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Evidence for shallow acceptors in GaN

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Two low-temperature photoluminescence lines in GaN, in the region of energies commonly interpreted as longitudinal optical-phonon replicas of free excitons, donor-bound excitons, or acceptor-bound excitons, are reinterpreted as acceptor-bound excitons (A^0X's) collapsing to $n=2$ and $n=3$ excited states, respectively, of the acceptors involved. Application of this model to two sets of A^0X-related lines in hydride-vapor-phase-grown GaN gives acceptor energies of 85±1, and 115±1 meV, respectively. The existence of such shallow acceptor states, if confirmed, is of great technological importance. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1364646]

I. INTRODUCTION

A wealth of photoluminescence (PL) lines is observed at low temperatures in the near-band-edge region of high-quality, *n*-type GaN.[1–7] The dominant spectral features are typically donor-bound exciton (D^0X) lines, having energies in the range 3.470–3.480 eV, depending on strain. Also prevalent are acceptor-bound exciton (A^0X) lines, appearing in the region 3.454–3.466 eV. Further features are often found at lower energies: 3.40–3.43, 3.38–3.39, 3.35–3.37, and 3.29–3.30 eV, Nearly all workers agree on the interpretations of the D^0X and A^0X lines; however, the lower-energy lines are open to some dispute. For example, features in the 3.42 eV range are sometimes attributed to excitons bound to stacking faults, free hole to oxygen–donor transitions, or donor–acceptor pairs, with the acceptor having a much lower energy ($<100\,\mathrm{meV}$) than that, say of $\mathrm{Mg}_{\mathrm{Ga}}(>200\,\mathrm{meV})$. The other lines mentioned above are often assigned to longitudinal optical (LO) phonon replicas of A^0X features.

The idea of a ''shallow'' acceptor, as mentioned in connection with the 3.40-3.43 eV lines, is highly attractive, because the control of such an entity would result in much superior *p*-type GaN. In fact, several workers have discussed just such a possibility. For example, Orton and Foxon[8] calculated a hole effective mass of $m_h=0.8\,m_0$ from the equation $m_h=m_e(E_D/E_X-1)$, where $m_e=0.22\,m_0$, $E_D=33\,\mathrm{meV}$ (the hydrogenic donor energy) and $E_X=26\,\mathrm{meV}$ (the exciton binding energy), and then calculated $E_A=(m_h/m_e)E_D=120\,\mathrm{meV}$. Also, Pödör[9] used Phillips' electronegativity theory to argue that E_A should be about 85 meV in GaN. Both of these analyses are of course simplistic, but some more detailed theoretical calculations support the idea of a shallow (100–130 meV) acceptor[10] while other calculations indicate that acceptors shallower than 200 meV are unlikely.[11] Experimentally, the most widely used acceptor, $\mathrm{Mg}_{\mathrm{Ga}}$, has a Hall-effect activation energy of about 160 meV, and a PL signature at about 210 meV.[12] Most other impurity acceptors which have been investigated are even deeper.

In this article, we offer evidence that there indeed may well be the signature of a shallow acceptor in GaN. Our evidence comes from a different interpretation of the lines falling in the regions 3.38–3.39 eV and 3.35–3.37 eV, respectively. We show that these lines are likely due to the involvement of *excited* states ($n=2$ and $n=3$, respectively) in certain acceptors, following the collapse of excitons bound to them. Such excited-state acceptor transitions, known as ''two-hole'' transitions, have been observed in the past, e.g., in InP[13] and in GaAs.[13,14]

II. EXPERIMENTAL DETAILS

In this investigation, two different GaN samples were studied. Both samples were grown on sapphire substrates by hydride vapor-phase epitaxy (HVPE). In sample #1, the GaN layer was grown to a thickness of 133 μm and was then removed from the substrate by laser-induced liftoff. Sample No. 2 was grown to a thickness of 93 μm but was not removed from the substrate. In both samples the *c* axis of the crystal is normal to the growth surface, with the Ga face on top. The PL was excited at 2 K with the 3250 Å line of a HeCd laser. The spectra were analyzed by a high resolution 4 m grating spectrometer equipped with an Radio Corporation of America C31034A photomultiplier tube for detection.

Electrical measurements were performed on the separated piece (No. 1) after removal of the highly conductive interface layer which always exists in HVPE GaN grown on sapphire.[15] This layer strongly affects the measured electrical properties but does not affect the PL, which is excited near the top of the sample. Although the effects of the layer on electrical properties can be removed by analysis,[15] it is better to physically remove the layer, and this is possible in a separated wafer. After removal, the 300 K mobility and carrier concentration were about 950 $\mathrm{cm}^2/\mathrm{V\,s}$ and $4.2\times10^{16}\,\mathrm{cm}^3$, respectively, and the donor and acceptor concentrations were

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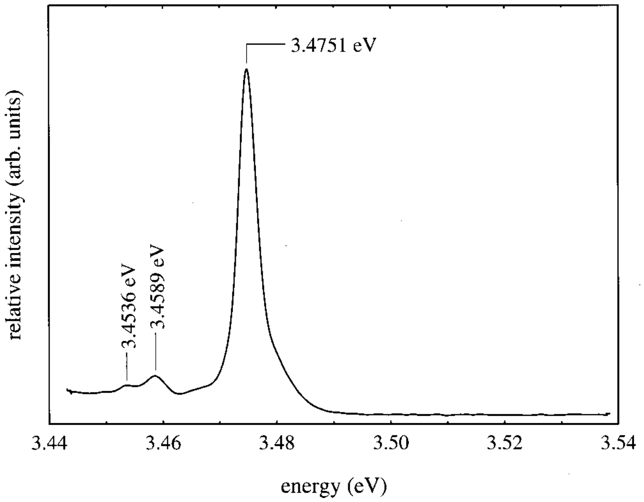

FIG. 1. Emission spectra for sample No. 1 (free standing layer) showing the D^0X transition and two A^0X ground–state transitions, A_1^0X and A_2^0X.

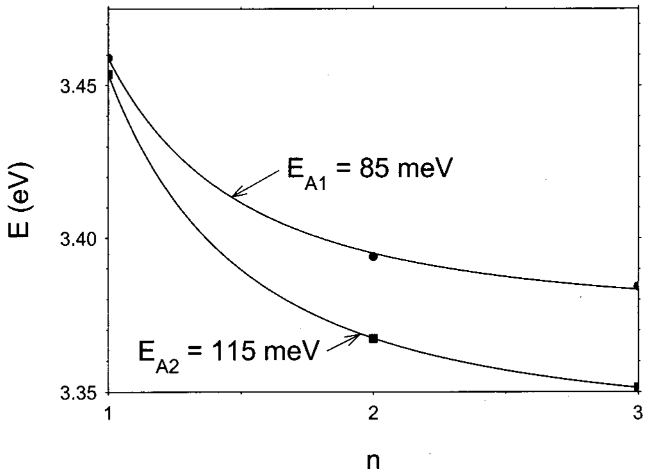

FIG. 3. Transition energies as a function of quantum number *n*.

about 7×10^{16} and $3\times10^{16}\,\mathrm{cm}^{-3}$, respectively. These values of donor and acceptor concentration are some of the lowest reported so far.

III. EXPERIMENTAL RESULTS

When an exciton bound to a neutral acceptor collapses, the acceptor is usually left in its ground state. The corresponding PL lines in GaN are those typically occurring in the region 3.45–3.46 eV. However, the acceptor may also be left in an excited state, $n=2,3,4,\ldots$, so that the transition will have to occur at a lower energy,[13,14] given by

$$E(n)=E_{\mathrm{FE}}-E_b-\Delta E(n), \tag{1}$$

where $E(n)$ is the transition energy, E_{FE} is the free exciton energy, E_b is the energy with which the exciton is bound to the acceptor, and $\Delta E(n)$ is the energy necessary to put the hole on the acceptor into an excited state n. In a hydrogenic model, Eq. (1) can be written as follows:

$$E(n)=E(1)-E_A(1-1/n^2), \tag{2}$$

where E_A is the ground-state acceptor energy. In Fig. 1, sample No. 1 displays the donor–bound exciton (D^0X) transition at 3.4751 eV as well as two ground-state ($n=1$) acceptor–bound exciton (A^0X) transitions at 3.4589 eV (A_1^0X) and 3.4536 eV (A_2^0X), respectively. In Fig. 2, the excited-state A^0X transitions are seen. We associate the 3.3939 and 3.3842 eV lines with the $n=2$ and $n=3$ transitions, respectively, of A_1, and the 3.3673 and 3.3515 eV lines with the corresponding transitions of A_2. All of these lines are plotted in Fig. 3, and it is seen that excellent fits to Eq. (2) can be obtained, with the following fitting parameters: $E_{A1}=85\pm1$ meV, and $E_{A2}=115\pm1$ meV. The lower energy transitions in this figure are LO-phonon transitions accompanying the excited-state transitions described above.

The transitions in Figs. 4 and 5 are associated with the HVPE layer (No. 2) in which the GaN is not separated from the sapphire substrate. In Fig. 4, essentially the same ground-state A^0X transitions are seen as those found in the separated layer; their energies are 3.4589 and 3.4534 eV, respectively.

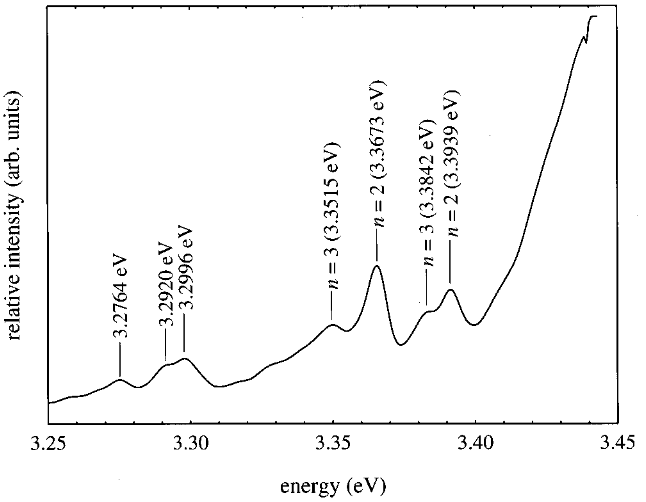

FIG. 2. The $n=2$ and $n=3$ excited–state transitions associated with the A^0X ground–state transitions shown in Fig 1.

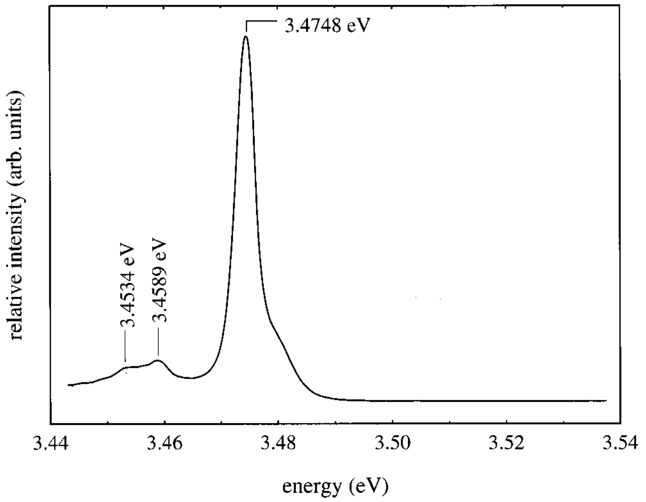

FIG. 4. Emission spectra from sample No. 2 (attached to the Al_2O_3 substrate) showing the D^0X transition and two A^0X transitions.

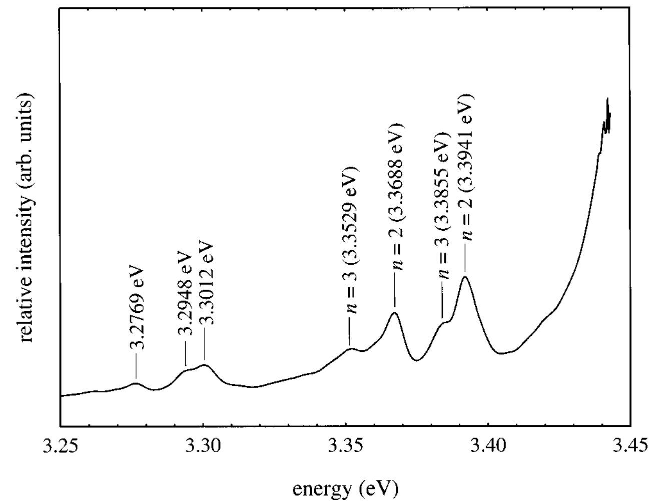

FIG. 5. The $n=2$ and $n=3$ excited–state transitions associated with the A^0X ground–state transitions shown in Fig 4.

In Fig. 5, the $n=2$ and $n=3$ states of the 3.4589 eV ground–state transition are observed at 3.3941 and 3.3855 eV, respectively. From these data, the activation energy of this acceptor (A_1) is again 85 meV. The $n=2$ and $n=3$ excited states of the 3.4534 eV ground–state transition are observed at 3.3688 and 3.3529 eV, respectively. From these excited state transitions the activation energy of acceptor A_2 is 113 meV, within error of the value found for sample No. 1.

Clearly, the excited states of both A_1 and A_2 follow a hydrogenic model quite well, but yet the ground–state energies of A_1 and A_2 differ considerably. Applying the simple relationship, $E_A=13.6m_h^*/\epsilon_0^2$, with $\epsilon_0=9.5$, gives $m_{h1}=0.56m_0$, and $m_{h2}=0.76m_0$. These values should not be taken as measured hole effective masses, but simply as the approximate magnitudes of the masses needed to explain activation energies in the 100 meV range. Interestingly, such low masses would predict hole mobilities much larger than those normally observed, about 10 $\mathrm{cm}^2/\mathrm{V\,s}$. Perhaps the hole mobilities in GaN are low not because of high effective masses, but because of the very high doping typically employed, and the concomitant poor structural properties.

Taking the free-exciton energy in GaN as 3.4814 eV,[16] the exciton is bound to acceptor A_1 with a binding energy of 22.5 meV. By Haynes rule,[17] the exciton is bound to the acceptor with some fraction of the ground–state energy. In this case, the Haynes factor is 22.4/85=0.26. For A_2, the exciton binding energy is 27.8 meV, and thus the Haynes factor is 27.8/115=0.24. For comparison, considering the D^0X line at 3.4751 eV, the binding energy of the exciton to the donor is 6.3 meV. Using a hydrogenic donor binding energy of 33 meV, the Haynes factor for the donor is 0.19.

The identities of A_1 and A_2 are unknown at this time. Secondary-ion mass spectroscopic measurements in similar GaN layers, grown in the same reactor and under nearly identical conditions, show both C and Mg at below the $1\times10^{16}\,\mathrm{cm}^3$ level. Indeed, there is evidence that the dominant acceptor in this material is the Ga vacancy; however, we have no concentration information on A_1 and A_2, so that they cannot be correlated with the Hall-effect acceptor mentioned earlier. In any case, the potential existence of a shallow (<100 meV) acceptor in GaN is intriguing, and should be further investigated.

IV. CONCLUSIONS

We reinterpret two rather common sets of lines in GaN to be two-hole (excited-state) transitions of acceptor–bound excitons. Fits to the data for two different acceptors give ground–state energies of 85±1 and 115±1 meV, respectively. The possibility of shallow (<100 meV) acceptors in GaN is of high technological importance, and further attempts to identify the acceptors observed here should be carried out.

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