Can Amorphous GaN Serve as a Useful Electronic Material?

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In this paper, we propose two structural models of amorphous GaN at different densities, obtained from approximate *ab initio* molecular dynamics. The network models we obtain are highly disordered but exhibit a large state-free optical gap, and have no homopolar bonds (or odd-membered rings). The radial distribution function, local bonding, and electronic density of states are described. We find that a model with many threefold atoms has weakly localized band tails, especially at the valence edge. This leads us to believe that amorphous GaN may have independent promise as a novel electronic material. [S0031-9007(97)03647-8]

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The dramatic success of crystalline GaN as an electronic and optical material has motivated an enormous effort to explore all aspects of the material and seek improved means of growth. During the early stages of GaN research in the 1970s, researchers grew amorphous GaN (a-GaN) [1]. Several a-GaN films were grown by reactive sputtering of gallium in nitrogen ambient. Little is known about a-GaN, since subsequently discovered crystal growth techniques diminished the interest in the amorphous phase of the material. Nevertheless, the well-known challenges of getting high quality crystals justifies an exploration of alternative wide gap materials.

Recently, experimental interest in growing a-GaN has been renewed [2,3]. Researchers [2] obtain transparent films with optical gaps as high as 3.9 eV. The band tailing of the optical absorption coefficient and no detectable x-ray diffraction lines imply the amorphous nature of these films. Electron spin resonance and subgap absorption measurements suggest a low midgap defect density of states [2].

In this Letter, we propose the first atomistic models of a-GaN, and characterize them as completely as possible [4]. Our motive is partly to determine experimental signatures of the amorphous state, which can presumably be present in some approaches to crystal growth. As a by-product we find that our networks show potential in their own right as novel electronic material, since they are shown to have a large, state-free band gap, *and* for a lower density form, weakly localized band tail states, suggesting that improved mobility may be possible compared to other amorphous semiconductors. Our calculation is exploratory, in the sense that we have not yet tried to optimize the density of the model or attempted different simulated annealing/cooling rates. Thus the "details" could differ somewhat from the laboratory material. Nevertheless, this work provides new insight into the character of bonding, defects, and their experimental signatures.

To construct the models, we used thousands of time steps of local basis *ab initio* molecular dynamics to form two 64 atom models. We used the program of Demkov, Ortega, Sankey, and Grumbach [5], "Fireball96," who generalized the non-self-consistent local basis Harris functional local density approximation (LDA) scheme of Sankey and co-workers [6] to an approximate self-consistent form. Spherical *charged* atom densities are used as Harris input fragments, and these charges are self-consistently determined. A minimal basis (one s and three p's per site) is employed. The method is very efficient, combining the advantages of charge transfer with a fixed atom-centered basis (and therefore efficient look-ups for matrix elements). The basis functions are slightly excited pseudoatomic orbitals with confinement radii [6] of $5.4a_B$ and $4.0a_B$ for Ga and N, respectively.

In zinc-blende (ZB) and wurtzite (WZ) GaN, FIREBALL96 produces a band structure in satisfactory agreement with the more accurate calculations of Lambrecht and Segall [7], even in the structure of the lower conduction states (which is *a priori* unexpected with a minimal basis, and is an empirical indication that d hybridization is not too important to these levels). All of the essential features of the band structure near the gap are reproduced. Our band structure has been published in Ref. [8]. From studies of crystalline phases of GaN we have found that we closely reproduce the essentially exact (within LDA) work of Neugebauer and Van de Walle [9] and Boguslawski *et al.* [10,11] for intrinsic defect relaxations, when the Ga $3d$ states are taken to be part of the core. The Ga $3d$ states have a significant effect on the lattice constant in plane wave self-consistent LDA calculations [9]. For the Hamiltonian we employ [5], retention of Ga $3d$ states in the core leads to a lattice constant 6% too small (compared to 3.1% with a plane wave basis [9]). The present method has been studied extensively for crystalline GaN, its intrinsic defects, and the electronic band structure for both WZ and ZB forms. Several detailed tests of intrinsic defect relaxations have been reported [8]. In particular, we find relaxations similar to the plane wave calculations for all cases, except for a very minor difference in the

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N vacancy in ZB GaN, for which the plane wave result [9] is a very small inward relaxation (0.01 Å) and ours is a small (0.05 Å) outward relaxation. In further agreement with the work of Refs. [9–11], we find that the N vacancy is a single donor, unlike tight binding [12] which predicts that the N vacancy is a triple donor. We note too, that the method has been used with success on GaN surfaces by Fritsch and co-workers [13].

For the work presented here, we have empirically repaired the error in the lattice constant (due mostly to keeping the Ga $3d$ states in the core) by rescaling the usual LDA repulsive pair interaction, such that the minimum energy occurs at the experimental lattice constant. The band structure is little affected, except for improving the gap [15% (20%) too large [14] for WZ (ZB) compared to experiment] and the bulk modulus of WZ-GaN, which is reproduced to within 9% of experiment (the bulk modulus of ZB-GaN is within 0.3%). Both the ZB and WZ forms of the crystal are well described, and the crystalline conformations are effectively degenerate (ZB is favored over WZ by 0.01 eV/atom). The uniformly satisfactory description of the properties of the crystalline forms of GaN provides a justification for our admittedly empirical fix to correctly reproduce crystalline bond lengths.

Since the density of a-GaN is unknown, but is probably similar to or less dense than crystalline GaN, we performed two calculations at the (wurtzite) crystalline experimental density (model A) and at 82% of the experimental density (model B). These choices clearly require further investigation in future modeling work; a first step should involve a study of energy vs density for thoroughly annealed cells at a range of densities.

The two structural models of this paper were formed by simulated quenching of liquid GaN. We began with a 64 atom (zincblende) cubic supercell of crystalline GaN, and randomized the atomic positions by performing a 400 fs molecular dynamics (MD) run starting at 10^4 K. Inspection of the network showed that it was substantially disordered, and a typical interatomic force was 5 eV/Å, implying that the structure was far from equilibrium. Then, Harris functional-LDA MD [6] was used to slowly cool the network over 7 ps to 300 K (a Berendsen [15] thermostat was used). The resulting network (model A) was then fully relaxed to equilibrium with the self-consistent method of Ref. [5]. A second, less dense sample (model B) was constructed by increasing the supercell lattice constant and atomic coordinates in the supercell by 6% and repeating the annealing process. We found that the self-consistent relaxation was essential to obtain reasonable network structure, an unsurprising result for such an ionic material.

As expected, the lower density model (B) contains more threefold coordinated atoms (42) than the denser model A (24). Possibly, there is a continuum of a-GaN possible with varying densities, as in a-C, for example. The first important property of both networks is the absence of wrong (homopolar) bonds (or odd-membered rings), which is likely to hold up in a wide range of densities for this stoichiometry. The lack of homopolar bonds (or odd-membered rings) is an indication of strong ionicity, and it is appealing that our short time scales can produce this result. It also implies that atomic segregation is unlikely, except for stoichiometries very different than 1:1. In the somewhat more ionic case of silica, Sarnthein *et al.* also obtained no homopolar bonds [16]. We discuss the structural and electronic properties of our models in three figures. Figure 1 provides the number density function $n(r) = 4\pi r^2 \rho g(r)$, for $g(r)$ the pair-correlation function, and ρ the number density. The average bond length of fourfold coordinated atoms is slightly higher (0.04 Å) for model B. Both materials show a well-defined nearest neighbor peak and a rapid loss of interatomic correlations typical of a highly disordered amorphous structure. The splitting in the nearest neighbor peak of model B is due to the slight bond length differences for three and four coordinated atoms. By taking (either) crystalline phase as reference, we find that the lower (higher) density model has a relative energy of 0.40 eV/atom (0.44 eV/atom) above the crystal. While one cannot directly connect these numbers to a given mode of growth, they show at a minimum that a-GaN is plausible from a theoretical perspective.

The energy density of states around the band gap is shown in Fig. 2 for both models. The size of the highest occupied and lowest unoccupied molecular orbital gap is roughly constant at 2.8 eV for both models and therefore independent of the material density. For the particular set of approximations we use (LDA *and* a minimal local basis set), it is probable that our estimate for the gap is somewhat *overestimated* [14]. The valence tail is barely broadened relative to the crystalline state density, while

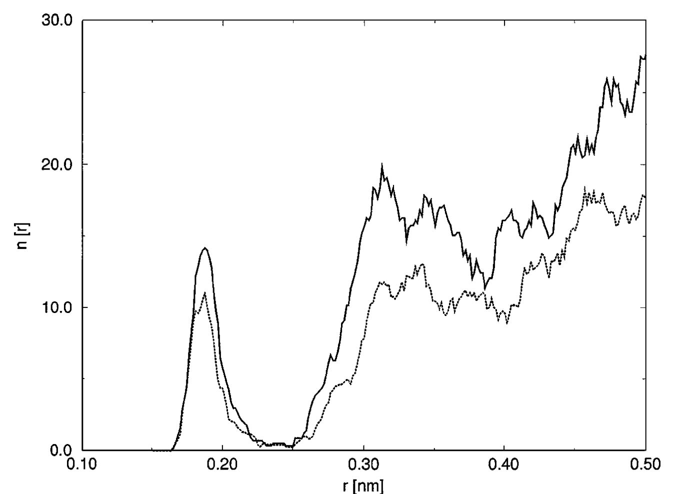

FIG. 1. Number density function $n(r)$ for both 64 atom models of a-GaN [solid line: model A (higher density); dotted line: model B (lower density)]. The broadening used was 0.03 Å.

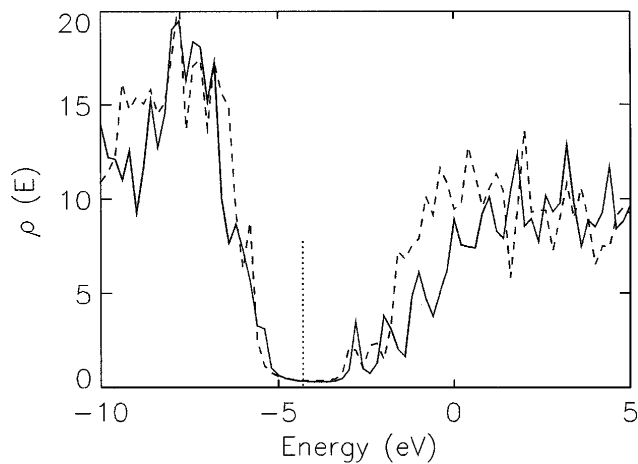

FIG. 2. Electronic density of states. The vertical dashed line is the Fermi level. We can roughly predict an experimental gap of 2.8 eV for both models, surprisingly independent of the threefold content. The broadening used was 0.1 eV.

the conduction tail states are significantly broadened by the topological disorder. Some measure of the ionicity of the models follows from our Mulliken populations, which show a typical net transfer of a 0.50 electron from Ga to N (with a fluctuation due to disorder of about 0.1 electron/atom).

It is quite promising that there are *no midgap states*, as one would certainly find in models of (unhydrogenated) amorphous Si or a-Ge. By analysis of the electronic eigenvectors, we find that the band tail states (on either side of the Fermi level) are significantly localized (as characterized by inverse participation ratio), with the valence tail states mostly localized on threefold N sites and the conduction tail states largely localized on threefold Ga sites.

Comparison of the localization of the band tail states for both models shows that tail states are more weakly localized in the lower density material (and more densely spaced) (see Fig. 3). In contrast, the higher density model has fewer but more localized states. This change towards less localization of the band tail states for the lower density model is expected, since the tail states are due to threefold coordinated atoms. As the number of threefold atoms increases, their associated localized eigenstates start to overlap and form an impurity band, *perhaps* eventually even exhibiting a local-to-extended [17] transition for a sufficient density of threefold sites. The remarkable drop in localization of the valence tail states in the lower density model is due to a large density of threefold N atoms with electronic energies nearly resonant, thereby producing considerable mixing and thus delocalization [18]. In contrast to a-C, for a-GaN we find that an increase in the threefold fraction in model B does not result in a smaller band gap, but instead, the density of the band tail states increases. *It is therefore probable that a-GaN could find use as an electronic material in its own right, since highly defective models possess no deep gap states and therefore no deep carrier traps—without defect passivating H, and exhibit much reduced band tail localization for the less dense model.*

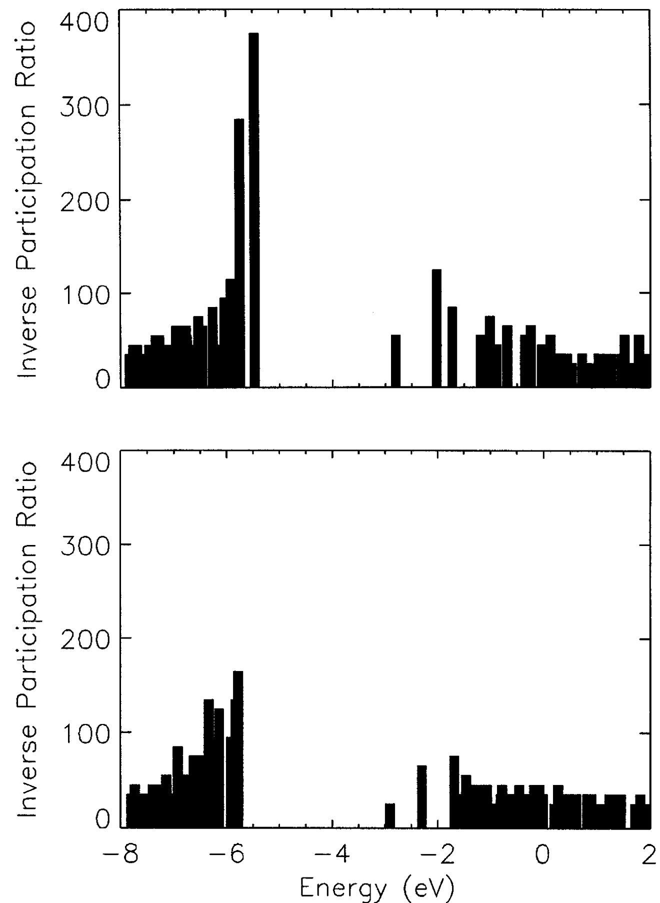

FIG. 3. Localization (inverse participation ratio) of the band gap states for model A (top) and model B (lower density) (bottom). The localization of the band tail states is decreased by up to 50% for the lower density model.

We have used approximate *ab initio* self-consistent density functional methods to model the microstructure and electronic properties of two models of amorphous GaN. There are no wrong bonds or odd-membered rings present in either model, and both models show a large, state-free band gap, despite the much larger threefold content of the lower density material. The localization of the band tail states is significantly decreased in the low density model, which should result in a higher mobility. The "simple physics" of this effect is that the creation of a *sufficient number of similar defects* in adequate proximity enables enough mixing or "banding" to yield tail states which may conduct, at least with some phonon assistance at finite temperature. Additional work on this material is needed: Larger models are desirable, and more accurate (albeit more costly) methods are also worth investigating.

Finally, simulations of doping and transport (using the Kubo formula and including finite-temperature effects) are needed to fully gauge the promise of this material. This work argues that any form of a-GaN may have utility as an electronic material and, particularly, low density phases (compared to the crystal) show special promise.

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