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Identification of Microscopic Hole-trapping Mechanisms in Nitride Semiconductors

John L. Lyons, Karthik Krishnaswamy, Luke Gordon, Anderson Janotti, and Chris G. Van de Walle

Abstract—Hole trapping has been observed in nitride heterostructure devices where the Fermi level is in the vicinity of the valence-band maximum. Using hybrid density functional calculations, we examine microscopic mechanisms for hole trapping in GaN and AlN. In defect-free material, hole trapping does not spontaneously occur, but trapping can occur in the vicinity of impurities such as C—a common unintentional impurity in nitrides. Using Schrödinger-Poisson simulations, we assess the effects of C-derived hole traps on N-face high-electron mobility transistors, which we find to be more detrimental than the previously proposed interface traps.

Index Terms—Hole traps, nitride semiconductors, first-principles calculations, impurities.

I. INTRODUCTION

A number of nitride semiconductor device designs employ heterostructures in which the Fermi level approaches the valence-band maximum (VBM) due to the effect of polarization fields. One case is a class of devices in which a polarization-induced hole gas is engineered to arise in a graded AlGaIn alloy [1]. Other examples occur in N-face high-electron-mobility transistors (HEMTs), in which a two-dimensional hole gas (2DHG) should be present at the interface between the AlGaIn back barrier and GaN buffer [2], and metal-face *p*-channel field-effect transistors, in which polarization engineering also leads to 2DHGs [3], [4]. A final example is interband tunneling junctions, in which trapping has been observed at interfaces [5]. In each of these heterostructures, the presence of hole traps has been found to adversely affect device performance. In the polarization-hole-doped heterostructures, such hole traps are thought to prevent the formation of free holes [1]. In N-face HEMTs, the hole traps have been proposed to cause large-signal dispersion that is observed in current-voltage curves [2], [6], and in tunnel junctions, such traps have been blamed for decreasing tunneling current [5].

Based on deep level transient spectroscopy, a donor-like defect with a transition level 60 meV from the VBM of GaN

was proposed to be responsible for hole-trapping behavior [2], [6]. Dispersion in the CV curves was suppressed with Si doping of the GaN buffer [6], as this *n*-type doping establishes the Fermi level far away from the VBM. However, the microscopic mechanism whereby the hole trapping occurs has not yet been established.

Here we examine possible hole-trapping mechanisms using hybrid density functional calculations. We find that self-trapping of holes does not occur in bulk material but can occur in the presence of impurities. We focus on C, an impurity almost always present in the nitrides due to unintentional incorporation. Using Schrödinger-Poisson (SP) simulations we examine the effect on N-face HEMTs of C hole traps distributed throughout the GaN layer, and compare this behavior with that of the interface traps that have been previously proposed. The distributed hole trap is found to deplete the hole gas at the AlGaIn/GaN back barrier interface in a fashion that is virtually indistinguishable from the interface traps, supporting our proposal that distributed C impurities are the cause of hole trapping in the heterostructures.

II. METHODS

We employ first-principles calculations based on the Kohn-Sham scheme [8] with the HSE hybrid functional [9] as implemented within VASP [10]. The use of the hybrid functional is necessary for an accurate description of the semiconductor band gap and for correctly describing hole localization at defects and impurities [7]. Calculations for trapped holes are carried out in 96-atom supercells; other details of the calculations are as in Ref. [7]. The SP simulations were carried out using the *nextnano*³ code [11].

III. RESULTS AND DISCUSSION

First-principles calculations of hole-trapping mechanisms. We first examine whether holes self-trap in bulk material (also known as small-polaron formation). In bulk GaN, we previously found that holes do not self-trap [12]. We have also examined whether a hole would self-trap in the presence of biaxial strain in pseudomorphic layers. Imposing a 2% biaxial strain does not alter the stability of the delocalized hole (the spin density remains similar to the unstrained case) with no tendency for hole localization. We also examined whether the presence of Al could lead to hole trapping in GaN by placing a single isoelectronic cation in the GaN supercell. Again, no self-trapping occurs. All of this is reassuring from the point of view of hole transport in GaN, for which hole self-trapping would be detrimental.

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Fig. 1. Spin densities a delocalized hole at a GaN/AlN interface.

A self-trapped hole can be stabilized in bulk AlN. Localization occurs mainly on a single N atom, accompanied by an increase in the bond length of the axial Al-N bond by 13%. However, the hole polaron is metastable, since the delocalized hole is lower in energy (by 0.30 eV) than the self-trapped hole. In equilibrium, we thus do not expect holes to self-trap in AlN. As for GaN, we also found that neither biaxial strain nor the presence of Ga leads to a trapped hole that is more stable than the delocalized hole.

To investigate whether holes might trap at an GaN/AlN interface, we constructed a GaN/AlN superlattice along the [0001] direction with 4 bilayers each of GaN and AlN, using the in-plane lattice constant of GaN and a (2×2) in-plane periodicity to allow for symmetry-breaking relaxations [Fig. 1]. A number of different distortions were explored, but none resulted in hole localization. Every structure tested relaxed into the delocalized-hole configuration shown in Fig. 1. The hole remains delocalized in the GaN part of the superlattice, as expected based on the valence-band offset between GaN and AlN, but near the [000 $\bar{1}$] end of the layer, consistent with the presence of polarization fields. Since the tendency for hole trapping should be strongest in AlN, as it has the highest hole mass and lowest-lying valence band, our results indicate that hole trapping will also not occur at AlGaIn/GaN interfaces.

Self-trapping of holes will therefore not occur in pristine material or near interfaces. Yet hole polarons may be stabilized at impurities [7]. In Fig. 2 we list candidate hole-trapping centers and their charge-state transition levels in GaN. Each of these impurities (or complexes) nominally acts as an acceptor [associated with a $(0/-)$ level], but (with the exception of Mg_{Ga}) they also exhibit a $(+/0)$ level near the VBM. Such a level is usually associated with donors, but due to its proximity to the VBM here it indicates that the impurity acts as a hole trap when the Fermi level is low in the gap.

Mg_{Ga} does not give rise to a hole trap by itself, but it can form a complex with hydrogen. Mg-H complexes are usually assumed to be electrically neutral (and need to be dissociated before Mg_{Ga} can become electrically active). However, we have found that Mg-H does exhibit a $(+/0)$ hole-trapping level 130 meV above the GaN VBM [13]. Such complexes could be present if intentional doping is performed in other regions of the heterostructure. Unintentional contamination with Mg (and formation of Mg-H complexes) could also occur if memory effects are present in a deposition system in which Mg-doped layers have previously been grown. Since the position of the

Fig. 2. Charge-state transition levels and charge-state regions of stability for acceptor impurities in GaN. Stability regions are color-coded by charge state as labeled for C_N : when the Fermi level is in the orange region, the $-$ charge state is stable; blue: neutral; and red: $+$. Mg_{Ga} has a $(0/-)$ transition level as expected for an acceptor. The other impurities and complexes also exhibit a $(+/0)$ level near the VBM, turning them into hole traps.

$(+/0)$ level in the Mg-H complex is similar to C_N , much of the discussion below will also apply to this complex.

The remainder of our discussion will focus on C, a common unintentional impurity in GaN and AlN. C_N acts as a deep acceptor, with a $(0/-)$ level at 0.90 eV above the VBM in GaN and 1.88 eV in AlN, but also features a $(+/0)$ transition level at 0.35 eV above the VBM in GaN and at 1.07 eV above the VBM in AlN [7]. C_N is the most stable form of C in unintentionally doped material. Similar to the case of Mg acceptors, a C-H complex can also form when H is present. This complex features a $(+/0)$ transition level at 0.25 eV above the VBM in GaN [Fig. 2].

Schrödinger-Poisson simulations of heterostructures. We now examine the effect of hole traps on nitride devices by performing Schrödinger-Poisson simulations. We use the N-face HEMT device structure shown in Fig. 3 (similar to the one investigated in [5]), which contains a 30 nm GaN channel, 30 nm of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ back barrier, and a 100 nm GaN buffer layer. Under zero bias this device exhibits a two-dimensional electron gas (2DEG) at the GaN channel/AlGaIn interface and a 2DHG at the AlGaIn/GaN buffer interface where the valence bands of GaN approaches the Fermi level (at zero energy on the left y -axis).

To investigate hole trapping in this HEMT we examine two cases. Case 1 reflects the proposal [2], [6] that hole traps at 60 meV above the VBM are present in a 0.2-nm-wide region at the AlGaIn/GaN buffer interface, with a sheet density between 0.1 and $1.5 \times 10^{12} \text{ cm}^{-2}$ (note that such a high interface trap density is unlikely to be caused by unintentional impurities; a 1-nm-wide region would mean a volume trap density of at least $1 \times 10^{18} \text{ cm}^{-3}$). In Case 2 we examine hole traps with a $(+/0)$ level at 350 meV above the VBM (as for C_N) distributed throughout the GaN buffer region with a density between 0.1 and $1.5 \times 10^{17} \text{ cm}^{-3}$; these C densities were chosen to reflect a realistic level of unintentional incorporation. We have also explored the presence of C in the AlGaIn back-barrier region,

Fig. 3. Band structure of a N-face HEMT with a design based on Ref. [6], in which a 2DHG accumulates at the AlGaIn/GaN buffer interface (at 60 nm along the x -axis). The Fermi level is at zero energy (left axis), indicated by the dotted horizontal line. The carrier distributions in the 2DEG and 2DHG are also shown (right axis).

Fig. 4. 2DHG density versus trap density for the case of a 60-meV hole trap located at the interface (Case 1, in red) and for the case of 350-meV C-related hole traps distributed in the GaN buffer (Case 2, in blue). Dotted lines indicate fits meant to provide estimates for carrier densities necessary for complete hole trapping.

but found it has a negligible effect on the 2DHG concentration.

The density of the 2DHG as a function of trap density for these two cases is shown in Fig. 4. In both cases, the traps reduce the density of the 2DHG: instead of polarization charges being compensated by free holes, holes are bound to the hole traps, and these positively charged centers compensate the polarization charge. In fact, Case 2 (C traps distributed throughout the GaN buffer) leads to a much greater reduction in the 2DHG density than the 60 meV interface traps at equivalent trap density. As a reduction in 2DHG density by donor-like traps has been linked to anomalous output conductance in N-face nitride-based HEMTs, our results suggest that C impurities in the buffer are a better candidate for the hole traps affecting these devices.

These results indicate that impurities can act as hole traps within nitride heterostructures, and that contamination by C

impurities or Mg-H complexes should be avoided. Hydrogenation, often used to passivate traps, would be ineffective here: both Mg-H and C-H complexes exhibit (+/0) trapping levels near the GaN VBM (see Fig. 2) and thus act as hole-trapping centers. Hydrogen is a ubiquitous impurity, present even in MBE growth environments. The concentration of hydrogen should thus be carefully monitored and controlled. In structures grown by metal-organic chemical vapor deposition where Mg doping is employed intentionally (as is the case, e.g., in Refs. [3] and [4]), post-growth annealing is performed in order to remove the hydrogen and activate the Mg acceptors. However, it is known that such an annealing procedure does not necessarily remove all of the hydrogen [14], and therefore some concentration of Mg-H complexes may still be present. Our results indicate the importance of keeping the concentration of such complexes low, ideally below 10^{16} cm^{-3} , because otherwise the 2DHG density may be affected (see Fig. 4). We note that, in structures of the type shown in Fig. 3, the electrostatics will inhibit the removal of hydrogen from the sample through the surface; structures with the p -type layer near the surface [3], [4] should therefore be favored.

IV. CONCLUSION

Using hybrid density functional calculations we have investigated microscopic mechanisms for hole trapping in GaN and AlN. Self-trapped holes are not stable in GaN or AlN. However, holes can trap at impurity sites, and we propose unintentionally incorporated C (or Mg-H complexes) as candidates for hole-trapping centers in nitride devices.

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