Shallow acceptors in GaN

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(Received 3 July 2007; accepted 6 August 2007; published online 25 September 2007)

Recent high resolution photoluminescence studies of high quality Mg doped GaN show the presence of two acceptors. One is due to Mg and the other labeled A1 has a shallower acceptor defect. The authors investigate likely candidates for this shallow acceptor and conclude that CN is the most likely possibility. The authors also show that the CN is passivated by H and the passivated complex is more stable than MgGaN-H. © 2007 American Institute of Physics. [DOI: 10.1063/1.2776852]

After Si, GaN is one of the most important semiconducting material and is unrivaled for bright light emission. As a result of technological advances in GaN epitaxy, nitrides are widely used to produce blue-green to ultraviolet emitters, ultraviolet photodetectors, and high electron mobility transistors. Notwithstanding remarkable success in fabricating these devices, the atomic processes that govern the incorporation of dopants intentional and otherwise and their interactions with native point defects are not yet fully understood. This is particularly true for p-type doping.

Whereas n-type doping is achieved with O and Si, p doping is problematic. Oxygen and Si donors have levels 33 and 30 meV, respectively, and these donors are ionized just above room temperature whereas the only useful shallow acceptor in GaN is Mg, which has an acceptor level about 220 meV. Growth of GaN doped with Mg leads to high resistivity material due, in part, to the formation of Mg–H pairs which are electrically inactive.1-12 These, however, can be eliminated either by thermal treatments at temperatures above ~350 °C (Ref. 3) or using electron irradiation13-15 leading to a very broad electron paramagnetic resonance signal attributed to substitutional Mg.2 The doping limit achieved with Mg is about 2 × 1018 cm−3 carriers with Mg concentrations about ten times larger. Increasing Mg leads to poorer material quality due to formation of VN donors and complexes with Mg. Thus, Mg is far from the ideal acceptor and it has generally been thought that there are no other choices. However, recent photoluminescence (PL) studies6 have shown that this picture is incomplete and the true situation is far more complex and intriguing.

The recent PL studies on high quality homoepitaxial Mg doped GaN layers grown on thick hydride vapor phase epitaxy GaN substrates by metal-organic chemical vapor deposition (MOCVD) in a Thomas Swann reactor reveal two emission lines due to acceptor bound excitons (ABEs) at 3.466 and 3.455 eV labeled ABE1 and ABE2 and due to two shallow acceptors labeled here A1 and A2.7

Correlated with each acceptor is a family of donor-acceptor pair (DAP) transitions. A1 is correlated with a DAP transition with a zero phonon line at 3.27 eV, while A2 is correlated with a broad peak with a maximum at 3.1 eV. Since the ABE1 binding energy is 0.01 eV less than ABE2 the A1 acceptor has, according to Hayne’s rule, a level about 0.1 eV shallower than A2. The ultraviolet light (UVL) or 3.27 eV DAP emission correlated with A1 increases in samples lightly doped with Mg but has been detected in material in which Mg is not present implying that A1 has nothing to do with Mg.5

It is known that the 3.27 eV DAP emission along with the ABE1 emission at 3.466 eV with which it is correlated are strongly reduced by low energy ionizing radiation even at cryogenic temperatures implying a radiation enhanced annealing of A1. Moreover, in p-GaN, the 3.27 eV UVL emission anneals around 500 °C (Ref. 8) but is thermally stable to higher temperatures in n-GaN. The effect of radiation and annealing suggest that the shallower acceptor A1 is a weakly bonded defect, but is certainly not Mg. Previous work7 has assigned A2 to MgGaN but left open the identity of A1. Thus, there are two shallow acceptors in MOCVD GaN doped with Mg. The presence of a second shallow acceptor might explain why electrical studies report an acceptor level at 0.15 eV rather than the optical level at 0.22 eV.3

Although A1 is not related to Mg, studies of the excitation power dependence of the intensity of ABE1 surprisingly show that both A1 and A2 increase with Mg concentration. This could be explained by the incorporation of Mg on Ga sites driving the A1 acceptor defect onto the N sublattice. We shall return to this below.

It is one of the principal aims of this letter to identify this center. We have investigated a number of candidates but the only defect which comes close to A1 is carbon at a nitrogen site (CN). We carry out spin-density-functional calculations using the aimpd code. The explicit treatment of electronic core states is avoided by using the pseudopotentials of Hartwigs7 et al.9 The calculations are done in 216 atom supercells for c-GaN and in 128 atoms for 2H-GaN. For the C and Mg acceptors in 2H-GaN convergence with respect to supercell size is verified with 300 atom supercells. The increase in supercell size leads to a difference of the acceptor levels of less than 0.01 eV for both acceptors. The basis set consists of Cartesian s-, p-, and d-type Gaussian functions centered on
each atom. Ga and N atoms contribute with a contracted basis consisting of (4, 4, 5) \((s, p, d)\) Gaussian orbitals optimized for bulk GaN.\(^{10}\) For C, Mg, and O we used a basis of (4, 12, 24) \((s, p, d)\) Gaussian orbitals.

We first investigate \(c\)-GaN since the acceptor levels of both C and Mg are known and lie at \(E_v + 0.215\) and \(E_v + 0.230\) eV.\(^{11, 12}\) We find that the Mg acceptor level is shallower than C\(_N\) but by only 0.17 eV. Thus, both defects are acceptors and the disagreement with the ordering of the experimental levels probably arises from the limitations of the theory.

For \(w\)-GaN, we found the same difference in acceptor level of C\(_N\) and Mg\(_{GaN}\). Hence, if we correct for the error we find in \(c\)-GaN, we conclude that the acceptor level of C\(_N\) in \(w\)-GaN would be 15 meV lower than that of Mg\(_{GaN}\) and lie at 0.210 eV. This is in good agreement with other theoretical results\(^{13}\) and experimental findings.\(^{14}\) We also looked at C\(_{Ga}\) and find its donor level to be deeper than Si\(_{Ga}\) by 0.2 eV.

The structure of hydrogen bound to C\(_N\) contrasts with that of Mg\(_{GaN}\). When bound to C\(_N\), H lies at an antibonding site to C with a C–H bond length of 1.11 Å. In contrast, when bound to Mg\(_{GaN}\), H lies at an antibonding site of a N neighbor of Mg\(_{GaN}\). The binding energy of H with C is 1.66 eV and larger than the binding energy of H with Mg which is 1.59 eV. In both cases, H passivates the acceptor action.

The \(V_{Ga}^{\pm}OH\) defect\(^{15}\) has been suggested as a candidate for A1. We find its acceptor level to lie about 0.8 eV above Mg\(_{GaN}\) and hence place it at \(E_v + 1.0\) eV. This rules this defect out as a candidate for A1. Hence, we conclude that the most likely candidate for A1 is C\(_N\).

We can suggest a mechanism for the annealing of A1 around 500 °C in \(p\)-GaN (Ref. 8) although it is stable at these temperatures in \(n\)-GaN. It has been found in positron annihilation (PAS) studies in GaN:Mg, that neutral V\(_{N}^{\pm}\)-Mg pairs are present in MOCVD grown material and these anneal around 500–800 °C with activation energy around 3 eV.\(^{16, 17}\) Hence, if the annealing occurs by dissociation followed by diffusion of V\(_{N}\) to the surface, as suggested by the PAS studies, then we can anticipate that defects on the N sublattice are also unstable at these temperatures. In other words, a migrating V\(_{N}\) defect will promote the diffusion of C\(_N\) which would then anneal around 500 °C. The samples studied by PAS were either highly resistive or \(p\) type. The situation in \(n\)-GaN counterdoped with Mg is different as then the formation energy of V\(_{N}\) is so large that such defects will not be present. Thus C\(_N\) defects will be stable in \(n\)-GaN to higher temperatures than in \(p\) type. In summary, there is the possibility that C\(_N\) is lost by instability of the N sublattice in \(p\)-GaN. It is less likely in \(n\)-GaN as the formation energy of V\(_{N}\) is then so large that such defects would be rare.

The second and more challenging property of the A1 acceptor to explain is its instability in the presence of \(e\)-\(h\) pairs. Low energy (10 keV) irradiation, producing \(e\)-\(h\) pairs, apparently removes A1 centers even at cryogenic temperatures.\(^{4, 5}\) It seems unlikely that C\(_N\) is unstable by itself in the presence of \(e\)-\(h\) pairs and so any instability must be due to the complexing with another mobile defect. Now, it is known that Mg–H defects are unstable in the presence of \(e\)-\(h\) pairs and dissociate producing H\(^0\) or H\(^+\) which are mobile. The dissociation energy of Mg–N–H being 1.59 eV is provided by the recombination energy of \(e\)-\(h\) pairs. Now, mobile H could be subsequently trapped by C\(_N\) or C\(_N\)–H defects. This would occur if the C–H bonded defect is more stable than the Mg–H defect or if it is not susceptible to the same radiation enhanced dissociation that Mg–H defects suffer. According to our calculations, C\(_N\)–H defects are passive. Hence, the effect of radiation is to activate Mg acceptors but passivate C acceptors. Clearly, this should increase the 3.1 eV DAP band and ABE2 intensity attributed to Mg and this is supported by experiments on lightly Mg doped metal-organic vapor-phase epitaxy GaN whereas the 3.27 eV band decreases, the band at 3.1 eV increases in intensity.\(^{5}\) Finally, we point out that there is evidence for C–H defects in undoped MOCVD GaN.\(^{18}\) Fourier transform infrared studies revealed modes at 2851, 2922, and 2956 cm\(^{-1}\). We find the stretch mode of the C–H defect to be 2855.5 cm\(^{-1}\) and very close to the first defect. The identity of the others is unclear at this stage.

In summary, we have found that C at a N site is a shallow acceptor and a strong candidate for the shallow acceptor observed in high quality grown Mg doped MOCVD GaN. We place its level 0.015 eV below Mg.

The authors thank Bo Monemar for helpful discussions.