# The influence of dopant type and carrier concentration on the effective mass and Seebeck coefficient of $GaN_xAs_{1-x}$ thin films

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We probe whether an enhancement in the Seebeck coefficient ($S$) could be obtained in $GaN_xAs_{1-x}$ through interactions between the N resonant states and the GaAs conduction band. Through experimental investigations, we then determined that an insufficient increase in the density of states effective mass ($m_d$) precludes such an enhancement. The relative influences of Group IV/VI dopants and the carrier concentration along with N passivation are discussed. © *2011 American Institute of Physics*. [doi:10.1063/1.3626041]

It has been recently shown that an enhancement of the Seebeck coefficient ($S$) may be obtained in PbTe doped with Tl due to a resonant interaction between the PbTe conduction band (CB) and the Tl energy levels.[1] Such an enhancement then increases the thermoelectric figure of merit, $Z\left(=\frac{S^2 ne\mu}{\kappa}\right)$, where $n$ is the carrier concentration, $e$ is electronic charge, $\mu$ is the carrier mobility, and $\kappa$ the thermal conductivity. We were then motivated by the possible application of this concept to the "highly mismatched alloy" systems,[2] such as N-doped GaAs, i.e., $GaN_xAs_{1-x}$, where resonant interactions between the N energy levels and the GaAs CB are prevalent. Such interactions, as described by the band anti-crossing (BAC) model, involved a splitting of the GaAs CB, which drastically reduced the electronic energy band gap but increased the effective mass, $m_d$, due to the decreased band curvature of the lower split-off branch (the $E_-$ band).[3] The increased $m_d$ then enhances $S$ at a given $n$, as is evident through the following relations derived [4–6] from the Boltzmann transport equation, assuming parabolic band structure and a relaxation time approximation, i.e., $\tau(E) = \tau_0 E^r$ where $\tau_0$ and $r$ are scattering constants (e.g., $r = -0.5$ for strong localized nitrogen impurity scattering,[7–9] $r = 1.5$ for weakly screened ionized impurity etc.[10])

$$n = \frac{1}{2\pi^2}\left(\frac{2k_B T m_d}{\hbar^2}\right)^{3/2}\left[F_{1/2}(\eta)\right], \quad (1)$$

$$S = \mp\frac{k_B}{e}\left[\frac{\left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta)} - \eta\right]. \quad (2)$$

In the above, $k_B$ and $\hbar$ are the Boltzmann and reduced Planck constants, $T$ is temperature, $\eta = \frac{E_F}{k_B T}$ is the reduced Fermi energy, where $E_F$ is the Fermi energy as measured from the CB minimum, and $F_j(\eta) = \int_0^\infty \frac{x^j}{e^{(x-\eta)}+1}dx$ is the $j$th order Fermi integral, which is always positive and increases with $\eta$ and $j$. It is then seen that as $\eta$ is increased (/decreased), this yields an increase (/decrease) of the $n$ and a decrease (/increase) of the $|S|$. Such a contrary relationship then dictates an optimal value for $\eta$ for maximizing the power factor, $S^2\sigma$.[4] However, if $m_d$ is increased, e.g., by the addition of N, while $n$ is held constant, $\eta$ would be reduced with an accompanying enhancement of the $|S|$. Additionally, increasing $r$ would also increase $|S|$.[4]

While N doping is expected to enhance $m_d$ and $|S|$, conventional carrier doping of GaAs, say, with Group IV (e.g., Si) or Group VI (e.g., Te, Se) elements should increase $n$, with minimal impact on the band structure and the $m_d$. However, while Te-doped $GaN_xAs_{1-x}$ have shown an increase in $m_d$,[8] there was a decrease in $m_d$ instead[9] in Se-doped samples. Additionally, mutual passivation of N and Group IV elements could reduce the effective number of N resonant states, thus weakening or even reversing the BAC effects through an increased band gap and a loss of donor contributed $n$.[11] Such passivation occurs when Si atoms which occupy the Ga lattice sites ($Si_{Ga}$) bond with Nitrogen on Arsenic site ($N_{As}$). On the contrary, direct bonding with $N_{As}$ is unlikely with Group VI elements which only occupy the As sites. While isolated N impurities could contribute to resonant energy levels within the host CB, N aggregates could also form *cluster states* with localized energy levels deep within the GaAs bandgap. In the linear combination of isolated nitrogen resonant states (LCINS) framework, such cluster states could yet interact with the $E_-$ band if the band minimum is sufficiently lowered,[12–14] and may also lead to $m_d$ enhancement. Since Si is a common dopant for GaAs, it is important to verify whether Si-N passivation would impact the expected enhancement of $m_d$ and $S$ in $GaN_xAs_{1-x}$. In this paper, we aim to investigate such a possible increase of $S$ in Si-doped $GaN_xAs_{1-x}$ thin films over a range of N content (from $x = 0$ to 0.025) with $n \sim 4\text{-}9 \times 10^{17}$ cm$^{-3}$.

$GaAs_{1-x}N_x$ thin films (~200 nm thick) were fabricated on semi-insulating (100) GaAs substrates through molecular beam epitaxy. The substrates were initially heated to 580 °C

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to desorb native oxide, and a 200 nm GaAs buffer layer was grown to reduce surface roughness. The substrate temperature was then lowered to ∼500 °C during the growth of the active $GaN_xAs_{1-x}$ layer, using elemental Ga and thermally cracked $As_2$ (from $AsH_3$), and N injected from a radical beam source. Si was injected through thermal evaporation. The temperature of the Si source ($T_{Si}$) was varied to modulate the carrier concentration, $n$. The growth rate for the buffer and active layer was ∼0.2 nm/s. The N concentration was estimated from the determined (using x-ray diffraction) film lattice parameters assuming a linear dependence (Vegard's law) between the lattice parameters of GaAs and GaN. The N concentration so estimated has been shown to be comparable to that determined by techniques such as secondary ion mass spectroscopy (SIMS),[15] for $x < 0.030$.[16] However, while the N as determined by SIMS and XRD may be comparable, the *effective* N concentration that actually contributes to effective mass/band gap reduction could be smaller, e.g., due to the formation of cluster states. For example, non-equilibrium synthesis of $GaN_xAs_{1-x}$ (e.g., using pulsed laser melting combined with rapid thermal annealing) has indicated a greater bandgap reduction compared to conventional thin film growth.[15,17] Additionally, ballistic electron emission microscopy photocurrent spectroscopy, and photoresponsivity could be used to measure the effective N concentration.

Patterned electrodes (constituted of Ge/Ni/Au layers of 20/20/100 nm thickness) were deposited, by electron beam evaporation, onto the film to serve as voltage, current, and temperature probes (in the four-wire configuration) for electrical conductivity (/n) and $S$ measurements.[18] It was necessary to anneal the samples at 450 °C in $N_2$ gas for reliable Ohmic contacts. The $n$ was determined from Hall coefficient measurements (in a magnetic field of 0.24 T), while $S$ was calculated from the voltage versus temperature difference ($\Delta T$) slope. The $\Delta T$ were calibrated through the electrical resistance variation and the measured temperature coefficient of resistance. The accuracy of our measurements was consistent with a number of previous studies,[8,9,19,20] as indicated in Figure 1. Comparison with calculations of Eqs. (1) and (2)

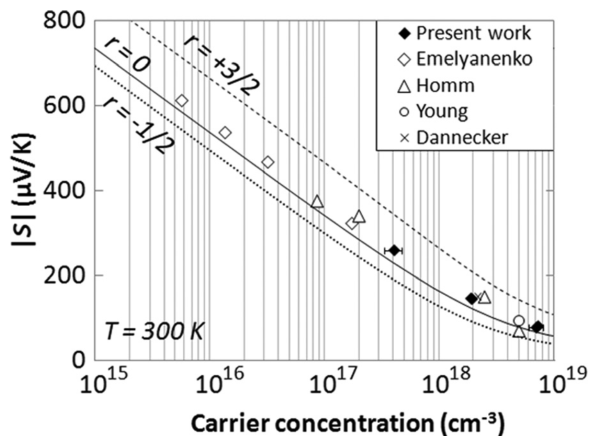


FIG. 1. Seebeck coefficient, $S$ *vs.* carrier concentration, $n$, of GaAs as measured in this work and compared to that of Emelyanenko *et al.* (see Ref. 19), Homm *et al.* (see Ref. 20), Young *et al.* (see Ref. 9), and Dannecker *et al.* (see Ref. 8). Calculated values assuming various $r$ values are indicated through lines.

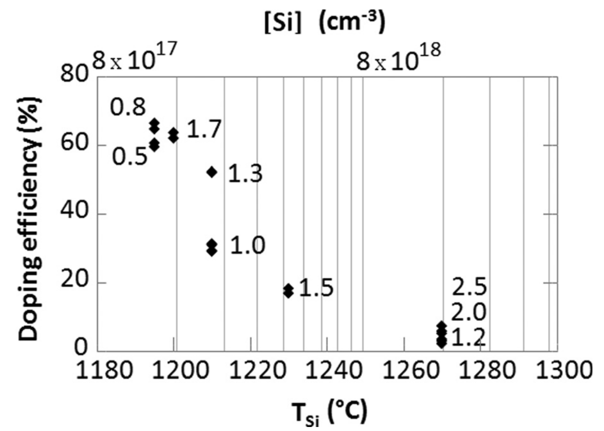


FIG. 2. Doping efficiency *vs* Si cell temperature, $T_{Si}$. The extrapolated Si concentration, $N_{Si}$ is shown on the top axis. The numbers, next to the data points, indicate the N content ($x$ in % in $GaN_xAs_{1-x}$). The $n \sim 4\text{-}9 \times 10^{17}$ cm$^{-3}$ for all the samples.

suggested that $r$ should be slightly greater than 0 for GaAs (e.g., previous measurements[9] suggest $r \sim 0.26$), which seems appropriate for polar optical phonon scattering[10] prevalent in III-V semiconductors at room temperature.[21] The increase in $m_d$ of GaAs from 0.067 to 0.090 $m_o$, as $n$ increases from $10^{16}$ to $10^{19}$ cm$^{-3}$, due to CB non-parabolicity,[22] was also considered.

We now report on the measurements of $GaN_xAs_{1-x}$. We define a *doping efficiency* as the percentage ratio of the measured $n$ in the in $GaN_xAs_{1-x}$ films to the Si concentration: [Si]—estimated from the $n$ measured in nitrogen-free GaAs, assuming $[Si] \approx n$. Such assumption neglects the Si donor ($Si_{Ga}$) compensation by Si acceptors (situated on As lattice sites: $Si_{As}$). However, [Si] may not be much underestimated, as we observed that: (a) the $n$ in GaAs increased exponentially with $T_{Si}$ with no saturation/reduction and (b) the maximum obtained $n$ of $9 \times 10^{18}$ cm$^{-3}$ coincides with the ∼30% compensation of $Si_{Ga}$ by $Si_{As}$.[23] Regardless, the reduction of doping efficiency (to 2%–70% seen in Figure 2) seems to be due to N incorporation. The low efficiency was surprising because, unlike compensation by $Si_{As}$ (which could be long-range), Si-N passivation requires Si to be adjacent to N, which should be rare given the low concentration of both N and Si. It was then probable that the spatial

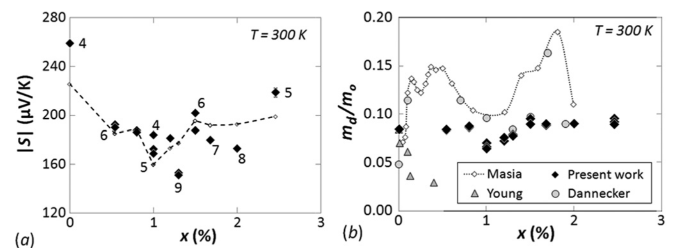


FIG. 3. (a) The Seebeck coefficient variation with percent nitrogen ($x$ in %) in $GaN_xAs_{1-x}$. The numbers, next to the data points, indicate $n$ in units of $10^{17}$ cm$^{-3}$. The dotted line indicate the extrapolation of $S$ to $n = 6 \times 10^{17}$ cm$^{-3}$. (b) The density of states effective mass ($m_d$, as a fraction of the free electron effective mass, $m_o$) as measured in this work, compared to literature, i.e., Young *et al.* (see Ref. 9), Dannecker *et al.* (see Ref. 8), and LCINS model based calculations by Masia *et al.* (see Ref. 14). The error bar for our data is invisible at this scale, while that for Dannecker *et al.*'s data, the error bars (= ±0.019) were omitted for clarity.

distribution of Si and N is not random, but maybe influenced, e.g., by Coulombic attraction between Si and N. Hall measurements on *pre*- and *post*- 450°C annealed samples indicate that much passivation occurred during growth. Extensive Si-N passivation was seen previously,[24] but was not observed when Si was ion-implanted *post*-growth, and annealing >600°C was required to stimulate passivation through Si diffusion.[11] The observed decrease (/increase) in doping efficiency (/passivation) with increasing $x$ and $T_{Si}$ or [Si] may be due to an enhanced surface diffusivity of Si adatoms.

A lower $|S|$ was generally observed with increasing N concentration, as shown in Figure 3(a). For comparison, we calculated the $|S|$ at a particular $n = 6 \times 10^{17}$ cm$^{-3}$ (chosen to coincide with the average carrier concentration in our samples, and to compare with literature[8]) with $m_d$ values determined from experimentally measured $n$ and $S$. The $m_d$—Figure 3(b), was calculated from Eq. (1), with a given $n$ and $T$, and the $\eta$ deduced from Eq. (2) and $S$. While $r = 0$ is assumed for GaAs, for $GaN_xAs_{1-x}$, the $r$ was reduced to $-0.5$, corresponding to previous measurements[9]/assumptions.[8] We note that the $|S|$ initially decreased significantly in the $x = 0$ to 0.005 range, but then increased slightly before exhibiting a minimum at $\sim x = 0.01$. In term of the $m_d$ variation, there seemed to be intriguing similarities and differences between our data and literature, e.g., the minimum at $x = 0.01$—Figure 3(b) predicted by the LCINS model.[8] However, our observed variation seems to be closer to the BAC model. The differences between our results and Dannecker *et al.*[8] could be related to their use of Te as the dopant. On the other hand, Young *et al.*[9] seem to observe an entirely opposite trend, see Figure 3(b), in Se doped $GaN_xAs_{1-x}$ samples (with higher $n \sim 6 \times 10^{18}$ cm$^{-3}$), where a diminished $m_d$ was attributed to band gap reduction as explained through k·p theory.[9]

From the BAC model, as N concentration is increased, the $E_-$ band should flatten and sweep into the band gap, with concomitant resonant interactions with *cluster states* from N aggregates (as specified through the LCINS model[12–14]). Such interactions may then produce an even greater increase in $m_d$. For example, the $m_d$ maxima at $x = 0.003$ and $x = 0.005$ in Figure 3(b) were attributed to interaction with N-Ga-N and N-Ga-N-Ga-N clusters, respectively. Correspondingly, the close relationship of the $m_d$ to the BAC model predicted variation could indicate the absence of such interactions. While passivation has been described in term of bonding of single $Si_{Ga}$ to single $N_{As}$, it is conceivable that Si could also replace Ga in N-Ga-N constituted clusters. Additionally, Si could be more strongly attracted, through Coulomb interactions, to larger N aggregates compared to single N, leading to a disproportionate passivation of the former. Considering that the dramatic increase in $m_d$ predicted by the LCINS model is due to N-Ga-N aggregates whose concentration "is expected to be only a small fraction of total N concentration,"[13] the passivation of such aggregates and the corresponding decrease in effective N clusters could dampen $m_d$ enhancement as observed in our work. Since mutual Si-N passivation is not observed for Group VI elements, similar behavior is unlikely in Se[9]/Te[8] doped samples. However, it is possible, that a pronounced $m_d$ modulation could yet be observed in Si-doped $GaN_xAs_{1-x}$, if Si-N passivation is avoided, say, through doping by *post*-growth ion-implantation.

In conclusion, we observed that the addition of N to Si-doped $GaN_xAs_{1-x}$ ($x = 0.005-0.025$) did not lead to an expected increase in $S$, due to insufficient increase of the $m_d$. However, we found an intriguing dependence of the $m_d$ on N concentration that differs in scale, but not in trend, from the LCINS model. We propose the possibility that Si-N passivation may play a role in disrupting formation of N-Ga-N aggregates, leading to dampened $m_d$ by N cluster states.

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