

Band gap engineering in amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$: Experiment and *ab initio* calculations

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Amorphous alloys of aluminum nitride and gallium nitride deposited at 100 K at compositions ranging from pure AlN to pure GaN with optical band gaps which vary linearly with composition from 3.27 eV (*a*-GaN) to 5.95 eV (*a*-AlN) have been synthesized. *Ab initio* molecular dynamics calculations for these alloys reproduce the band gap versus composition data and give specific information on the electronic localization of the band tail states. There are no midgap states in amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys. The calculated models have mixed four-fold and three-fold coordination and have no wrong (homopolar nuclear) bonds, demonstrating the strong ionicity in amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys. It has been found that the valence band tail states are mostly localized on the three-fold coordinated N sites while the conduction band tail states are mostly localized on the three-fold coordinated Ga or Al sites. © 2000 American Institute of Physics. [S0003-6951(00)02434-7]

The crystalline nitride semiconductors are used for many photonic applications, most notably light emitting diodes in the green to blue visible spectral range.^{1,2} The crystalline AlGaN alloys also are used for light emitters at intermediate colors. The crystalline AlGaN alloys, grown by metalorganic chemical vapor deposition, for example, are known to have a nearly linear relationship in composition versus band gap, with values ranging between 3.42 eV for GaN and 6.2 eV for AlN.^{3,4} Amorphous AlN and GaN have been grown using reactive sputtering at 100 K.^{5,6} Both of these materials are easily grown in standard, scalable, commercial sputtering system. The most critical aspect of deposition is the cooling of the substrate. The properties of amorphous GaN have been calculated using *ab initio* methods in Refs. 7 and 8. Surprisingly, amorphous AlGaN materials, like their crystalline counterparts, are transparent, (i.e., there is no midband gap state), and are therefore useful as hosts for optically active dopants and possibly for electronic purposes. In this letter we will show experimentally that alloys of amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ also exhibit a nearly linear relationship between band gap and metal composition. *Ab initio* calculations for the band gap engineering that support the experimental data and provide insight to tail states are also presented.

The amorphous films are grown with a reactive sputtering technique described in Ref. 5. The films are deposited onto a liquid nitrogen cooled substrate which reaches 100 K during deposition. The pure films have been grown by reactive sputtering of a liquid gallium target, a pure aluminum target, and by argon ion sputtering from a pressed-powder GaN target. The alloys are grown by simultaneous sputtering of the Al and Ga sources, or the Al and GaN sources. The relative composition is determined by regulating the power to each sputtering source, and the composition is monitored during growth by individual quartz crystal thickness monitors facing each of the targets. In practice, the alloy compo-

sition is determined from the equivalent thicknesses of each nitride component as determined from the thickness monitor. The absolute composition of these alloy films has been checked by rutherford backscattering spectroscopy, as reported in Refs. 5 and 6. The optical band gap is measured with a spectrophotometer. This procedure has been used for the pure amorphous films and reported in Refs. 5 and 6. Typical parameters for film growth are as follows: For the Al, Ga targets: gas ratio 80:20, nitrogen to argon, Al direct current (dc) power 80–150 W, Ga radio frequency (rf) power 40–100 W. Films have been deposited on Si(001) and quartz. For the Al and GaN targets: gas ratio 50:50, nitrogen to argon, Al dc power 100–200 W, GaN rf power 50–120 W. Films have been deposited on glass, quartz, and Si(001). In the GaN target series, some films were codoped with Er for luminescence purposes, see Refs. 5 and 6.

We applied an approximate self-consistent *ab initio* molecular dynamics approach based on the density functional theory with local density and pseudopotential approximations.^{9,10} The basis functions are slightly excited pseudoatomic orbitals. In our calculations, the minimal basis with one *s* and three *p* orbitals was employed per site. This approach has been extensively applied in the calculation of amorphous alloys^{11–13} and reproduces all the essential features of band structures of wurzite and zinc blende of GaN and AlN¹⁴ in the near band gap in agreement with more accurate local density approximation calculations.¹⁵

We constructed five initially random 216-atom models for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, with the Al fraction *x* being 0%, 25%, 50%, 75% and 100%. For each cell, the first 4.4 ps molecular dynamics simulations were performed for the initial random configuration at the temperature of 10⁴ K. The network was then equilibrated at 8 × 10³ K and then 6 × 10³ K, each for 2.2 ps, respectively. Slow dynamical quenching was performed to fully relax the system to zero temperature. The simulation was done at constant volume. Charge transfer was calculated self-consistently in the simulations, which is es-

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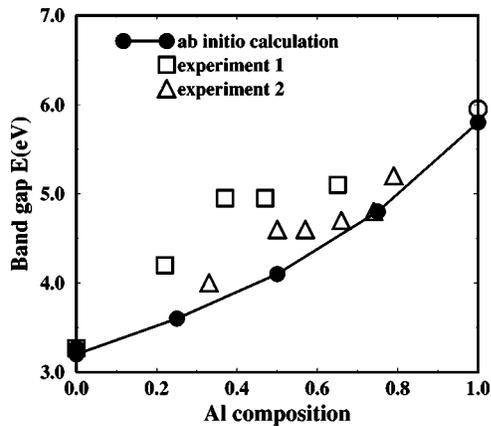


FIG. 1. The band gap engineering of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys vs Al composition x . The \square , \triangle , and \circ are experiment results, in which \square are grown from Ga metal and Al targets, and \triangle are grown from GaN and Al targets. The solid circles \bullet are from *ab initio* calculations.

sential in modeling these significantly ionic materials.

Figure 1 shows the band gap engineering of two sets of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy film data versus x , the Al composition by both experimental and *ab initio* calculations. It can be seen that the band gaps determined by theoretical calculations show a small downward bowing behavior. The average slope of band gap versus x by theoretical calculations is around 0.026 eV/% Al composition. While the slope of the band gap versus x measured by experiment is around 0.027 eV/% Al composition. The calculated results are in good agreement with experiment.

For our amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, we define the band gap as the difference between the mobility edge located at both conduction band (CB) and valence band (VB) edges (see Fig. 2). By this definition, we find that the calculated band gap is larger than the experiment by about the same amount of 1.4 eV for both amorphous GaN and AlN. This is consistent with a recent *ab initio* calculation of crystalline wurzite and random GaN and AlN.¹⁶ We found that the cal-

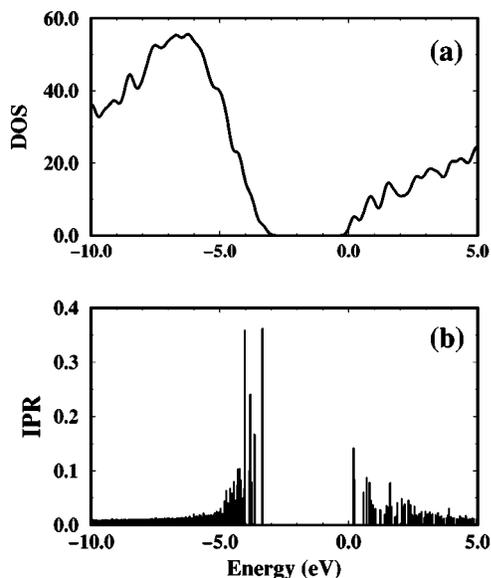


FIG. 2. (a) The electronic density of state of $\text{Al}_{50}\text{Ga}_{50}\text{N}$ alloy. The Fermi level is -1.2534 eV. The broadening factor is 0.05 eV. (b) The electronic localization (inverse participation ratio) of amorphous $\text{Al}_{50}\text{Ga}_{50}\text{N}$ alloy of the band gap state.

culated band gap for end point pure amorphous GaN and AlN is 4.62 and 7.24 eV, respectively, while the experimental results are 3.27 and 5.95 eV. The calculated results are 1.4 eV larger than the experiment. Thus we are able to reliably calculate the variation of the electronic bandgap energy as a function of Al composition. Figure 1 shows the theoretical calculated bandgap shifted downwards by 1.4 eV.

Figure 2(a) shows the electronic density of state (EDOS) for a specifically chosen composition of amorphous AlGa_xN alloys, the $\text{Al}_{50}\text{Ga}_{50}\text{N}$. The EDOS exhibits a large, state-free gap. No midband gap state appears. Therefore, no deep carrier traps exist, which is consistent with the experimental observation. In addition, the CB edge displays more tailing than the VB edge. For increasing Al content, it is found that the band gap opens up as indicated in Fig. 1. The electronic localization of band tail states is estimated by the inverse participation ratio of $q_2(\epsilon_i) = \sum_{n=1}^N q(n, \epsilon_i)^2$, where n and ϵ_i denote the number of atom and the eigenvalue, respectively. A completely localized state is described by $q_2=1$, and a completely delocalized state by $q_2=1/N$. The electronic localization of amorphous $\text{Al}_{50}\text{Ga}_{50}\text{N}$ is illustrated in Fig. 2(b). It is also observed that the location of the VB edge is weakly sensitive to the Al composition fraction. An analysis of the structural models demonstrates that no wrong bonds, i.e., homopolar nuclear bonds, are present. It also implies that amorphous $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys are strongly ionic. Furthermore, we did not observe any five-fold sites: only three-coordinated defects are present. We found that the number of three-fold defects in our *ab initio* calculations decreases with increasing Al composition for the five models. The VB tail states are mostly localized on the three-fold coordinated N sites, and the CB tail states on the three-fold Al or Ga sites.

Both experiment and simulation of these materials suggest that the coordination of both cation and anion sites is remarkably variable, and implies that the amorphous III-N alloys are quite different structurally and electronically from their crystalline counterparts. Despite these significant differences, the amorphous nets never exhibit deep traps and have large gaps with moderate bandtailing. These materials have proven utility as a host for rare-earth photonic devices and the robust lack of midgap states suggests their possible exploitation as an electronic material. Clearly the latter goal is far from certain, but these amorphous wide gap materials have special advantages: (1) a natural tendency to a state free gap without hydrogenation, a situation quite different than that for Si or diamond and, (2) these materials might be able to accommodate growth on a variety of substrates. As a final note, our work offers another hint about the surprising effectiveness of crystalline III-N materials in the presence of defects. In a crude sense our amorphous nitrides are exceedingly defective (from the perspective of the crystalline phases); yet even here there is a wide state-free gap. It leads us to speculate that even in the crystalline systems there may be remnants of the amorphous phases we report here and these would not be easily differentiated from the crystal, at least optically.

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- ¹S. C. Jain, M. Willander, J. Narayan, and R. Van Overstraeten, *J. Appl. Phys.* **87**, 965 (2000).
- ²S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, *J. Appl. Phys.* **86**, 1 (1999).
- ³M. R. H. Kahn, Ykoide, H. Itoh, N. Sawaki, and I. Akasaki, *Solid State Commun.* **60**, 509 (1986).
- ⁴H. S. Kim, R. A. Mair, J. Li, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* **76**, 1252 (2000).
- ⁵K. Gurumurugan, H. Chen, G. R. Harp, M. W. Jadwisienczak, and H. J. Lozykowski, *Appl. Phys. Lett.* **74**, 3008 (1999).
- ⁶H. Chen, K. Gurumurugan, M. E. Kordesch, W. M. Jadwisienczak, and H. J. Lozykowski, *MRS Internet J. Nitride Semicond. Res.* **5S1**, W3.1b (2000).
- ⁷P. Stumm and D. A. Drabold, *Phys. Rev. Lett.* **79**, 677 (1997).
- ⁸M. Yu and D. A. Drabold, *Solid State Commun.* **108**, 413 (1998).
- ⁹O. F. Sankey and D. J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989).
- ¹⁰A. A. Demkov, J. Ortega, O. F. Sankey, and M. P. Grumbach, *Phys. Rev. B* **52**, 1618 (1995).
- ¹¹D. A. Drabold, P. A. Fedders, S. Klemm, and O. F. Sankey, *Phys. Rev. Lett.* **67**, 2179 (1991).
- ¹²P. A. Fedders, Y. Fu, and D. A. Drabold, *Phys. Rev. Lett.* **68**, 1888 (1992).
- ¹³X. Zhang and D. A. Drabold, *Phys. Rev. Lett.* **83**, 5042 (1999).
- ¹⁴P. Stumm and D. A. Drabold, *Mater. Res. Soc. Symp. Proc.* **449**, 941 (1997).
- ¹⁵E. A. Albanesi, W. R. L. Lambrecht, and B. Segall, *Phys. Rev. B* **48**, 17841 (1993); W. R. L. Lambrecht, B. Segall, in *The Properties of III-Nitrides*, edited by J. H. Edgar (INSPEC, London, 1994).
- ¹⁶J. Fritsch, O. F. Sankey, K. E. Schmidt, and J. B. Page, *J. Phys.: Condens. Matter* **11**, 2351 (1999).