Zeeman spectroscopy of shallow donors in GaN

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Gallium nitride grown by hydride vapor phase epitaxy has been studied by infrared spectroscopy in the region of donor intrasite electronic excitations as a function of magnetic field and temperature. Infrared-absorption features which are present only when the sample temperature is cooled to near 4 K have been observed. These features are identified as due to $1s\text{-}2p_{\pm}$ transitions which split in a magnetic field, and a $1s\text{-}2p_0$ transition which does not split. A donor effective mass of $0.22m_0$ is calculated from the rate of splitting with field. We assume that the lower-energy transition occurs at an effective-mass donor and calculate donor binding energies of 31.1 and 33.8 meV for the two donors observed, and a static dielectric constant of 9.8. [S0163-1829(97)01344-1]

Wide-band-gap nitride semiconductors are becoming available with qualities approaching those required for production of commercially competitive visible and near-ultraviolet lasers and for high-frequency transistors. Within this family, GaN, and its alloys with Al and In, are widely produced members.

Typical GaN epitaxial films can have conductivity which varies from highly conducting n type to high resistivity, and the conductivity often varies unpredictably with growth parameters or modifications to the growth apparatus. The identities of the impurities and/or defects responsible for establishing the conductivity of undoped films is not yet known, and the energy levels of intentionally and unintentionally introduced donors and acceptors are topics of ongoing study. Even common dopants such as Si have characteristic energy levels which are not known accurately.

Advances in material quality will be facilitated by improvements in techniques for identifying and quantifying electrically active impurities and native defects. Infrared studies of absorption by electronic intrasite transitions is a nondestructive quantitative analysis technique which easily identifies and quantifies neutral electrically active impurities or defects; in many cases this can be done even when their positions in the band gap are indistinguishable by other means. Usually these studies require films with a thickness ranging from several microns to a few hundred microns. The most successful techniques at this time for growing thick, high-quality films suitable for infrared studies of impurities are metal-organic chemical-vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE).

There is no clear identification of the native donors produced unintentionally during growth by either technique, and no convincing data indicating that they are the same have been published. Therefore, there is the possibility that the unintentionally introduced donors in as-grown materials are not the same for the two techniques. It is also not established that the dominant unintentionally introduced impurities are the same in materials grown in different laboratories. Materials intentionally doped with a specific impurity, e.g., Si, should show similar properties irrespective of the grower or the growth technique. However, the possibility of amphoteric behavior, e.g., Si having different preferred sites for different growth parameters, is present.

Donor activation energies determined by various methods differ widely. For example, Si donors in MOCVD material can have activation energies determined from Hall effect as a function of temperature which are as low as 12 meV.[1] A larger apparent activation energy has been determined from a magneto-optical experiment[2] in which an activation energy of 29.0 meV is quoted based on a linear extrapolation of a feature identified as a $1s\text{-}2p_+$ transition to zero magnetic field, and an assumed effective-mass ground-state energy. An electron effective mass of $0.20m_0$ also was estimated.

It must be recognized that the $1s\text{-}2p_+$ transition energy varies as the cyclotron resonance energy only at high magnetic fields[3] and this requires fields of the order of 120 T or greater for GaN ($m_{\perp}^* \cong 0.22m_0$). When the field is adequately low the $1s\text{-}2p_+$ transition energy varies approximately as half the cyclotron resonance energy. When considering the data of Wang *et al.*[2] we could assume the field is high, expect data varying as the cyclotron resonance energy, and find an effective mass of $0.267m_0$; alternatively, we could assume the field is low, expect data varying as half the cyclotron resonance energy, and find a mass of $0.134m_0$. Both these assumptions appear to be incorrect; their data appear to be in an intermediate-field region. The $1s\text{-}2p_+$ transition energy varies slower than cyclotron resonance, but faster than half that rate. Theory predicts the behavior of excited states in the intermediate-field region, but requires that the effective mass be known and used as an input parameter in that prediction. Consequently, in the intermediate-field region the donor binding energy cannot be found accurately from a linear extrapolation, and effective masses cannot be obtained from the $1s\text{-}2p_+$ transition.

The splitting between the $2p_+$ and $2p_-$ states is, to a good approximation, equal to the cyclotron resonance energy at all magnetic fields, and therefore an observation of the separation between $1s\text{-}2p_-$ and $1s\text{-}2p_+$ transitions in a

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magnetic field can be used to determine effective masses. When this experiment is done at zero magnetic field, the energy of the degenerate $1s$-$2p_\pm$ transition determines the excited-state binding energy and the ground-state binding energy if the donor is well described by effective-mass theory.

In previous work on HVPE materials, the effective-mass transverse to the c axis has been determined from cyclotron resonance, yielding a value of $0.22m_0$.[4] Also in that work, an electronic intrasite transition, assumed to be $1s$-$2p_\pm$, at an unknown donor was observed in transmission at 26.7 meV. A donor that is well described by the effective-mass model, i.e., one with a negligible chemical shift, and that has a 26.7-meV $1s$-$2p_\pm$ transition energy should have its ground state at 35.5 meV.[4,5] This donor's thermal activation energy was estimated based on thermal depletion of the strength of the $1s$-$2p_\pm$ transition of the neutral impurity, and assumption of an $E_D/2$ dependence. A thermal activation energy $E_D = 20$ meV ($E_D/2 = 10$ meV) was determined. This is significantly smaller than the $\cong 35.5$ meV optical activation energy.

The observation of different activation energies in thermal equilibrium experiments, including Hall effect, and optical experiments is similar to early work on CVD 3C-SiC grown on Si, in which the dominant donor, identified as substitutional N, had a thermal activation energy of the order of 15 meV but an optical value near 54 meV (Ref. 6) in the same samples. There is not yet complete agreement on the origin of this discrepancy in SiC, and we know of no fully satisfactory theory which models a donor that exhibits simultaneously a binding energy reduced by a high donor concentration in thermal equilibrium experiments and optical properties characteristic of isolated centers.

A specific donor can, however, exhibit different properties in different regions of a sample. For example, activation energies measured by the temperature-scanned Hall effect are not necessarily the same as activation energies determined from infrared transmission on the same sample. A thick epitaxial film with a low donor concentration throughout most of its thickness but with a thin, degenerate n-type layer adjacent to the substrate[7] may have transport which is noticeably affected by the degenerate layer and optical properties reflecting primarily the low-concentration bulk region. Donor excitation features of the degenerate layer may be sufficiently broadened to be unobservable in infrared transmission measurements.

In this paper, we present results of infrared transmission measurements which show clear $1s$-$2p_\pm$ donor excitation spectra of two donors in undoped HVPE GaN in magnetic fields to 10 T. We determine the transverse effective mass from the $2p_\pm$ splitting, estimate the binding energies of the donors using effective-mass theory, and derive a value for the static dielectric constant. An absorption identified as a $1s$-$2p_0$ transition also is observed.

The GaN films were grown by HVPE in a vertical reactor configuration on (0001) sapphire substrates utilizing a ZnO pretreatment.[8] The films were approximately 20 and 40 μm thick, and optical microscopy did not reveal any thermally induced cracks. Room-temperature electron concentrations, as measured by Hall and Hg-probe capacitance-voltage measurements, were $< 1 \times 10^{17}$ cm^{-3} and room-temperature Hall mobilities were usually 500–880 cm^2 V$^-$ s^{-1}.
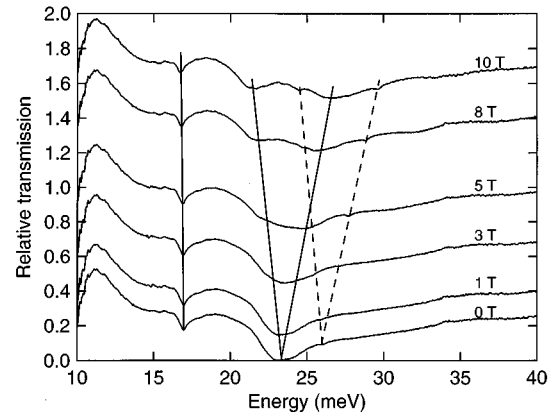

FIG. 1. Infrared transmission spectra for magnetic fields to 10 T with $E \perp B$ and $B \| c$ axes. Spectra are offset by an amount proportional to the magnetic field. The measurement temperature was near 4.2 K.

Samples were wedged on the substrate side to minimize interference effects, mounted in a light pipe containing a low-pressure He atmosphere for efficient cooling, and placed in a superconducting magnet cooled to 4.2 K. Infrared spectra were acquired with a Bomem DA 3.02 Fourier transform infrared (FTIR) spectrometer. The sample plane, perpendicular to the crystalline c axis, was oriented with the magnetic field parallel and the infrared electric field perpendicular to the c axis (Faraday orientation).

The observed infrared-absorption lines were identified as electronic in origin by warming the samples above 4.2 K. The warming experiment was performed with the samples attached by rubber cement to a cooled Cu block with a calibrated heat sensor. The cementing procedure did not provide a tight thermal coupling to the cooled block so the temperature of the samples was not known accurately. Warming caused rapid reduction in strength of the transitions identified as electronic and none were visible at 300 K.

Two HVPE samples were studied. Both had the same set of donor excitation absorption lines, but one sample exhibited significant overabsorption at the strongest line. Only the sample having the lower donor content was studied as a function of field, since its narrower lines facilitated observation of the field-induced splitting.

The spectra acquired are shown in Fig. 1, and the observed absorption line positions are plotted in Fig. 2 as a function of magnetic field. Three electronic absorption lines are present at $B = 0$, a weak absorption at 25.95 meV, a strong absorption at 23.30 meV, and an intermediate strength one at 16.96 meV. As the field increases, the 25.95- and 23.30-meV lines can be seen to split by an equal amount. The 16.96-meV transition does not split by an observable amount for fields up to 10 T.

We identify the 23.30- and 25.95-meV lines as $1s$-$2p_\pm$ transitions at shallow donors. The line at 16.96 meV cannot be a $1s$-$2p_\pm$ transition because it does not split with magnetic field. In a magnetic field the $2p_\pm$ state is expected to split with a separation given by

$$\Delta E = \frac{h}{2\pi m^*} B = \frac{h}{2\pi m_0} \frac{B}{m^*/m_0} = 0.1158 \frac{B}{m^*/m_0}, \quad (1)$$
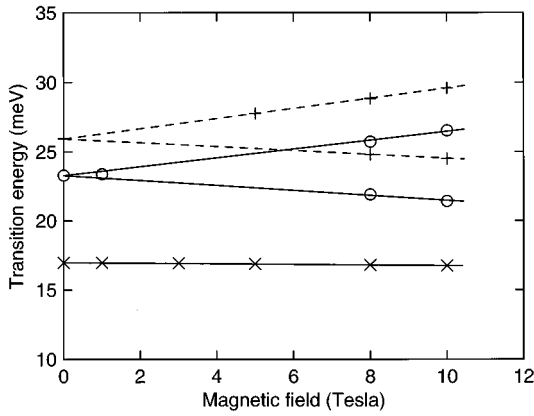
FIG. 2. Positions of the electronic absorption lines in Fig. 1 as a function of the magnetic field.

where ΔE is in meV and B is in T. So the effective mass is given by

$$\frac{m^*}{m_0} = 0.1158 \, \frac{B}{\Delta E}. \tag{2}$$

For the rate of splitting of the $1s$-$2p_{\pm}$ transition observed here, 0.519 meV/T, we determine the transverse effective mass to be $m_{\perp}^* = 0.22m_0$, a value in excellent agreement with the cyclotron resonance.[4]

High-lying components of the donor excitation sequence have not yet been observed in GaN. Therefore, the limiting energy of the sequence, the conduction band, cannot be established experimentally. Excited states of impurities are very well described by effective-mass calculations, even when chemical shifts of the ground states are large.[9] Positions of the donor excited states can be calculated if the electron effective mass and the static dielectric constant are known; similarly, if the excited-state position and effective mass are known, the static dielectric constant can be determined to a good approximation. The excellent agreement between our determination of electron transverse effective mass and that from cyclotron resonance gives us confidence in the mass value, but the static dielectric constant is still only approximate.

Chemical shifts usually increase an impurity binding energy above the effective-mass value; we will, then, assume that the shallowest observable donor has a negligible chemical shift and a ground-state binding energy equal to the effective-mass value. Any deeper donors will be assumed to have observable chemical shifts. The donor producing the $1s$-$2p_{\pm}$ transition at 23.30 meV is the shallower of the two donors observed in this experiment, and the shallowest GaN donor for which an electronic $1s$-$2p$ transition has been observed. If we assume that this shallower donor is well described by the effective-mass approximation, we can calculate the donor ground-state binding energy and the static dielectric constant from its $1s$-$2p_{\pm}$ transition energy.

Effective-mass theory[10] locates the $2p_{\pm}$ excited state at $0.25E_D$ for an isotropic effective mass, where E_D is the effective-mass ground-state binding energy given by

$$E_D = \left(\frac{m^*/m_0}{\varepsilon_0^2} \right) 13.606 \ \text{eV}, \tag{3}$$

m^* is the effective mass, and ε_0 is the static dielectric constant. Then the $1s$-$2p_{\pm}$ transition energy $E(1s$-$2p_{\pm})$ is $0.75E_D$. For $E(1s$-$2p_{\pm}) = 23.3$ meV and $m^* = 0.22m_0$ the donor binding energy is 31.1 meV, and the static dielectric constant is 9.8. Static dielectric constants determined in this way may differ slightly from electrical or optical values due to averages over anisotropies and small departures from effective-mass theory.

The weak line at 25.95 meV is identified as a second donor. It cannot be the $3p_{\pm}$ transition of the first donor, because its energy is about 1.6 meV too low, and there is no indication of interaction as the excited-state transitions cross. This donor has a small chemical shift which places it 2.65 meV deeper than the assumed effective-mass donor. Thus its binding energy is approximately 33.8 meV. This transition is near that observed previously in HVPE material by Meyer et al.[5] at 26.7 meV. However, the approximately 0.7-meV difference in transition energy is considerably larger than typical errors in FTIR spectroscopy for narrow absorption lines, so we believe that the donor observed by Meyer et al. is a third donor. If our shallower donor is effective-mass-like, then the Meyer et al. donor has a chemical shift of 3.36 meV, and a 34.5-meV binding energy.

Cubic semiconductors with isotropic conduction bands are expected to have an isotropic dielectric constant and zero-field $2p_{\pm}$ and $2p_0$ excited states at the same energy.[10] However, this expectation does not necessarily hold for crystals with wurtzite structure such as GaN, even though the conduction band is nearly isotropic.[11] Accordingly, we assign the transition at 16.96 meV to the $1s$-$2p_0$ transition of the 31.1-meV donor.

Although these HVPE films are known from secondary-ion-mass spectroscopy data to contain Si and O impurities, we cannot reliably identify the dominant donor found in these IR transmission measurements as Si based on this knowledge alone. However, when we compare our data on HVPE GaN with previous experiments on Si-doped MOCVD GaN by Wang et al.,[2] we find supporting results. The IR spectra from Wang et al. reproduced in their Fig. 3 has been normalized to their zero-field transmission spectrum. A strong peak can be seen in their data near 192 cm^{-1} (23.8 meV), which is identified as related to zero-field results. We find, as seen in Fig. 1, a strong absorption at 23.3 meV. When we normalize our spectra to our zero-field data, we find a similar strong peak at 23.3 meV. We conclude, based on this observation, that the strong peak in the Wang et al. spectra is produced by division by a zero-field spectrum with a transmission minimum at 23.8 meV, and suggest that the $1s$-$2p_{\pm}$ transition at Si donors is responsible for that minimum. These absorption lines are sufficiently broad that we cannot state with confidence that the 0.5-meV difference in position is meaningful. It is probable that the 23.3-meV absorption in our HVPE samples and the 23.8-meV absorption in the MOCVD sample of Wang et al. are the same, and both are likely due to Si. Future studies with samples having lower Si donor concentrations should resolve the remaining uncertainty.

In summary, we have observed clear $1s$-$2p_{\pm}$ transitions from two donors in undoped GaN. These transitions split with magnetic field consistent with a transverse effective mass of $0.22m_0$. By assuming that the shallower donor is well described by effective-mass theory, we find a donor effective-mass binding energy of 31.1 meV, and a static dielectric constant of 9.8. This donor is believed to be Si. A second donor is observed at lower concentration, with a binding energy of 33.8 meV. The same set of donor-induced absorptions were observed in two HVPE GaN samples. These absorptions have positions which are unique to a specific donor, and strengths proportional to the donor's concentration. Thus the IR transmission technique should be capable of providing quantitative donor identification in currently available HVPE material.

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