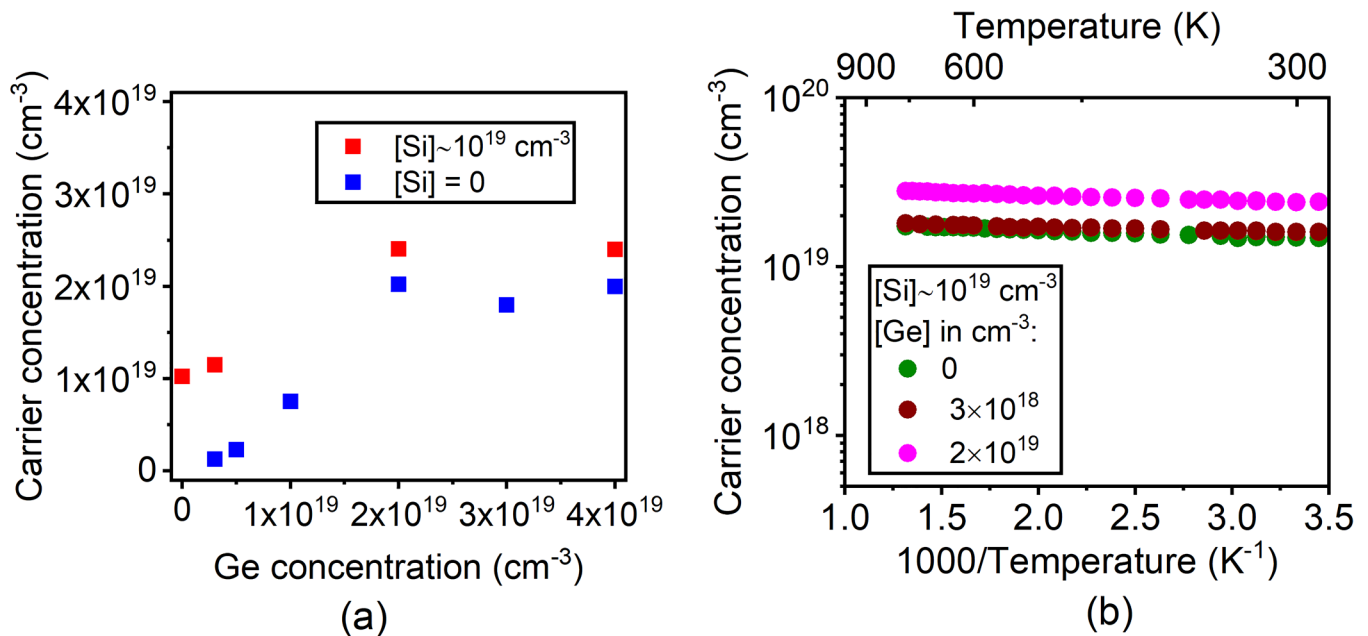


FIG. 1. (a) RT free carrier concentration in $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$ as a function of $[\text{Ge}]$ in the absence (blue) and presence of 10^{19} cm^{-3} Si (red); (b) temperature-dependent carrier concentration for $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$ co-doped with 10^{19} cm^{-3} Si and different amounts of Ge.

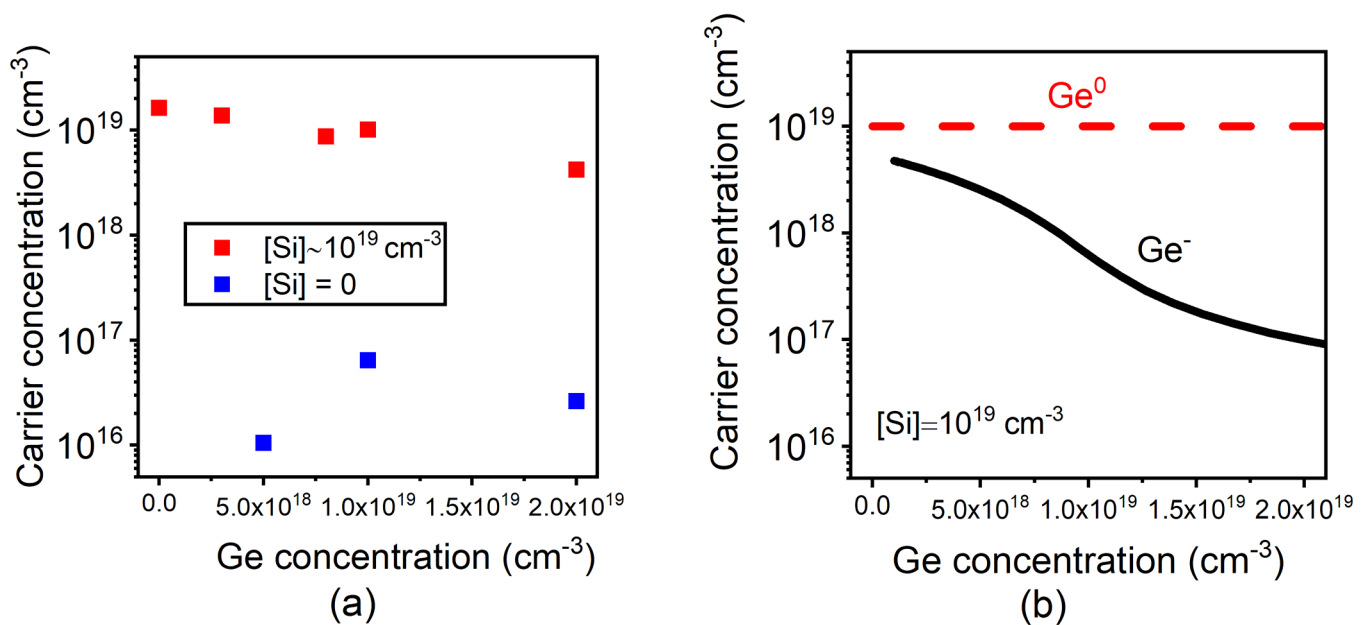


FIG. 2. (a) RT free carrier concentration in $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ as a function of $[\text{Ge}]$ in the absence (blue) and presence of 10^{19} cm^{-3} Si (red); (b) free carrier concentration as a function $[\text{Ge}]$ in Si-doped $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$, calculated from Eq. (1) for Ge^0 (red) and Ge^{-1} (black).

electron concentration should decrease with [Ge] based on the charge balance equation as follows:

$$n = [\text{Si}] - \frac{[\text{Ge}]}{1 + g_A \exp\left(\frac{E_A - E_F}{k_B T}\right)}, \quad (1)$$

where g_A is the degeneracy factor, E_A is the energy level of the Ge acceptor state, and E_F is the Fermi level. Equation (1) assumes negligible compensation, which is reasonable for all total dopant concentrations below $\sim 3 \times 10^{19} \text{ cm}^{-3}$. For the calculations, the ionization energy is assumed to be 150 meV as measured previously.⁷ The calculated carrier concentration for the two scenarios (D^0 and DX^{-1}) is depicted in Fig. 2(b).

As shown in Fig. 2(a), co-doping of Si-doped $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ with Ge resulted in practically constant electron concentrations for a wide range of Ge concentrations. Hence, comparing Figs. 2(a) and 2(b), we may conclude that Ge in $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ has to be in a neutral deep donor state and not in a negative DX^{-1} acceptor state, as the latter should have resulted in the reduction of carrier concentration as [Ge] increases and consequently negligible free electron concentration once [Ge] surpassed [Si]. Interestingly, beyond the knee concentration of Ge, it is expected to self-compensate by forming complexes with V_{III} .¹⁵ Therefore, self-compensation accounts for the minor decrease in free carrier concentration, as shown in Fig. 2(a), which is related to $V_{\text{III}}\text{-nGe}_{\text{III}}$ complex formation; the “knee” in Fig. 2(a) is consistent with that in Fig. 1 and previous studies of heavily doped samples.¹⁵

Figure 3(a) shows the free carrier concentration as a function of temperature in Si-doped (10^{19} cm^{-3}) $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ co-doped with various amounts of Ge. In the absence of Ge, Si behaves as a shallow donor with low ionization energy ($<30 \text{ meV}$) over the entire studied temperature range of 300–900 K. However, all Si and Ge co-doped AlGaIn layers show a second donor that is ionized at higher temperatures, i.e., a deep donor with a higher ionization energy corresponding to the Ge deep donor state. Therefore, the electron concentration of AlGaIn layers is dominated mainly by Si as a source at room temperature where the Ge donor is neutral and negligibly ionized. Expectedly, it does not affect either the Fermi level or the carrier concentration, due to its high activation energy. However, it is ionized at elevated temperatures, resulting in an increase in free carrier concentration beyond [Si], as shown in Fig. 3(a). This is possible only by the presence of a deep donor and not for an acceptor state, as calculated in Fig. 3(b), where Ge acting as a deep acceptor shows a single high ionization energy corresponding to the energy barrier between DX^{-1} and d^+ . The presence of two ionization energies (two slopes) is not predicted considering the charge balance equation for Ge acting as DX^{-1} and is exclusively a signature of two donors. Hence, Ge exhibits a deep (0/+) donor-type thermodynamic transition rather than a (−/+) transition as suggested by prior work.⁷

In Fig. 4, we study the transition of Ge from shallow to deep donor as a function of alloy composition. For all compositions, Ge and Si concentrations are kept constant at $\sim 8 \times 10^{18}$ and $\sim 1 \times 10^{19} \text{ cm}^{-3}$, respectively. All other impurities are at least one order of magnitude lower due to the active management of compensators during the growth.^{12,25} Figure 4(a) indicates the expected

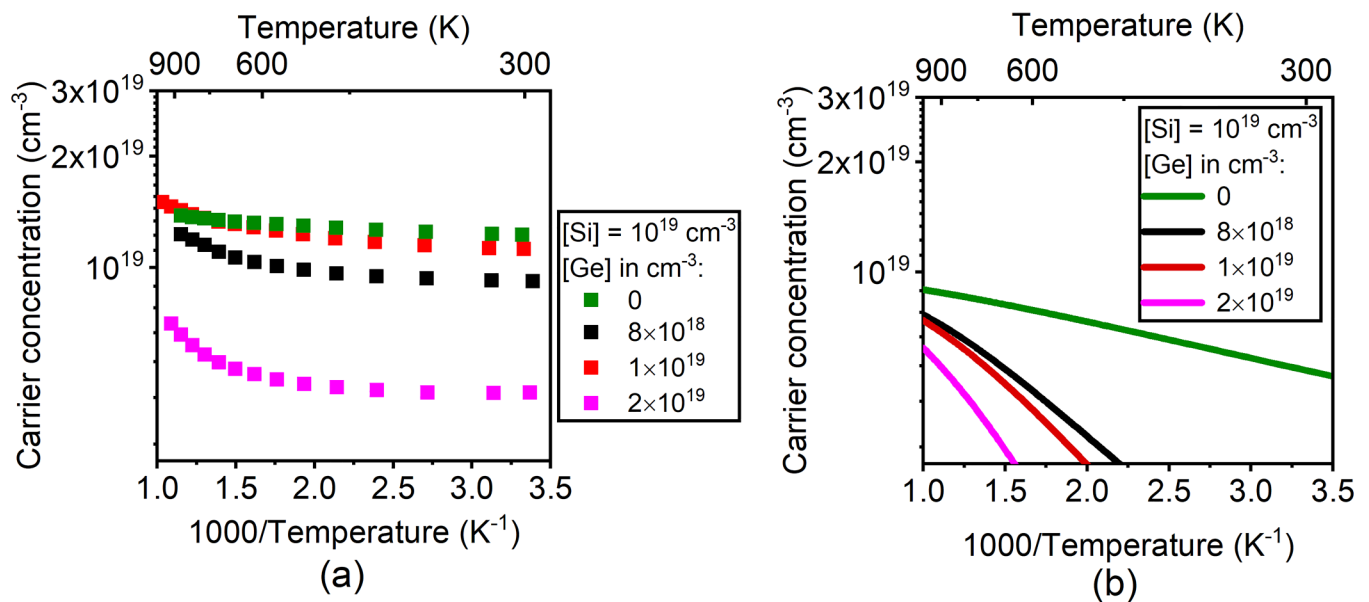


FIG. 3. (a) Temperature-dependent free carrier concentration in $\text{Al}_{0.65}\text{Ga}_{0.35}\text{N}$ co-doped with a constant [Si] of $\sim 1 \times 10^{19} \text{ cm}^{-3}$ and variable [Ge]. (b) Calculated temperature-dependent free carrier concentration simulating doping concentrations in (a) but assuming the coexistence of Ge^{-1} and Si^{+} . Notably, the expected behavior is completely different from that of the experimental data.

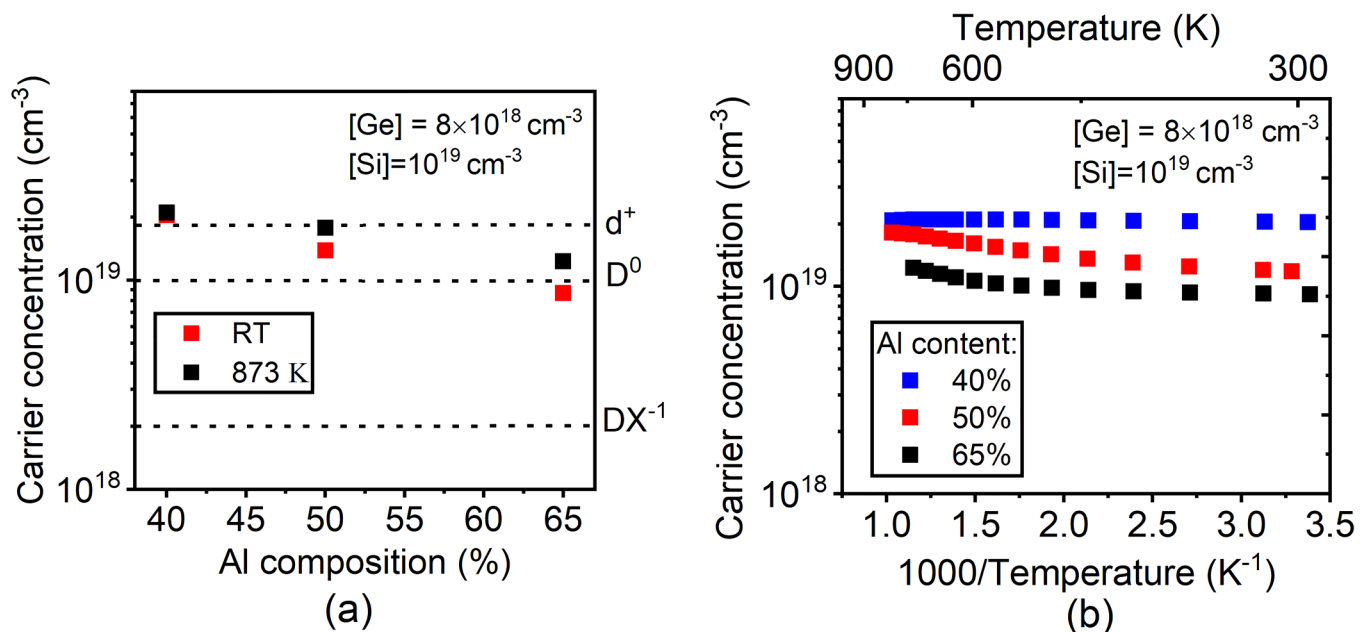


FIG. 4. (a) Free carrier concentration as a function of AlGaIn composition for co-doped samples (Si, $\sim 10^{19} \text{ cm}^{-3}$ and Ge, $\sim 8 \times 10^{18} \text{ cm}^{-3}$) at RT and 873 K. (b) Temperature-dependent carrier concentration of samples in (a).

carrier concentrations for Ge in d⁺, D⁰, and DX⁻¹ states, while Si is at d⁺ state with constant concentration at $1 \times 10^{19} \text{ cm}^{-3}$. While dopant concentrations remain constant, the increase in the Al content causes a reduction in the room temperature carrier concentration. The corresponding reduction is approximately equal to the Ge concentration, as expected from its transition to a deep donor. In contrast, a reduction in carrier concentration twice that of the Ge concentration was observed previously in GaAs co-doped with Te and Ge where Ge was in a DX⁻¹ state.⁵⁴ At higher temperatures, the difference in carrier concentrations decreases due to the partial ionization of the deep Ge donor. Interestingly, in Al_{0.5}Ga_{0.5}N, a distribution of shallow and deep Ge donor states is observed, where at higher temperatures, almost full ionization of the donors is witnessed. In Al_{0.4}Ga_{0.6}N, both Ge and Si are shallow donors with full ionization at room temperature. As for Al_{0.65}Ga_{0.4}N, Si is a shallow donor and Ge is a deep neutral donor.

The change of carrier concentration with temperature for the same samples grown at different Al contents is shown in Fig. 4(b). In Al_{0.4}Ga_{0.6}N, one single ionization energy (<30 meV) is observed, indicating that Ge and Si are both shallow donors with similar ionization energies. On the other hand, Al_{0.65}Ga_{0.4}N shows two ionization energies (two slopes), one for shallow Si and one for deep Ge donor. Al_{0.5}Ga_{0.5}N exhibits the two ionization energies as well and shows a saturation of carriers at the intended doping concentrations at higher temperatures, indicating that a full ionization of the deep Ge donors occurs, as expected.

The observation of Ge as a deep donor requires a revision of the models proposed to explain donor states in Al-rich AlGaIn and AlN.⁴² This work shows that Ge in Al_{0.65}Ga_{0.35}N is neutral with a

(0/+) thermodynamic transition. Consequently, the deep donor state should exhibit a Ge_{III} configuration with a relatively small lattice displacement or relaxation. Since Ge, as the most stable state in Al_{0.65}Ga_{0.35}N, occupies the neutral charge state, the DX⁻¹ state with large lattice relaxation and bond rupturing becomes unstable. As such, the deep donor state is the most stable state in Al_xGa_{1-x}N for $x > 0.6$ where the ionization energy is expected to increase by increasing Al content (>150 meV respectively).

The co-doping experiment is a direct proof of the Ge transition to a deep donor in AlGaIn. It could suggest a similar behavior for other donors, such as Si and O. Recently, a similar distribution of shallow and deep states was reported in Si-implanted AlN, supporting the expectation of a similar behavior for other donors in Al-rich AlGaIn and AlN.^{61,62} As discussed in the Introduction, the DX formation is dependent on the energy shifts of the various Brillouin zone critical points that determine the conduction band minima as a function of alloy composition and pressure. As such, there exists a contrasting behavior between the arsenide systems with a cubic crystal structure and the nitride systems with a wurtzite crystal system. This finding has profound technological consequences: while the DX formation caps the achievable free carrier concentration at a very low level, deep donor formation allows for technologically relevant conductivity. This should inspire additional theoretical studies to understand the nature of the shallow to deep donor transitions in these ultra-wide-bandgap semiconductors.

CONCLUSION

In conclusion, Ge and Si co-doping experiments were used in Al_xGa_{1-x}N ($0.4 < x < 0.65$) to establish the electron occupancy of

the Ge state in AlGa_{0.6}N. Both Ge and Si acted as shallow donors in Al_{0.4}Ga_{0.6}N, exhibiting a single, low ionization energy and practically complete ionization. However, in Ge-doped Al_{0.65}Ga_{0.35}N, carrier concentrations at room temperature were orders of magnitude lower than [Ge]. Co-doping with Si, which served as a source of free electrons, revealed that Ge was neutral at room temperature (neither generating electrons nor causing compensation); at elevated temperatures, Ge behaved as a donor with high ionization energy. No DX⁻¹ with a (-/+) thermodynamic transition was observed. Ge as a deep donor with (0/+) thermodynamic transition was the most stable state in the band; Si is expected to behave similarly in Al-rich AlGa_{0.6}N and AlN. This is at variance with the AlGaAs system, where the donor-related DX⁻¹ was previously proven to be the stable state in AlGaAs (or GaAs under hydrostatic pressure) based on the Chadi-Chang model. The different behaviors of the donors may stem from the basic differences in the arsenide and III-nitride crystal systems and corresponding band structures. The fact that the neutral deep donors are the most stable states (rather than the negatively charged acceptor states) creates a great opportunity in III-nitrides as there are no intrinsic limitations in n-type doping of these ultra-wide-bandgap semiconductors. This should allow for technologically relevant n-type conductivity in Al-rich AlGa_{0.6}N and AlN for applications in optoelectronics and electronics.

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DATA AVAILABILITY

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

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