The effects of biaxial strain and chemical ordering on the band gap of InGaN

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We have performed first-principles calculations to examine the effects of biaxial strain and chemical ordering on the band gap of wurtzite $In_xGa_{1-x}N$ in the range $0 \leq x \leq 0.5$. Our results for unstrained, random alloys are in good agreement with theoretical estimates and measurements on unstrained zinc-blende alloys, but are in poor agreement with recent measurements on strained wurtzite alloys which display significantly lower gaps. Biaxial strain is found to have a non-linear effect on calculated alloy gaps, increasing them for $x < 0.25$ and decreasing them for $x > 0.25$. However, the overall agreement with measured wurtzite values remains poor. Chemical ordering along the [0001] direction in strained alloys is found to decrease the band gaps considerably, yielding much improved agreement with measurements. We discuss our results with regard to current theories concerning the optical properties of wurtzite InGaN alloys.

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Wurtzite $In_xGa_{1-x}N$ has a direct band gap that can potentially be varied from 3.42 ($x = 0$) to 1.89 eV ($x = 1$), making it useful for fabricating blue and green light-emitting diodes. Recent experimental studies have begun to provide valuable insights into the properties of InGaN,[1-5] and two noteworthy observations have emerged from these studies: 1) InGaN layers up to 2500 Å thick can be grown coherently on GaN in spite of the sizeable lattice mismatch ($\approx 2.7\%$ mismatch at $x = 0.25$, for instance), and 2) The peak in photoluminescence (PL) spectra is often observed at a lower energy than the absorption edge typically used to define the band gap. Chichibu *et al.*[6] proposed that the redshift in the PL signal (sometimes referred to as the Stokes shift) arises from the recombination of excitons localized in indium-rich regions of the alloy, and this view has recently been extended by O'Donnell *et al.*[7] who speculated that quantum dots exist within the alloy matrix having compositions approaching InN. Coherent growth results in compressive biaxial strain within the alloy which can change its band structure, and may also generate an internal electric field causing field-induced tail states to appear below the absorption edge via the Franz-Keldysh effect.[8] Wetzel *et al.*[8] proposed that the redshift in the PL signal in strained alloy films originates from these tail states, thereby providing an explanation that does not require the presence of composition fluctuations or quantum dots.

Notwithstanding the different proposed explanations for the redshift in the PL signal, alloy band gaps as measured by absorption-related techniques (absorption, photoreflectance and spectroscopic ellipsometry) vary significantly between films grown by different groups. This is illustrated in Fig. 1 where we plot the gap deviations, $\Delta E_g = E_{g,InGaN} - xE_{g,InN} - (1 - x)E_{g,GaN}$, from five sets of InGaN films. (The gap deviation is used here in order to emphasize the band-gap bowing and to facilitate comparisons between theory and measurements, and wurtzite and zinc-blende results.) We note that the gap deviations for biaxially strained wurtzite films are consistently below the values for unstrained zinc-blende films, whereas strain is expected to increase the band gap. One purpose of this study was therefore to carefully examine the effect of biaxial strain in wurtzite $In_xGa_{1-x}N$ films. We have also examined the effect of chemical ordering on the band gaps of strained wurtzite $In_xGa_{1-x}N$. This work was motivated by experimental

studies showing evidence of cation ordering along the [0001] direction in wurtzite alloys.[9] Furthermore, a recent theoretical study by Northrup et al.[10] reported that indium atoms have a 0.5 eV bias to incorporate at one of the two possible sites at a step edge in wurtzite InGaN, thereby providing a mechanism for ordering along the [0001] direction. For future reference, we note that this mechanism does not apply to cubic structures so this type of ordering should not be present in zinc-blende InGaN.

Our calculations were performed using the Kohn-Sham formulation of density-functional theory[11] with 192-atom supercells consisting of 4×4×3 primitive wurtzite cells. We considered the set of x values 0.0625, 0.125, 0.1875, 0.250, 0.375, and 0.5, and for each x we generated five separate configurations in order to assess the variation in the computed alloy properties with atomic configuration and the finite-sized supercell used in these calculations. Ordered configurations were generated by constraining indium atoms to reside on alternating planes along the [0001] direction and randomly occupying cation sites within a plane. Random configurations were generated by randomly occupying the cation sites. The atom positions were fully relaxed for all of the supercells considered, and the cell shapes for unstrained cells were adjusted until the diagonal elements of the stress tensor were equal to zero. For strained cells, the lattice constant in the (0001) plane was fixed at the theoretical value for GaN, and the lattice constant along the [0001] direction was adjusted until the corresponding component of the stress tensor was equal to zero. The calculations were performed using the plane-wave, ultrasoft pseudopotential formulation,[12] employing pseudopotentials developed by Grossner et al.[13] The Brillouin zone was sampled using the Γ-point, and tests using Monkhorst-Pack[14] parameters {2,2,2} verified the adequacy of this sampling.

We first briefly discuss results related to alloy lattice constants and mechanical properties. The a lattice constants of the unstrained supercells were found to be within 0.4% of the composition-weighted averages of the constituent values and the c lattice constants were within 0.3%, indicating that Vegard's law[15] is valid for wurtzite InGaN. The c lattice constants of the strained, random supercells were within 0.2% of the values predicted using composition-weighted lattice and elastic constants,[16] indicating that no

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unusual behavior exists in terms of the mechanical response of InGaN to biaxial strain. Finally, negligible differences were found in the strain along the c-axis between ordered and random structures.

In Fig. 2, we present our results for unstrained, random wurtzite alloys. For each composition we show the average of the gaps from the five configurations and the standard deviation. The band gap dependence on composition is nearly parabolic with bowing parameter, b, ranging from 1.2 ($x = 0.5$) to 1.5 eV ($x = 0.1875$) where the bowing parameter is defined in terms of the expression $\Delta E_g = -bx(1 - x)$.. Our results are compared with measurements on unstrained zinc-blende alloys and theoretical estimates for zinc-blende alloys obtained using special quasirandom structures (SQS).[17] The calculated wurtzite and zinc-blende gap deviations are in good agreement, providing confidence in the often made assumption that nitride alloys having these two structures should have similar band-gap bowing. The theoretical results are in very good agreement with measurements by Goldhahn *et al.*,[4] and somewhat worse agreement with the results of Brandt *et al.*[5] beyond $x = 0.1$.

In Fig. 3, we display all of our results for wurtzite alloys. Straining the random alloy to be coherent with GaN increased the gaps for $x < 0.25$ and decreased them for $x > 0.25$. A similar non-linear behavior was found for wurtzite GaN under biaxial strain in the (0001) plane over the range $-0.04 \leq \varepsilon_{\parallel} \leq +0.01$ where $\varepsilon_{\parallel}$ is the in-plane strain. Zinc-blende GaN displayed similar non-linear behavior for trigonal strain, but only weakly non-linear behavior for tetragonal strain over the same range of strain values. As a check that these results were not an artifact of the pseudopotential approximation, the same calculations were performed using the all-electron, full-potential, linear muffin-tin orbitals method. Almost exact agreement was found both in the absolute values of the band gaps and their strain dependence. Similar calculations were carried out for zinc-blende GaP under trigonal strain and roughly comparable non-linearities were found. Further studies are underway to determine the origin of this surprising behavior.

Ordering the strained alloys reduced their band gaps considerably (Fig. 3). Before comparing these results to measurements, we note that the strain-induced electric field discussed by Wetzel et al.[8] can alter the alloy band structure aside from causing field-induced tail states. To estimate the magnitude of this effect, we note that the field will exert a force on an atom proportional to its ionic charge. If we assume a charge of −1 for nitrogen ions, +1 for cations, and a field strength of 1 MeV/cm, then the force on an atom will be 0.01 eV/Å in magnitude. These forces will tend to lengthen the cation-nitrogen bond oriented along the c-axis and, as a secondary effect change the c lattice constant. We estimated the field effect on the band gap by displacing the atoms in an $x = 0.5$ ordered alloy and relaxing the c-axis in response to these displacements. The resulting change in the alloy gap was +25 meV. If we assume that this effect scales linearly with composition, then it will have little bearing on the comparisons or discussion presented below and we therefore neglect it.

Our strained wurtzite results are compared with corresponding measurements in Fig. 3. The results for random alloys fall above the measurements and are in poor agreement with them. The results for ordered alloys are in much better agreement with the measured values, especially those of Wagner et al.[3] In addition, we note that O'Donnell et al.[18] estimated a gap deviation of $\Delta E_g = -1.45x$ eV for $In_xGa_{1-x}N$ in the range $0 \leq x \leq 0.4$. A linear fit to our strained, ordered results yields $\Delta E_g = -1.5x$ eV in excellent agreement with their estimate. O'Donnell et al.[18] also emphasized that their measurements showed no evidence of a parabolic form for the gap deviations, and the same might be said for the experimental results shown in Fig. 3. Our calculations indicate that this behavior arises mainly from the non-linear response of the alloy gap to biaxial strain, although ordering enhances the linearity beyond $x = 0.25$.

In summary, our results for unstrained, random wurtzite alloys and our estimates for zinc-blende alloys are in good agreement with each other, and in good agreement with zinc-blende measurements.[19] Our results for random alloys indicate that biaxial strain by itself cannot account for the differences in measured gap deviations between wurtzite and zinc-blende samples. However, we do find an interesting, non-linear band-gap

dependence on strain, both for InGaN and for bulk compounds. Cation ordering along the [0001] direction considerably reduces the band gap of strained wurtzite alloys as compared with random alloys, and yields much improved agreement with measured values. The presence of chemical ordering may therefore provide an explanation for the different gap deviations of wurtzite and zinc-blende samples, since this type of ordering should not occur in zinc-blende InGaN. In light of these results, it seems worthwhile to look for evidence of ordering in a broader set of wurtzite samples than has been examined up to now. The presence of composition fluctuations or indium-rich quantum dots in wurtzite InGaN and their absence in zinc-blende InGaN could possibly account for the differences in wurtzite and zinc-blende gap deviations. However, a more complete theory of how these fluctuations affect absorption is needed as well as an explanation of why the fluctuations apparently do not exist in zinc-blende alloys.

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A. Measurements of the gap deviation in InGaN alloys. The gap deviations for zinc-blende were computed assuming a band gap of 1.8 eV for zinc-blende InN.

B. Calculated gap deviations for random, unstrained wurtzite InGaN, estimated gap deviations for zinc-blende InGaN, and corresponding experimental results for zinc-blende InGaN. The symbols for the wurtzite results show the average of the gaps from the five configurations and the vertical lines give the standard deviations. The gap deviations for the experimental results were computed assuming a band gap of 1.8 eV for zinc-blende InN.

C. Theoretical and experimental gap deviation results for wurtzite. The symbols for the wurtzite results show the average of the gaps from the five configurations and the vertical lines give the standard deviations. Note that we have offset the compositions for the random results by ± 0.003 to make them easier to distinguish.
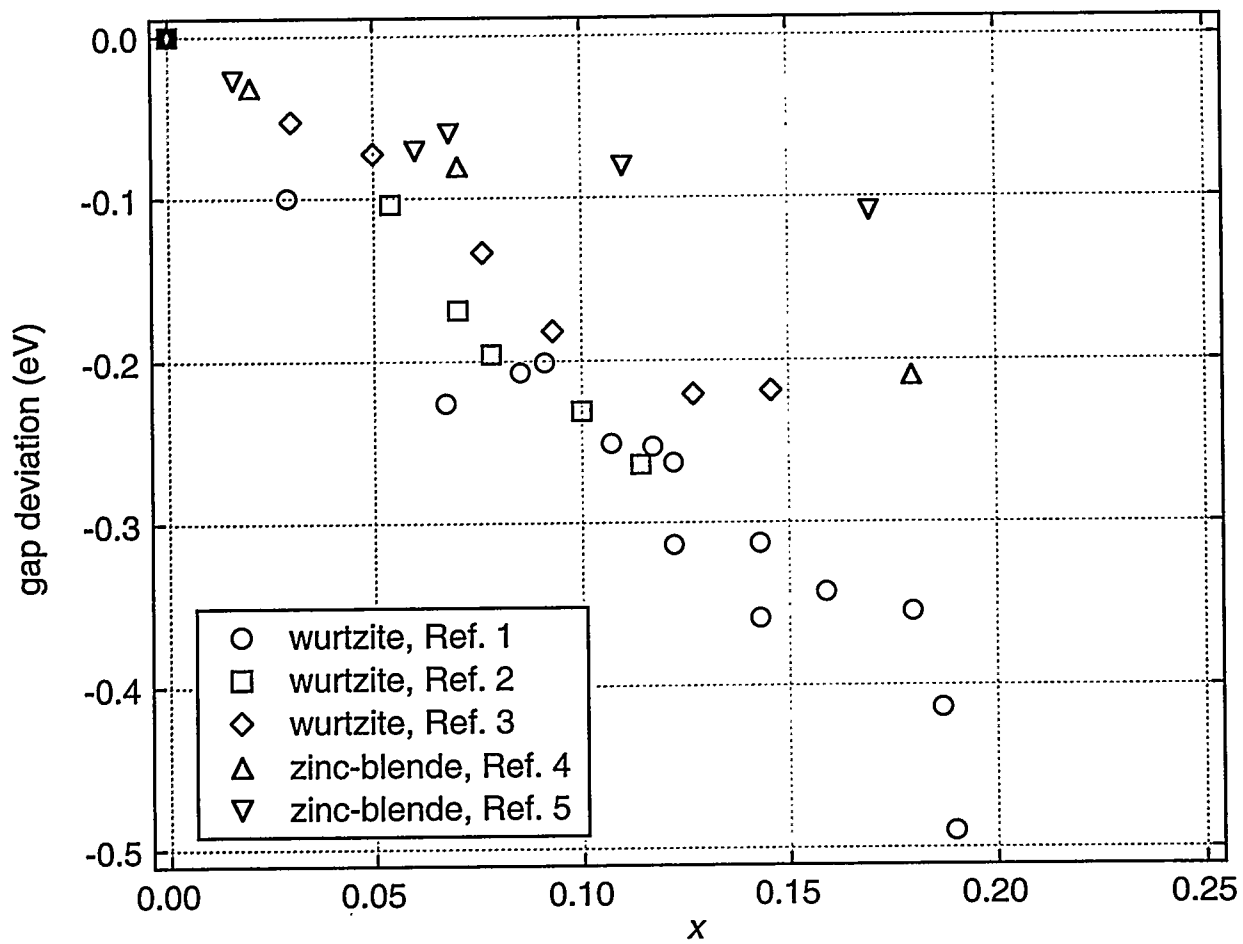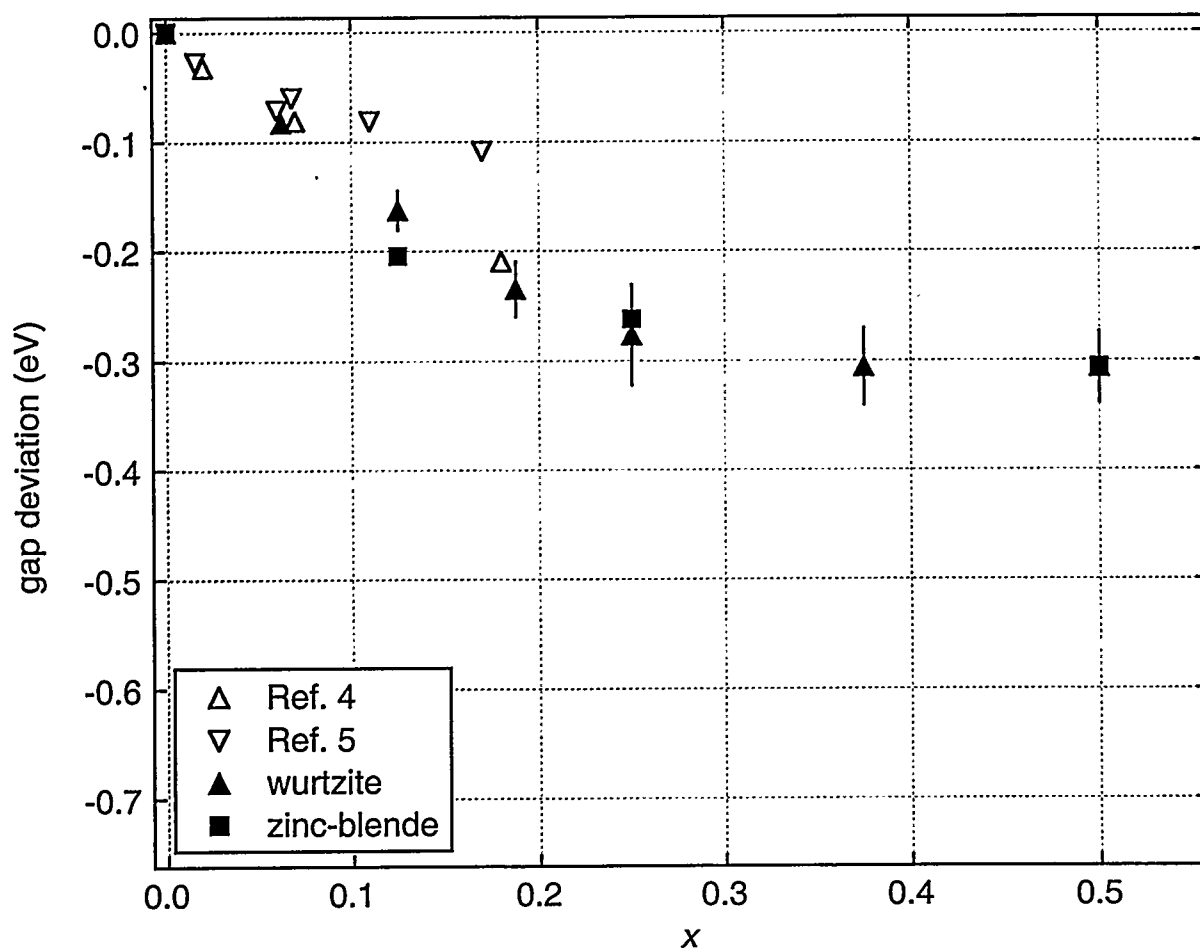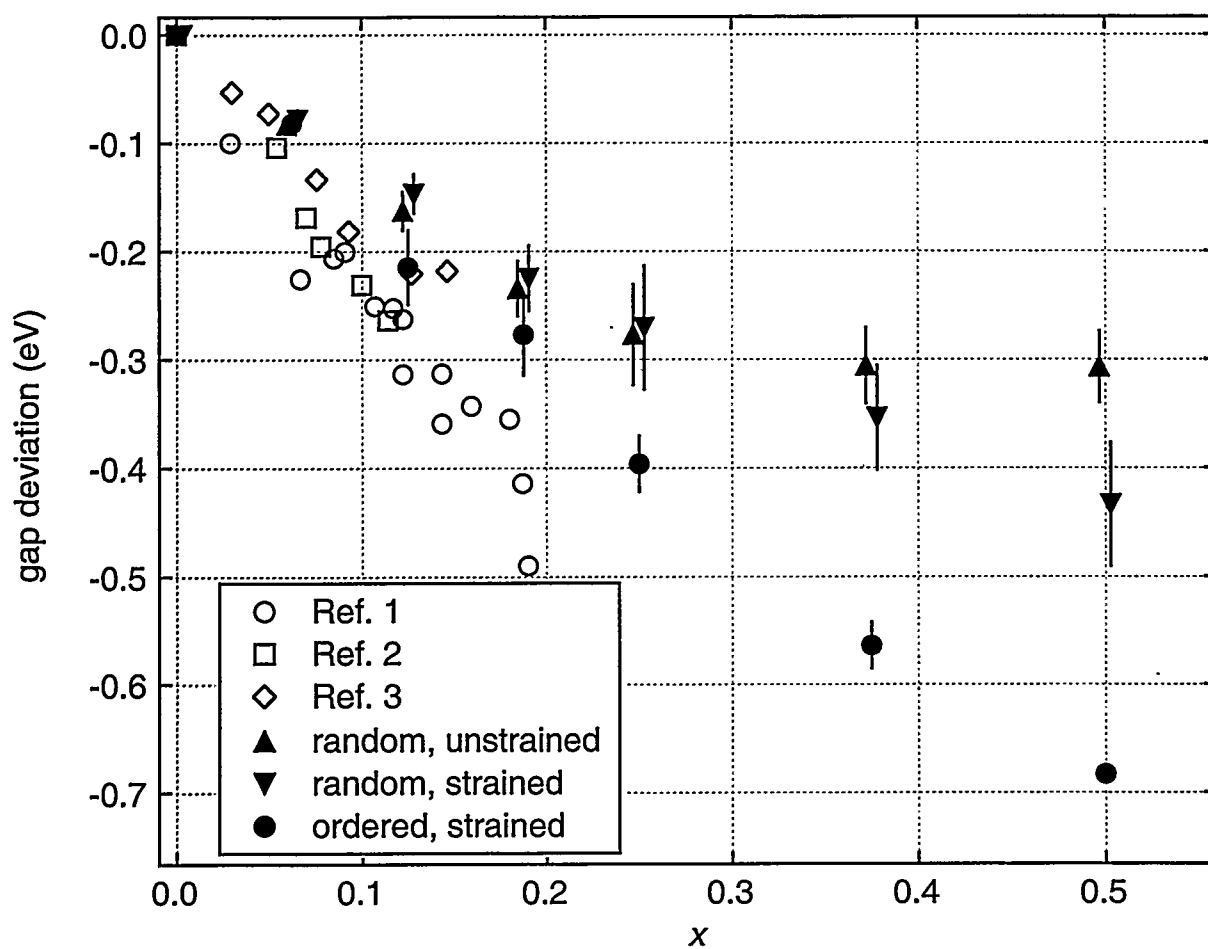
Fig. 1

Fig. 2.

Fig. 3