Electron effective mass in unintentionally doped In$_{0.33}$Ga$_{0.67}$N determined by mid-infrared optical Hall effect

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Mid-infrared optical Hall effect measurements are used to determine the free charge carrier parameters of an unintentionally doped wurtzite-structure c-plane oriented In$_{0.33}$Ga$_{0.67}$N epitaxial layer. Room temperature electron effective mass parameters of $m_\parallel^* = (0.205 \pm 0.013) m_0$ and $m_\perp^* = (0.204 \pm 0.016) m_0$ for polarization perpendicular and parallel to the c-axis, respectively, were determined. The free electron concentration was obtained as $(1.7 \pm 0.2) \times 10^{19} \text{ cm}^{-3}$. Within our uncertainty limits we detect no anisotropy for the electron effective mass parameter and we estimate the upper limit of the possible effective mass anisotropy is $7\%$. We discuss the influence of band nonparabolicity on the electron effective mass parameter as a function of In content. The effective mass parameter is consistent with a linear interpolation scheme between the conduction band mass parameters in GaN and InN when the strong nonparabolicity in InN is included. The In$_{0.33}$Ga$_{0.67}$N electron mobility parameters were found to be anisotropic supporting previous experimental findings for wurtzite-structure GaN, InN, and Al$_x$Ga$_{1-x}$N epitaxial layers with c-plane growth orientation.

Variation of indium content in wurtzite-structure In$_x$Ga$_{1-x}$N permits tuning its bandgap from the near-infrared (NIR) (NIR: InN) to the ultraviolet (UV) (UV: GaN) spectral range.$^\dagger$ Device heterostructures employing low-In content In$_x$Ga$_{1-x}$N alloys ($x < 0.3$) are widely used in blue light emitting diodes, laser diodes and vertical-cavity surface-emitting lasers. On the other hand, higher In content ($x > 0.3$) In$_x$Ga$_{1-x}$N optoelectronic devices for operation at long wavelengths are still emerging. The high electron saturation drift velocity of the two dimensional electron gas in In$_x$Ga$_{1-x}$N ($\sim 2 \times 10^7 \text{ cm s}^{-1}$) makes the material also promising for high frequency and high power electronic switch and transistor applications.$^\ddagger$ Knowledge of free charge carrier properties of In$_x$Ga$_{1-x}$N alloys, and their dependencies on carrier density and In content is prerequisite for device design and operation, and for developing new device architectures. However, reports on electron effective mass, concentration and mobility parameters in In$_x$Ga$_{1-x}$N are scarce.

Density functional tight binding calculations predict nearly linear variation of the electron effective mass parameter in wurtzite-structure In$_x$Ga$_{1-x}$N as a function of In content with a small bowing parameter of $2.27 \times 10^{-3}$. Cyclotron resonance and Shubnikov-de Haas measurements, which can typically be used to experimentally determine the effective mass, require high mobility parameters and thus low temperatures, and/or very high magnetic fields.$^\ddagger$ Alloy disorder and relatively high density of defects in alloyed thin films typically reduce the mobility parameters compared to the binary compounds rendering Cyclotron resonance and Shubnikov-de Haas measurements inapplicable to currently available In$_x$Ga$_{1-x}$N materials. The determination of free charge carrier effective mass at room temperature or higher (under device operation condition) temperature is still a challenging task. There are only few reports which estimate experimentally the effective mass parameters in In$_x$Ga$_{1-x}$N.$^{\ddagger}$ Eljarvat et al. estimated an isotropic average of the electron effective mass parameter between 0.14 $m_0$ and 0.16 $m_0$ ($m_0$ is the free electron mass) for multilayer quantum well structures of In$_{0.05}$Ga$_{0.95}$N and In$_{0.2}$Ga$_{0.8}$N layers using a numerical Kramers-Kronig extension of electron energy loss spectra. Yadav et al. investigated polycrystalline In$_x$Ga$_{1-x}$N layers and estimated isotropically averaged electron effective mass parameters for In contents from 0.4 to 1 combining parameters obtained from electrical Hall effect and optical reflectivity measurements.$^\ddagger$ The reported values vary between 0.13 $m_0$ and 0.42 $m_0$, and carry large uncertainty limits of more than 50%. Furthermore, values determined from the measured plasma frequencies and the estimated energies of Burstein-Moss shifts assuming parabolic bands differ substantially among the reported set.$^\ddagger$

It is well known that the conduction band of InN exhibits nonparabolicity, while in GaN the conduction band is nearly parabolic.$^\ddagger$ Therefore, the electron effective mass increases in InN with increasing free electron density, which was experimentally verified by Hofmann et al. using optical Hall effect measurements.$^\ddagger$ Due to the uniaxial symmetry of the wurtzite lattice structure, the electron effective mass parameter at the conduction band minimum in InN is anisotropic with $m_\parallel^* = 0.050 m_0$, $m_\perp^* = 0.037 m_0$.$^\ddagger$ With increasing carrier concentration the anisotropy vanishes.$^\ddagger$ For GaN the effective mass parameter at the conduction band minimum exhibits negligible anisotropy below 1% with $m_\parallel^* = 0.0237 \pm 0.006 m_0$, $m_\perp^* = 0.228 \pm 0.008 m_0$.$^\ddagger$ With increasing carrier concentration the small anisotropy remains.$^\ddagger$ Feneberg et al. used infrared spectroscopic ellipsometry and showed that the electron effective mass in GaN remains constant for free electron concentrations up to the low $10^{19} \text{ cm}^{-3}$ range, as expected for a parabolic conduction band of GaN.$^{\ddagger}$ Hence, conduction band nonparabolicity is anticipated in In$_x$Ga$_{1-x}$N alloys, and which may vary as a function of the In content. To this end, no ac-
curate effective mass and anisotropy determination has been reported yet for any In content $0 < x < 1$.

Measurements of the optical Hall effect (OHE) provide access to the free charge carrier parameters, including their anisotropy, in contactless manner and does not require prior knowledge of band curvature and band gap parameters.\cite{8,11,12} The OHE is a physical phenomenon that occurs in conductive samples upon interaction with electromagnetic waves with intermediate to terahertz frequencies and in the presence of an external magnetic field. The OHE is manifested in optical birefringence caused by the motion of the free charge carriers under the influence of the Lorentz force, and can be measured by generalized ellipsometry. The free charge carrier properties are then obtained from the ellipsometry data analysis based on parametrized physical model.\cite{13}

In this work we determine the electron effective mass, mobility and concentration parameters of wurtzite In$_{0.33}$Ga$_{0.67}$N using mid-infrared (MIR) OHE measurements. We discuss the results on the electron effective mass parameter in terms of In content and free electron concentration dependence, and estimate the upper limit of the electron effective mass anisotropy that may remain hidden within our present experimental error bars.

An In$_{0.33}$Ga$_{0.67}$N layer with a nominal thickness of 300 nm was grown on an AlN template layer on c-plane sapphire ($\alpha$-Al$_2$O$_3$) substrate by molecular beam epitaxy. Both AlN and In$_{0.33}$Ga$_{0.67}$N epilayers have wurtzite crystal structure with their c-axes perpendicular to the sample surface. The In content was determined using X-ray diffraction measurements. MIR-spectroscopic ellipsometry (SE) measurements (IR-VASe, J.A. Woollam Co., Inc.) at zero magnetic field were carried out in the spectral range from 300-1200 cm$^{-1}$ with a resolution of 1 cm$^{-1}$, and at 55° and 65° angles of incidence. MIR-OHE measurements were performed within the spectral range of 800-1100 cm$^{-1}$ with a resolution of 1 cm$^{-1}$, and at 45° angle of incidence using a custom-built Fourier transform-based generalized ellipsometer system operating in the polarizer-sample-rotating analyzer arrangement.\cite{14} The MIR-OHE measurements were performed at magnetic field strengths of $-6$ T, 0 T and 6 T with the magnetic field vector oriented parallel to the incoming beam. All measurements were performed at room temperature. The optical response of the sample was recorded in terms of $\Psi$ and $\Lambda$ for the MIR-SE, and in terms of Mueller matrix elements for the MIR-OHE measurements.\cite{15}

We employed the following optical model for the data analysis: surface-charge-depleted In$_{0.33}$Ga$_{0.67}$N/conductive In$_{0.33}$Ga$_{0.67}$N/AlN/sapphire. The model dielectric function (MDF) of all constituents contain contribution from IR optical phonon modes, while the surface-charge-depleted and conductive In$_{0.33}$Ga$_{0.67}$N layers contain an additional contribution from free charge carriers. The phonon contribution to the MDF, $\varepsilon_{\omega}^{\text{ph}}$, is accounted for by\cite{16,14}

$$\varepsilon_{\omega}^{\text{ph}} = \varepsilon_{\omega,0} \prod_{j} \left[ \frac{\omega_{\text{TO},j}^{2} - \omega^{2} - i\omega\gamma_{\text{TO},j}}{\omega_{\text{TO},j}^{2} - \omega^{2} - i\omega\gamma_{\text{TO},j}} \right],$$

where $\varepsilon_{\omega,0}$ is the high frequency dielectric constant, $k$ denotes the number of active phonon modes for polarization parallel $j = "||"$ (A$_1$ symmetry) and perpendicular $j = "\perp"$ (E$_1$ symmetry) to the c-axis; $i$ is the imaginary unit; $\omega$ is the angular frequency; $\omega_{\text{TO},j}$, $\omega_{\text{LO},j}$ and $\gamma_{\text{TO},j}$, $\gamma_{\text{LO},j}$ are the transverse optical phonon (TO) and longitudinal optical phonon (LO) modes frequency and broadening parameters, respectively.

The magnetic field dependent free charge carrier contribution, $\varepsilon_{\omega}^{\text{FCC}}$, to the dielectric response of the surface-charge-depleted and conductive In$_{0.33}$Ga$_{0.67}$N layers is accounted for by the classical Drude model augmented by the Lorentz force:\cite{17,14}

$$\varepsilon_{\omega}^{\text{FCC}} = -\varepsilon_{0}^{-1} \left( \omega^{2} + i\omega\gamma - i\omega\omega_{\text{c}} \begin{pmatrix} 0 & -b_x & b_y \\ -b_x & 0 & -b_z \\ b_y & b_z & 0 \end{pmatrix} \right)^{-1},$$

where $I$ is the identity matrix and the magnetic field vector is defined as $\vec{B} = |\vec{B}|(b_x, b_y, b_z)$ in the laboratory coordinate system. At zero magnetic field, the classical Drude contribution is described by the screened plasma frequency tensor, defined as $\omega_p^2 = Nq^2m^{*}-1/\varepsilon_0\varepsilon_{\infty}$, and the plasma broadening tensor $\gamma = \mu m^{*-1}$, which depend on the free charge carrier concentration parameter $N$, and anisotropic mobility $\mu$ and effective mass $m^{*}$ tensors ($\varepsilon_0$ is the vacuum dielectric permittivity, and $q$ the carrier unit charge). At non-zero magnetic field, the cyclotron frequency tensor appears, $\omega_{\text{c}} = q|\vec{B}|m^{*-1}$, which provides independent access to $m^{*}$ and the conductivity type ($\gamma = \pm e$, where $e$ is the electron charge and "$+$" corresponds to p-type while "$-$" to n-type conductivity).

The AlN and sapphire MDFs were obtained from previous investigations (Ref. [14] and [15]) and not varied during the analysis. The MDFs of the conductive and the surface charge depletion In$_{0.33}$Ga$_{0.67}$N layers shared the same phonon mode contributions with the phonon parameters coupled between the two layers. We found during the MIR-SE data analysis that a MDF containing one TO-LO phonon mode pair for $j = "\perp"$ (E$_1$ symmetry) and one phonon mode pair $j = "||"$ (A$_1$ symmetry) suffices to excellently match the experimental data. This is in agreement with the one phonon mode behavior previously reported for InGaN A$_1$(TO) phonon mode from Raman scattering experiments.\cite{16,17} Our result on the one phonon mode behavior of the E$_1$(TO) presents the first experimental confirmation of earlier theoretical predictions using the modified random-element isodisplacement and a rigidion model.\cite{18} The TO and LO mode broadening parameters cannot be differentiated in the case of one phonon mode behavior, and were thus coupled together in our analysis. For wurtzite III-nitride layers with c-plane orientation, SE data are not sensitive to the A$_1$(TO) phonon parameters.\cite{19} Thus, in the data analysis the A$_1$(TO) frequency was set to 504 cm$^{-1}$ according to a linear interpolation between frequencies for GaN and InN.\cite{20} Due to limited sensitivity, the E$_1$(LO) phonon frequency $\omega_{\text{E}_1,\perp}$ was fixed to the linearly interpolated value between the binary parent compounds of 692 cm$^{-1}$.\cite{21} We further assumed an isotropic high-frequency dielectric constant ($\varepsilon_{\infty} = \varepsilon_{\infty,||} = \varepsilon_{\infty,\perp}$). The following parameters: $\varepsilon_{\infty,||}/\varepsilon_0 = (5.48)$, the combined thickness ($d = 302$ nm) of the In$_{0.33}$Ga$_{0.67}$N depletion and conductive layers, and the AlN layer thickness


(d_{AlN} = 1024 nm) were determined from analysis of NIR-UV SE measurements and not varied during the MIR-SE and OHE data analysis. The optical model parameters varied during the MIR-SE and OHE data analysis were the remaining phonon and free charge carrier parameters of the conductive and surface depletion In_{0.33}Ga_{0.67}N layers. The thickness of the surface depletion layer $d_{dep}$ was varied while the combined In_{0.33}Ga_{0.67}N layer thickness was held constant. MIR-SE data ($\Psi$, $\Delta$) and MIR-OHE difference data ($\Delta M$), obtained by subtracting OHE data at 6 T ($M(6 \text{T})$) and 0 T ($M(0 \text{T})$), and -6 T ($M(-6 \text{T})$) magnetic fields, were matched simultaneously.

Measured and the best-match model calculated MIR-SE $\Psi$ and $\Delta$ spectra at 55° and 65° angles of incidence are depicted in Fig. 1. An excellent agreement between measured and calculated spectra is observed. The strong feature at around 950 cm$^{-1}$ is assigned to the A$_1$(LO) phonon coupled to free charge carriers in the conductive In_{0.33}Ga_{0.67}N layer. The subtle spectral feature at around 700 cm$^{-1}$ is associated with the uncoupled A$_1$(LO) phonon in the surface depletion layer by virtue of the Berreman effect. A similar behavior was observed and explained for c-plane oriented Si-doped GaN, and Mg-doped InN layers.$^{19,20}$ The broad feature at around 460 cm$^{-1}$ (Fig. 2) can be represented by a weak Lorentz oscillator with polarization perpendicular to the c-axis, a small TO-LO splitting and a large damping parameter, assigned as an impurity mode. Such low-polarity modes were also observed previously in doped GaN and InGaN.$^{21,22}$

Figure 2 depicts experimental and best-match calculated OHE data in terms of Mueller matrix block off-diagonal element ($\Delta M_{ij}, i j = 13, 31, 23, 32$) difference data between $M(0 \text{T})$ and $M(-6 \text{T})$ data sets. Note that all block off-diagonal Mueller matrix elements are zero without external magnetic field, and all differences therefrom are caused by the magnetic-field induced free charge carrier response in the InGaN layer.

The best-match model parameters for the In_{0.33}Ga_{0.67}N conductive and surface depletion layers are listed in Table 1. We note that a surface depletion in In$_x$Ga$_{1-x}$N films should occur for In contents below 4 where surface accumulation was observed which is consistent with our findings. Our OHE data analysis the effective mass and mobility parameters were allowed to have different values for polarization perpendicular $m^*_\perp$, $\mu^*_\perp$ and parallel $m^*_\parallel$, $\mu^*_\parallel$ to the c-axis. A higher mobility is found along the c-axis with $\mu^*_\parallel = 65 \pm 7 \text{cm}^2/(\text{Vs})$ and $\mu^*_\perp = 30 \pm 1 \text{cm}^2/(\text{Vs})$. A similar anisotropy of the electron mo-
isotropically averaged electron effective mass parameters of GaN and InN for different electron concentrations, assuming parabolic bands in GaN and considering the nonparabolicity in InN. The GaN value reported by Kasic et al. is considered to be independent on the electron concentration.

The linear interpolation for the lowest carrier concentration of $10^{15} \text{cm}^{-3}$ may be seen as the curvature of the conduction band bottom in In$_x$Ga$_{1-x}$N. The electron effective mass parameter determined in this work is larger than the value at the bottom of the conduction band predicted by the linear interpolation. In principle, this may be due to two effects: i) a nonparabolic conduction band in In$_{0.33}$Ga$_{0.67}$N leading to dependence of the electron effective mass on carrier concentration, and/or ii) a nonlinear dependence $m^*(x)$ with significant bowing parameter. A very small effective electron bowing parameter was theoretically predicted for In$_x$Ga$_{1-x}$N. We therefore compare our effective mass parameters with the linear interpolation for the electron concentration in our sample of $1.7 \times 10^{19} \text{cm}^{-3}$. It can be seen from Fig. 3 that within the error bar our result is consistent with this linear interpolation, and thus indicative for nonparabolicity in In$_{0.33}$Ga$_{0.67}$N. A larger bowing parameter, however, cannot be ruled out. Further accurate effective mass parameters in In$_x$Ga$_{1-x}$N with different electron concentrations and different In contents are needed.

In conclusion, the room temperature electron effective mass parameters perpendicular and parallel to the $c$-axis of In$_{0.33}$Ga$_{0.67}$N epilayer are determined to be $m^*_\parallel = (0.205 \pm 0.013) m_0$ and $m^*_\perp = (0.204 \pm 0.016) m_0$ for a free electron concentration of $(1.7 \pm 0.2) \times 10^{19} \text{cm}^{-3}$. Within our uncertainty limits, the electron effective mass parameter is found to be isotropic and the upper limit of the possible relative anisotropy is estimated to be 7%. Our results indicate that nonparabolicity of the conduction band in In$_{0.33}$Ga$_{0.67}$N is likely present. The free electron mobility is found to be is anisotropic with $\mu_\parallel = 30 \pm 1 \text{ cm}^2/\text{Vs}$ and $\mu_\perp = 65 \pm 7 \text{ cm}^2/\text{Vs}$. Our results confirm previous experimental and theoretical findings for the one mode behavior of the $A_1$(LO) phonon and provide experimental support for the theoretical predictions of a one mode behavior of the $E_1$(TO) phonon in InGaN.

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![Electron effective mass parameter in In$_x$Ga$_{1-x}$N as a function of In content $x$. MIR-OHE results determined in this work (● - $m^*_\parallel$, ○ - $m^*_\perp$); InN effective mass from Ref. 8 (● - $m^*_\parallel$, ○ - $m^*_\perp$) and GaN effective mass from Ref. 9 (▲ - $m^*_\parallel$, △ - $m^*_\perp$). The solid lines indicate the linear interpolation of the results in Refs. 8 (InN) and Refs. 9 (GaN), considering the nonparabolicity in InN, and assuming full parabolic behavior in GaN. The color coding represents the free electron concentrations in In$_x$Ga$_{1-x}$N.](image-url)
5

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