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Boron alloying in GaN

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Using first-principles calculations in the local density approximation, we studied effects of adding up to 6% boron to zinc-blende GaN. We found that the band gap increases monotonically with boron incorporation, in agreement with experiment. A composition-independent band-gap bowing parameter of 4.30 eV was determined, and proved to be large compared to bowing for other mixed cation systems. The formation enthalpy of mixing, ΔH, was determined for $B_xGa_{1-x}N$, $B_xGa_{1-x}As$, and $GaAs_{1-x}N_x$. A comparison of enthalpies indicates that the production of $B_xGa_{1-x}N$ films with boron concentrations of at least 5% may be possible. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644910]

Alloying in the group-III nitrides has diversified the properties of semiconductor materials, enabling the production of commercially important light emitting devices covering many regions of the visible spectrum.[1] Ongoing efforts to expand the range of available materials for III–V semiconductor applications include advancing epitaxial growth techniques and engineering energy band gaps.[2–4]

A potential candidate for band-gap modification in the nitrides is boron.[5–9] It has been reported that the nitride binary compound, GaN, alloyed with boron is a potential material for UV laser devices, in part since adding boron to GaN increases the band gap from the blue to the UV spectral region.[10] While prospects are positive for $B_xGa_{1-x}N$ alloys as viable III–V semiconductor materials, single phase $B_xGa_{1-x}N$ has not been achieved for boron concentrations necessary to effect significant change in structural and electronic properties of GaN.[8] Experimental work shows that phase separation occurs for boron content in excess of 2%, a consequence of the large lattice mismatch between BN and GaN that causes internal strain during processing.[6,7,9–15]

Experimental studies of high concentration, single-phase $B_xGa_{1-x}N$ rely on advances in growth techniques that are expected with sustained interest in these material systems.[8] Computational simulations can complement experimental efforts to expedite research. In this work, structural and electronic properties calculations for zinc-blende $B_xGa_{1-x}N$ with boron concentrations as high as 6% were carried out in the local density approximation (LDA) using the supercell approach and first principles pseudopotentials code (VASP).[16] Zinc-blende (zb) structures are utilized for computational convenience, but also serve as a model system for the wurtzite (wz) phase. We performed preliminary calculations using wurtzite supercells and found that wz-$B_xGa_{1-x}N$ band gaps are slightly larger than those for the zinc-blende alloy, as expected, since the reduced symmetry of wurtzite structures leads to coupling between conduction band minimum (CBM) and valence band maximum (VBM) states that raises the conduction band.[17] Bowing parameters for the two structures are also similar. We found that formation enthalpies for wz-$B_xGa_{1-x}N$ are higher than for the zinc-blende alloy. This result implies that the zinc-blende structure will have a greater boron solubility than the wurtzite structure.

Band-gap energy calculations were used to determine the $B_xGa_{1-x}N$ bowing parameter, a key factor in ternary semiconductor energy band-gap engineering.[4] Calculation and comparison of formation enthalpies for $B_xGa_{1-x}N$, $B_xGa_{1-x}As$, and $GaAs_{1-x}N_x$ predict that $B_xGa_{1-x}N$ films with boron concentrations of at least 5% are possible, a result that should encourage efforts to overcome the limitations of current growth techniques.

Calculations employed the gallium pseudopotential with Ga $3d$ states treated as valence states. More recent articles report that these states must be included in the pseudopotential since total energy characteristics are influenced by coupling of high energy gallium states to nitrogen valence states.[18,19] Earlier work treats the Ga $3d$ states as core states with[20] and without[21] correction. We find that including the Ga $3d$ states diminishes energy band gaps overall, an effect arising from Ga d and N p coupling that raises the VBM.[22] We also note that formation enthalpies are qualitatively different when Ga $3d$ states are pseudized away.

Supercells chosen for the study maximize nearest neighbor distances between alloying elements, with substitution at one gallium site. To test how well these supercells mimic true random systems, we calculated band gaps at $x=6\%$ for one boron atom in a 32-atom cell and for two boron atoms in a 64-atom cell. The latter configuration models a random system with more accuracy and effort than the single site substitution cell since a boron pair may occupy lattice sites in one of five symmetrically inequivalent pair configurations. Pair coordinates (from Ref. 23) are listed with corresponding calculated band gaps in Table I, with the total band-gap energy given as the weighted average of the five gaps ($\overline{E_g}$). A band gap of 2.7 eV was obtained for the one boron in a 32-atom cell, a mere 15 meV larger than the weighted average band gap for the 64-atom cell. This minor discrepancy indicates that for small alloy concentrations, single impurity supercells in this study represent random alloys sufficiently.

Determination of the band-gap bowing parameter, $b=4.30$, follows from the definition:

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TABLE I. Boron pair locations and band-gap energies for the $x=6\%$, 64-atom supercell. Similar band gaps for configurations indicate that supercells are sufficient approximations of random systems.

Boron coordinates	Weight	E_g (eV)
(0,0,0), $(0,\frac{1}{2},\frac{1}{2})$	12	2.2432
(0,0,0), (1,0,0)	3	2.2874
(0,0,0), $(1,\frac{1}{2},\frac{1}{2})$	12	2.2694
(0,0,0), (1,1,0)	3	2.2348
(0,0,0), (1,1,1)	1	2.2767
		$\overline{E}_g=2.2579$

$$E_g(x)=\overline{E}_g(x)-bx(x-1), \tag{1}$$

where $\overline{E}_g$ is the weighted linear average of the individual band gaps of the pure constituents and $E_g(x)$ is the alloy band gap at concentration x. The pure constituents linear average band gap (solid line) and a quadratic fit to the alloy band-gap energies (dashed line) are plotted in Fig. 1. Band-gap energies used in the bowing calculation (Table II) represent the energy difference at the gamma point, E_g^{Γ}. For direct band-gap materials, this is the energy difference between the VBM and the CBM. For $x=6\%$, the weighted average band gap of the five different configurations was used. The band-gaps are direct and increase monotonically with increasing concentration, in agreement with previously estimated trends that were verified through photoluminescence spectra.[8,14] Band gaps for the pure constituents were also calculated at the gamma point. For BN, an indirect band-gap material, the energy gap at gamma is not the energy difference between the VBM and the CBM. The indirect band gap of BN is not relevant to the bowing effects of the alloy, and is not reported in this work.[23] The calculated band gaps were 8.87 and 2.09 eV for BN and GaN, respectively, compared to accepted experimental values, 8.5–10 and 3.2 eV.[24,25] Theoretical band gaps are ~1–2 eV smaller than experimental due to LDA error.[26] This does not affect the accuracy of bowing calculations in which, to lowest order, LDA errors cancel.[23]

As seen in Table III, $B_xGa_{1-x}N$ exhibits the highest bowing relative to other mixed-cation systems, which tend to have low bowing. Band-gap bowing for the boron alloy is large, even compared to mixed-anion systems, such as $GaAs_{1-x}N_x$, which demonstrates giant and composition-dependent bowing.[2,27] These results indicate that alloying with boron will affect the band gap energy of III–V compounds significantly with adequate boron content. Also evident from Table III is the rough proportionality between bowing and lattice constant mismatch. When the alloy constituents suffer a large lattice mismatch, the coupling potential introduced during alloy formation is large. The resulting level repulsion drives the CBM and VBM closer together, effectively reducing the alloy band gap relative to the linear average band gap of the constituents. Positive bowing characterizes this effect, with greater reductions corresponding to larger bowing.[27,28]

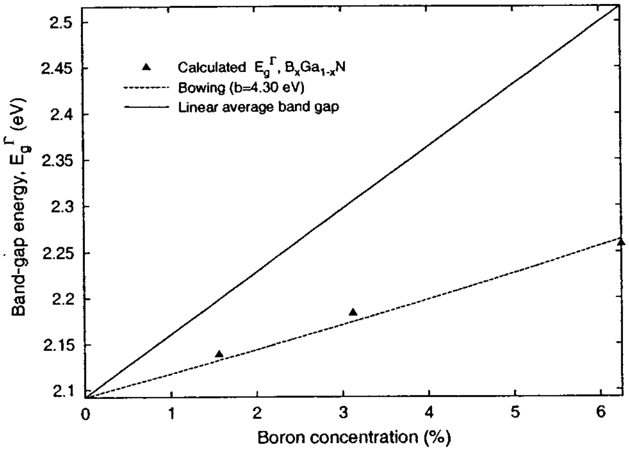

FIG. 1. Band gaps calculated for $B_xGa_{1-x}N$ deviate from the linear average of the calculated band gaps for BN and GaN to give a relatively large and composition-independent bowing parameter for the alloy.

TABLE II. Zinc-blende $B_xGa_{1-x}N$ energy band gaps, E_g^{Γ} (eV), at concentration x are used to determine the bowing parameter, b.

E_g^{Γ} (eV) vs x				Bowing, b (eV)
0%	1.5%	3%	6.25%	
2.0922	2.1381	2.1830	2.2579	4.30

In the case of cubic GaN alloyed with boron, there is a 24% lattice mismatch between BN and GaN that leads to internal strain, driving the alloy toward phase separation. For this reason, high crystalline quality $B_xGa_{1-x}N$ for boron concentrations exceeding 2% are presently unattainable.[9] It is possible that with continued effort $B_xGa_{1-x}N$ films with 5% boron could be produced. This assessment follows from a comparison of formation enthalpies of mixing for $B_xGa_{1-x}N$, $B_xGa_{1-x}As$, and $GaAs_{1-x}N_x$. Figure 2 illustrates trends for calculated formation enthalpies that were determined by taking the difference in energy between the alloy and the weighted sum of the constituents A and B:

$$\Delta H(x)=E_{\text{alloy}}-[(1-x)E_A+xE_B]. \tag{2}$$

With increasing concentration, each of the alloys exhibits increasing formation enthalpy. Higher formation enthalpies imply a strain energy contribution associated with deforming

TABLE III. Comparison of bowing parameters for zinc-blende III–V semiconductor alloys demonstrates that $B_xGa_{1-x}N$, with its large bowing parameter, is a potential candidate for band-gap engineering applications. The data also indicates a rough proportionality between bowing and lattice misfit.

Ternary alloy	Bowing parameter[a]	Lattice mismatch
Mixed cations		
$B_xGa_{1-x}N$	4.30	24%[b]
$B_xGa_{1-x}As$	3.50[c]	15%
$Ga_xIn_{1-x}N$	3.00	10%
$Al_xIn_{1-x}As$	0.70	7%
$Ga_xIn_{1-x}P$	0.65	7%
$Ga_xIn_{1-x}As$	0.48	7%
$Al_xGa_{1-x}N$	0.00	3%
$Al_xGa_{1-x}As$	−0.127–1.183	0.02%
Mixed anions		
$GaAs_{1-x}N_x$	5–20[d]	20%
$InP_{1-x}N_x$	15	15%
$InAs_{1-x}N_x$	4.22	18%
$GaP_{1-x}N_x$	3.90	17%
$GaAs_{1-x}P_x$	0.19	4%

[a] Bowing parameters and lattice constants used to obtain mismatch are given in Ref. 2 unless noted.
[b] Reference 9.
[c] Reference 23.
[d] References 27, 31, and 32.

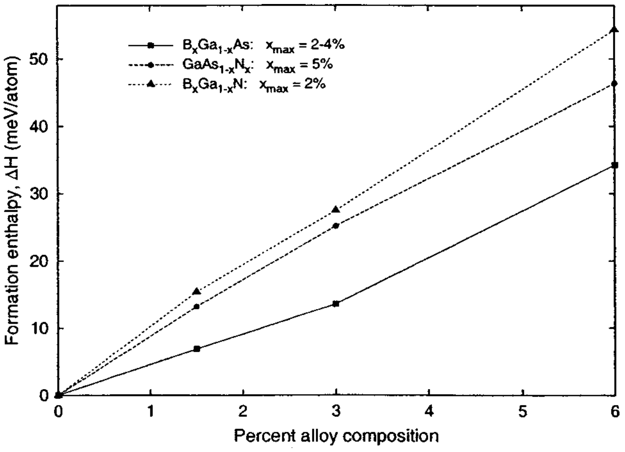

FIG. 2. Comparison of formation enthalpies of mixing shows similar trends and magnitudes between $B_xGa_{1-x}N$ and $GaAs_{1-x}N_x$, indicating that high quality $B_xGa_{1-x}N$ films with boron concentrations of at least 5% could be achieved. Lines between data points are meant only as guides for the eye.

the pure constituents into the alloy lattice.[23] If strain effects are not counterbalanced by chemical effects (i.e., enhanced bonding) during alloying, there is a net increase in the energy of the system and poor crystalline quality results. For this reason, trends in enthalpy of mixing can forecast the range of possible alloy compositions for a high quality material system. Figure 2 shows that the $B_xGa_{1-x}As$ system demonstrates the greatest range of possible alloy compositions with the lowest overall enthalpy of mixing. High alloy compositions are most difficult for $B_xGa_{1-x}N$ and are similar in trend and magnitude to those of $GaAs_{1-x}N_x$, suggesting that the range of possible boron concentrations for $B_xGa_{1-x}N$ should, in practice, parallel the range of nitrogen concentrations for $GaAs_{1-x}N_x$. This comparison is only applicable to the degree that strain due to lattice mismatch is the dominating factor leading to poor crystalline quality in these three alloys. Since high quality single crystals with nitrogen concentrations up to 5% have been achieved[29] (claims of 14.8% exist[30]), it is reasonable to conclude that 5% boron in GaN may be possible.

In summary, boron, with its relatively large bowing parameter is suitable for band-gap engineering III–V semiconductors. We also predict that boron solubility is greater in the zinc-blende structure than in the wurtzite structure. While the band-gap engineering potential of boron is limited by the difficulty of producing high quality $B_xGa_{1-x}N$ films, boron alloys do show promise, as illustrated by similarities between formation enthalpies for $B_xGa_{1-x}N$ and $GaAs_{1-x}N_x$. These studies indicate that higher concentration boron alloys are possible. Relative to $GaAs_{1-x}N_x$, a heavily studied ternary, $B_xGa_{1-x}N$ has had minimal attention. With increasing interest in $B_xGa_{1-x}N$ alloys it is probable that higher quality, higher concentration $B_xGa_{1-x}N$ films will be produced.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode: GaN Based Light Emitters and Lasers* (Springer, Berlin, 1997), pp. 1–5.
[2] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).
[3] A. Mascarenhas, Y. Zhang, J. Verley, and M. J. Seong, Superlattices Microstruct. **29**, 395 (2001).
[4] W. Lin and Y. Kuo, Proc. SPIE **4913**, 236 (2002).
[5] S. Sakai, Y. Ueta, and Y. Terauchi, Jpn. J. Appl. Phys., Part 1 **32**, 4413 (1993).
[6] C. H. Wei, Z. Y. Xie, J. H. Edgar, K. C. Zeng, J. Y. Lin, H. X. Jiang, C. Ignatiev, J. Chaudhuri, and D. N. Braski, Mater. Res. Soc. Symp. Proc. **537**, G3 (1999).
[7] V. Vezin, S. Yatagai, H. Shiraki, and S. Uda, Jpn. J. Appl. Phys., Part 2 **36**, L1483 (1997).
[8] T. Honda, M. Shibata, M. Kurimoto, M. Tsubamoto, J. Yamamoto, and H. Kawanishi, Jpn. J. Appl. Phys., Part 1 **39**, 2389 (2000).
[9] L. K. Teles, L. M. R. Scolfaro, and J. R. Leite, Appl. Phys. Lett. **80**, 1177 (2002).
[10] T. Honda, M. Kurimoto, M. Shibata, and H. Kawanishi, J. Lumin. **87–89**, 1274 (2000).
[11] A. Y. Polyakov, M. Shin, M. Skowronski, D. W. Greve, R. G. Wilson, A. V. Govorkov, and R. M. Desrosiers, J. Electron. Mater. **26**, 237 (1997).
[12] C. H. Wei and J. H. Edgar, J. Cryst. Growth **208**, 179 (2000).
[13] C. H. Wei, Z. Y. Xie, J. H. Edgar, K. C. Zeng, J. Y. Lin, H. X. Jiang, J. Chaudhuri, C. Ignatiev, and D. N. Braski, J. Electron. Mater. **29**, 452 (2000).
[14] V. K. Gupta, C. C. Wamsley, M. W. Koch, and G. W. Wicks, J. Vac. Sci. Technol. B **17**, 1246 (1999).
[15] L. K. Teles, J. Furthmüller, L. M. R. Scolfaro, A. Tabata, J. R. Leite, F. Bechstedt, T. Frey, D. J. As, and K. Lischka, Photonics Spectra **13**, 1086 (2002).
[16] Calculations employ ultrasoft pseudopotentials and a 4×4×4 mesh of Monkhorst and Pack special points for binary constituents and equivalent *k*-points for alloys. Plane-wave expansions for nitrogen-containing systems were restricted by an energy cutoff of 25.57 Ry. Energy cutoff for $B_xGa_{1-x}As$ and BAs was 18.90 Ry, and 15.70 Ry for GaAs. In all calculations, cell volume and cell-internal parameters were fully relaxed [H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976)].
[17] C.-Y. Yeh, S.-H. Wei, and A. Zunger, Phys. Rev. B **50**, 2715 (1994).
[18] L. E. Ramos, L. K. Teles, L. M. R. Scolfaro, J. L. P. Castineira, A. L. Rosa, and J. R. Leite, Phys. Rev. B **63**, 165210 (2001).
[19] M. Suzuki and T. Uenoyama, in *Properties, Processing and Applications of Gallium Nitride and Related Semiconductors*, edited by J. H. Edgar (INSPEC, London, 1999), pp. 159–167.
[20] R. Miotto, G. P. Srivastava, and A. C. Ferraz, Surf. Sci. **426**, 75 (1999).
[21] S. J. Jenkins, G. P. Srivastava, and J. C. Inkson, J. Phys. C **6**, 8781 (1994).
[22] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).
[23] G. L. W. Hart and A. Zunger, Phys. Rev. B **62**, 13 522 (2000).
[24] S. Rumyantsev, M. Levinshtein, A. D. Jackson, S. N. Mohammad, G. L. Harris, M. G. Spencer, and M. Shur, in *Properties of Advanced Semiconductor Materials*, edited by M. E. Levinshtein, S. L. Rumyantsev, and M. S. Shur (Wiley, New York, 2001), pp. 67–91.
[25] V. Bougrov, M. Levinshtein, S. Rumyantsev, and A. Zubrilov, in *Properties of Advanced Semiconductor Materials*, edited by M. E. Levinshtein, S. L. Rumyantsev, and M. S. Shur (Wiley, New York, 2001), pp. 1–30.
[26] W. R. L. Lambrecht, E. A. Albanesi, and B. Segall, Inst. Phys. Conf. Ser. **1994**, 457.
[27] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).
[28] S.-H. Wei and A. Zunger, Phys. Rev. B **39**, 3279 (1989).
[29] K. Uesugi, N. Morooka, and I. Suemune, Appl. Phys. Lett. **74**, 1254 (1999).
[30] W. G. Bi, C. W. Tu, D. Mathes, and R. Hull, Mater. Res. Soc. Symp. Proc. **449**, 203 (1997).
[31] W. G. Bi and C. W. Tu, Appl. Phys. Lett. **70**, 1608 (1997).
[32] J. Salzman and H. Temkin, Mater. Sci. Eng. **50**, 148 (1997).