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Magneto-optical studies of free-standing hydride-vapor-phase epitaxial GaN

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Magneto-optical studies of donor excitation in hydride-vapor-phase epitaxial GaN are reported. Donor ground-to-excited state transitions are observed in the infrared for Si, O, and a third unidentified donor as a function of magnetic field to 11 T. Transitions from the ground state to $2p_{\pm}$ and $3p_{\pm}$ excited states are studied. Values for effective mass ground and excited state binding energies are determined from the observed excited-state separation. We find a value of 29.1 ± 0.5 meV for the effective-mass donor binding energy in GaN. Ground state binding energies for Si_{Ga} and O_N are 30.18 ± 0.1 meV and 33.20 ± 0.1 meV, respectively. Separation rates for the $2p_+$ and $2p_-$ excited states with magnetic field are consistent with an electron effective mass of $0.22m_0$.

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Epitaxial GaN is an emerging candidate material for fabrication of a variety of optical and electrical semiconductor devices having good high-frequency and high-temperature operational characteristics. Routine production of these devices will depend on the ability to produce layers with engineered electrical properties and on the availability of high-quality substrates onto which the epitaxial layers can be grown by techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). We consider here the properties of unintentionally-introduced impurities in thick wafers of GaN grown by hydride-vapor-phase epitaxy (HVPE), a process potentially capable of providing high-quality substrates for epitaxy.[1]

Although it was observed some time ago that doping with Si or O makes GaN *n*-type, the accurate positions of these donors in the forbidden gap have been known only recently.[2] Donor activation energies have been studied by various techniques including photoluminescence (PL), temperature-scanned Hall effect, and infrared (IR) transmission, often with contradictory results. Here we use IR transmission to study donor excitation transitions in a magnetic field and attempt to reconcile these data with previous observations.

GaN materials used in this study are thick (>100 μm) wafers grown by HVPE that have been removed from their sapphire substrates by laser liftoff.[3] We have studied several unintentionally-doped *n*-type HVPE GaN wafers and have found conductivity dominated by either O or Si donors. Material grown by Samsung Advanced Institute of Technology (SAIT) typically has *n*-type conductivity and a dominance of O donors over Si donors. Background O and Si concentrations in the studied SAIT wafers are in the low 10^{16} cm^{-3} and low 10^{15} cm^{-3} range, respectively, lower concentrations than those typically found for GaN. By these criteria these wafers are of unusually high quality. Both IR transmission and PL data exhibit narrow features, again attesting to the high quality of these wafers. Several wafers were surveyed for donor content and were found to have similar characteristics. The magnetic field study reported here was carried out on one representative SAIT wafer.

A sample cut from a 160-μm-thick 2″ wafer of free-standing *n*-type hexagonal GaN was wedged on the substrate side to an average thickness of 145 μm for IR transmission studies. The slice was placed in a light pipe between condensing cones and inserted into an 11-T superconducting magnet in the Faraday geometry ($E \perp B$) with a gallium-doped germanium IR detector below the sample and outside the magnetic field. The light pipe was filled with a low pressure He gas for thermal contact between the sample and the liquid He cryogen. This cooling technique minimized unintentional strain that could broaden or split the donor excitation transitions. IR transmission spectra were collected with a Bomem DA8 Fourier transform IR spectrometer as a function of magnetic field from the detector low-energy limit at about 70 cm^{-1} to about 500 cm^{-1} where GaN optical phonon absorption became dominant.

Transmittance spectra, as a function of magnetic field in 1 T increments from zero field to 11 T are shown in Fig. 1. Several IR features are observed and most are attributed to ground-to-excited state transitions at three donors designated Si, O, and N3. Details of the identification of dominant donor IR absorption features as intrasite transitions at Si on the Ga site, Si_{Ga}, and O on the N site, O_N, have been published.[2] The donor N3, present in low concentration, remains unidentified. Identifications for most transitions are given at the top, adjacent to the transition at a field of 11 T. Dotted lines are provided as an aid to the eye. Spectral positions observed in these experiments with free-standing samples are shifted toward low energy by approximately 0.3 meV compared with previous observations on sapphire-backed samples[2,4] due, we assume, to reduced strain in wafers removed from their substrates.

All clearly-observed features are identified as transitions from $1s$ ground states of the three donors to their $2p_+$ and $2p_-$ excited states or to the $3p_+$, and $3p_-$ excited states of

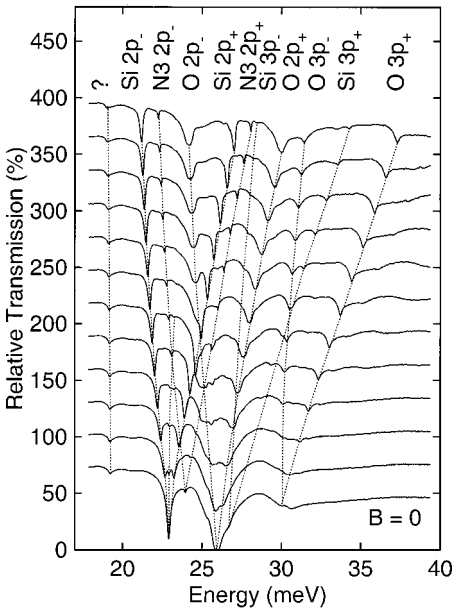

FIG. 1. Transmission spectra as a function of magnetic field in 1 T increments from $B=0$ at the bottom to 11 T at the top. Identifications of absorption lines are given at the top. Dotted lines are a guide to the eye.

Si_{Ga} and O_N with two exceptions. The exceptions are the transitions at the Si donor that is either a transition to $2p_0$ and/or $2s$ and an unidentified transition labeled with a question mark. These spectra clearly show transitions terminating on $3p$ excited states in GaN.

Spectral positions for all clearly-observed absorption lines are plotted in Figs. 2–4 as a function of magnetic field. For clarity, data are presented for each donor separately. Figure 2

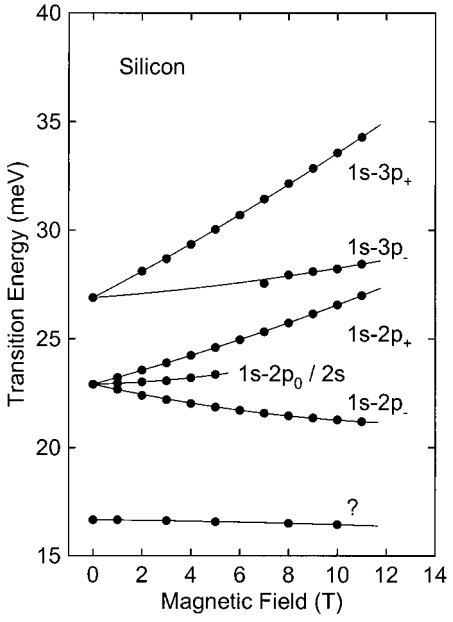

FIG. 2. Positions of transitions associated with Si on the Ga site as a function of magnetic field. The transition near 17 meV was taken from Ref. 4.

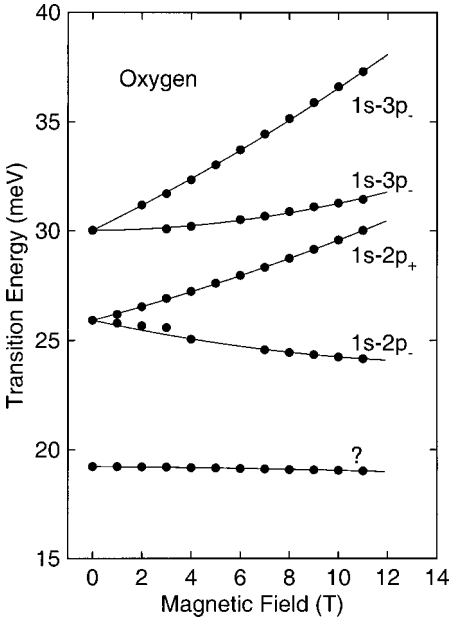

FIG. 3. Positions of transitions associated with O on the N site as a function of magnetic field.

gives line positions for transitions at Si_{Ga}; we observe transitions from $1s$ to $2p_+$, $2p_-$, $3p_+$, $3p_-$, especially at high fields, and to $2p_0$ and/or $2s$ at low fields. In Fig. 2 we have chosen to plot the unidentified transition associated with Si previously observed at 16.96 meV in sapphire-backed HVPE GaN[4] where it should appear (shifted -0.3 meV) in these reduced-strain materials if the concentration of Si were high enough. Similar spectral positions for all clearly-observed transitions at O_N are given in Fig. 3. We observe a transition (19.23 meV at $B=0$) associated with O that can be seen to be similar to the previously observed transition at 16.96 meV associated with Si. Identification of these transitions is not yet clear and will be discussed. Transitions at the unidentified donor N3 are given in Fig. 4.

Electrons or holes weakly bound to donors or acceptors will experience predominantly the Coulombic field of their parent if they are farther than one or two nearest neighbors from their parent donor/acceptor. When closer than a few

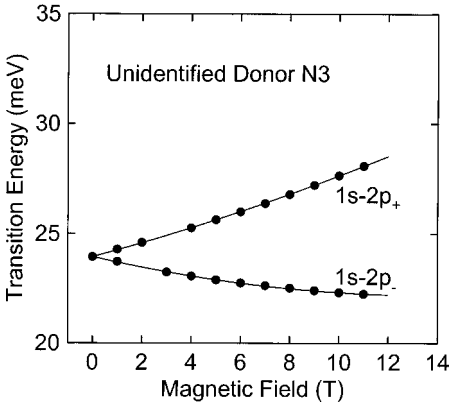

FIG. 4. Positions of transitions at an unidentified donor as a function of magnetic field.

nearest neighbors they can experience details of the parent impurity's local environment. Differences in the local environment cause modifications of the impurity binding energies known as the core shift for different nearly effective-mass centers. The local environment is felt less strongly by *p*-like excited states than by *s*-like ground states so the binding energies of *p*-like excited states typically are in better agreement with values calculated using the effective mass approximation (EMA) than are ground states.[5] Here we observe transitions to two *p*-like excited states at zero field, $1s\text{-}2p_{\pm}$ and $1s\text{-}3p_{\pm}$, for both Si and O. When longitudinal and transverse electron effective masses are the same, the EMA predicts[6] that the binding energies of $2p_{\pm}$ and $3p_{\pm}$ are, respectively, 1/4 and 1/9 times the EMA ground state. Therefore, when two or more *p*-like excited states are observed we can extract EMA ground and excited-state binding energies from the more accurate experimental *p*-like excited state energies alone.

Excitation spectra give the difference in energy between $2p_{\pm}$ and $3p_{\pm}$ as 3.99 meV and 4.10 meV, respectively, for Si and O. We average these experimental determinations to get a value of 4.045 ± 0.06 meV for the $2p_{\pm}$ to $3p_{\pm}$ separation. EMA theory predicts that this separation is 0.1389 times the ground state binding energy, yielding 29.1 ± 0.5 meV for the EMA donor effective Rydberg in GaN.

The donor effective Rydberg found here differs from that calculated by scaling the atomic hydrogen binding energy with the electron effective mass and usual values for static dielectric constant.[7] However, consistency between these approaches is not always found. For example, we have optimized fits of experimental 4.2 K excitation spectra of N in cubic SiC[8] to theory[6] with the dielectric constant as a parameter finding 9.82 for the static dielectric constant. Subsequently we found an accurate static dielectric constant of 9.28 at 4.2 K using IR interference fringes.[9]

From the effective Rydberg we find the EMA $2p_{\pm}$ and $3p_{\pm}$ binding energies and, with experimental $1s\text{-}2p_{\pm}$ transition energies, find Si_{Ga} has its ground state at 30.18 ± 0.1 meV below the conduction band, approximately 1.1 ± 0.5 meV deeper than EMA. Similarly, we find O_N has its ground state at 33.20 ± 0.1 meV below the conduction band, approximately 4.1 ± 0.5 meV deeper than EMA. The conduction band electron effective mass found from the $2p_-$ to $2p_+$ separation is $0.22m_0$, a value consistent with several previous determinations.[4,10,11]

We have carried these measurements to the low energy limit of the Ge:Ga detector in our system, approximately 9 meV, and do not see any donor excitation transitions below the Si transitions. The magnetic field is extremely helpful in making this determination since a moving absorption line is quite easily distinguished from the background of stationary features. Energies of the transitions given in Figs. 2 and 3 show that, at 11 T, the energy of the $1s\text{-}2p_+$ transition is approximately 4.1 meV greater than it is at zero magnetic field. Similarly, the energy of the $1s\text{-}3p_+$ transition is approximately 7.3 meV greater than at zero field. This means we would observe, at 11 T, $1s\text{-}2p_+$ transitions that appear at 4.9 meV at zero field if such transitions were present and we would observe $1s\text{-}3p_+$ transitions which appear at 1.7 meV at zero field if these transitions were present. No transitions are observed at energies lower than those of Si.

Binding energies of donor/acceptor centers near the effective mass energy vary due to center-dependent variations in the local core environment. Centers shallower than effective mass are attributed to negative core shift, that is, an environment within a few nearest neighbors of the center that repels the bound electron/hole. Odd parity excited states typically do not experience even large positive core shifts[5] so they would be expected to have binding energies independent of negative core shifts also. A $1s\text{-}2p_+$ transition at 4.9 meV could be associated only with a donor whose ground state is no deeper than 12.2 meV and a $1s\text{-}3p_+$ transition at 1.7 meV could be associated only with a donor whose ground state is no deeper than 5.0 meV. Therefore, the failure to observe donor excitation lines below the Si lines allows us to set an upper limit of 1×10^{14} cm^{-3} on the concentration of unobserved neutral donors with binding energies between 12.2 meV and 30.2 meV. Similarly, we set the upper limit of 4×10^{15} cm^{-3} on the concentration of unobserved neutral donors with binding energies between 5.0 meV and 12.2 meV.

The unidentified transition at 19.23 meV in Fig. 3 is analogous to the transition plotted in Fig. 2 near 16.66 meV. We earlier attributed[4] that feature to a $1s\text{-}2p_0$ transition of Si_{Ga} shifted from its expected degeneracy with $2p_{\pm}$. However, there are other possibilities. Although $1s\text{-}2s$ transitions are IR forbidden, they sometimes can be observed weakly.[5] One would expect some core shift of a $2s$ state from its expected EMA position if the $1s$ state is core shifted. Here, however, the required core shift of the $2s$ states associated with both Si and O would have to be larger than the observed core shift of their $1s$ states. Other possible origins of these features are transitions at widely separated donor pairs or triads.[12–15] The observation of these transitions associated with both Si and O suggests that these transitions are real and their transition energy follows the impurity's core shift; their identification, however, is not yet clear.

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