

Influence of the dipole interaction energy on clustering in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys

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The interactions of the polarization-induced dipole moments at each unit cell in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have been studied using analytical electrostatic dipole energy calculations to determine their potential influence on local material composition. Clustering of In atoms along the [0001] direction and anticlustering of In in the (0001) plane are shown to be energetically favorable. Comparisons of the dipole interaction energy to the strain energy and the energy associated with the decreased entropy of the ordered configurations show that the dipole interaction energy could have a substantial influence on local composition in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys. © 2001 American Institute of Physics. [DOI: 10.1063/1.1366651]

The InGaN/GaN material system is of great interest for optical devices such as blue/green light-emitting diodes and lasers, but questions still remain regarding the detailed mechanisms responsible for the high emission efficiencies observed.¹ In a quantum well, the electric field caused by the polarization in the material has a large impact on the degree of wave function overlap between electrons and holes and, therefore, affects the recombination efficiency of the device.² Evidence of compositional inhomogeneities (clustering or phase separation) has also been reported in InGaN/GaN quantum well structures.^{3–5} In many structures these inhomogeneities are believed to play a major role in the attainment of high emission efficiencies,⁶ but the physical mechanisms responsible for such clustering have not been extensively explored. These inhomogeneities can affect device performance via localized variations in energy band gap and polarization field, and it is, therefore, essential to understand their origin.

The polarization fields that arise in III–V nitride compounds due to the spontaneous polarization and piezoelectric effect have been shown to be exceptionally large.⁷ Thus, small fluctuations in the chemical composition or strain within a ternary or quaternary III–V nitride alloy layer can lead to pronounced local variations in the polarization fields, and thereby modify device characteristics. For example, the fluctuation of the dipole moments present at each unit cell of an AlGaIn/GaN heterostructure has recently been shown to decrease the mobility of carriers in the two-dimensional electron gas of a heterostructure field-effect transistor due to scattering from the random distribution of dipole moments.⁸

It is possible that the electric field from such dipole moments could also influence the material composition locally by favoring configurations that would minimize the dipole interaction energy. Such a process would be present in InGaN, AlGaIn, and AlInGaIn alloys, and could cause short-range clustering to occur in these compounds. In this letter, we focus on understanding the impact of the local dipole moment interaction energy on InGaN compounds by exam-

ining how this energy can be configurationally minimized and how this phenomenon may contribute to clustering in ternary nitride alloys.^{3,4,9,10} Studies in other material systems have shown that surface reconstruction that occurs during growth can also have a significant influence on ordering.¹¹ In addition, surface phenomena in III–V nitride semiconductors such as the presence of metallic Ga/In layers during growth¹² and termination of dipole fields by surface charges may influence alloy clustering or ordering. Although it is possible that such mechanisms influence InGaN in a similar manner, the present investigation will neglect such effects in an attempt to gain a basic physical understanding of the influence of the dipole interaction energy. Our results show that clustering of In atoms along the [0001] direction and anticlustering of In atoms in the (0001) plane are energetically favorable.

In an InGaIn compound, microscopic dipoles are caused by a separation of charge between In or Ga atoms and N atoms which are aligned along the [0001] direction as shown in Fig. 1. The average polarization of the material, defined as the dipole moment per unit volume, is the sum of the micro-

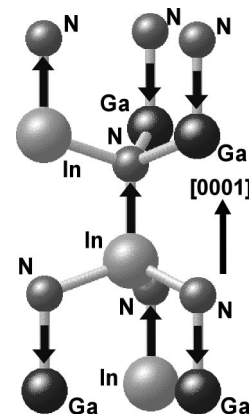


FIG. 1. Crystal structure of InGaIn showing the directions of the dipole moments along In–N and Ga–N bonds. The figure depicts one dipole in the center position with its six “vertical nearest-neighbors.” Each of the three dipoles above and below the central dipole are “horizontal nearest-neighbors” to each other.

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scopic dipole moments divided by the volume of the crystal. To estimate the size of the microscopic dipole moment for an In–N (Ga–N) dipole in an $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy coherently strained to the relaxed GaN lattice constant, the polarization for InN (GaN) strained to a GaN substrate can be multiplied by the volume that the dipole occupies, given by $\Omega(x) = \sqrt{3}c(x)a_{\text{sub}}^2/4$, where $c(x)$ is the lattice constant of the coherently strained material and a_{sub} is the lattice constant for the GaN substrate.⁸ Possible additional lattice distortions arising from local compositional fluctuations are neglected. The polarization for In–N and Ga–N dipoles includes the spontaneous polarization of the binary alloy and, for In–N dipoles, also includes a piezoelectric component given by $P_{\text{pz}} = 2[(a_{\text{sub}} - a_{\text{InN}})/a_{\text{InN}}][e_{31} - e_{33}(c_{13}/c_{33})]$, where a_{InN} is the lattice constant of unstrained InN and e_{31} , e_{33} , c_{13} , and c_{33} are the piezoelectric coefficients and elastic constants for InN. Calculating the dipole moment associated with In–N and Ga–N dipoles using this model yields values of $5.24 \times 10^{-28} \text{ C cm}$ and $-0.67 \times 10^{-28} \text{ C cm}$, respectively, and with these values, it is possible to calculate the interaction energy between two dipoles as

$$U_{\text{dipole}} = \frac{1}{4\pi\epsilon_0\epsilon_{\text{InGaN}}} \left[\frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r^3} - 3 \frac{(\mathbf{r} \cdot \mathbf{p}_1)(\mathbf{r} \cdot \mathbf{p}_2)}{r^5} \right], \quad (1)$$

where ϵ_{InGaN} is the relative dielectric constant of $\text{In}_x\text{Ga}_{1-x}\text{N}$. Equation (1) is in fact a conservative estimate of the dipole interaction energy: the interaction energy of dipoles that are located within a few unit cells may be larger because the relative dielectric constant of InGaN used in Eq. (1) is a macroscopic quantity for the bulk material, whereas nearby dipoles are less affected by the surrounding crystal and the dielectric constant used in Eq. (1) should be closer to the dielectric constant of vacuum.

Two principal strategies were employed to evaluate the potential influence of the dipole interaction energy on clustering. First, the dipole interaction energy was calculated for two isolated dipoles with their relative positions corresponding to positions in the InGaN crystal structure. This enabled a clear determination of where the dipole interaction is strongest and what sites were favored by specific group III atoms. The energy arising from the interactions of all the dipoles in the crystal was then computed, thereby yielding more accurate information regarding the favorability of certain configurations. Finally, the magnitudes of the energies obtained with these techniques were compared to the strain energy in an $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy coherently strained to GaN, and to the change in energy associated with the configurational entropy change in going from a random distribution of atoms to an ordered configuration. The values for the physical constants were taken from Bernardini *et al.*⁷ and Wright.¹³

Using Eq. (1), the dipole interaction energy for two isolated In–N dipoles was calculated; the results are shown in Fig. 2. The relative separation of the two dipoles is represented in the figure by fixing one dipole at the origin, marked with an ‘‘X,’’ and locating the other dipole at the position shown in the schematic $[11\bar{2}0]$ view of the crystal. A negative interaction energy indicates that the presence of an In atom at that site is favored when an In atom is located at the site marked with an X. Since the interaction is symmetric

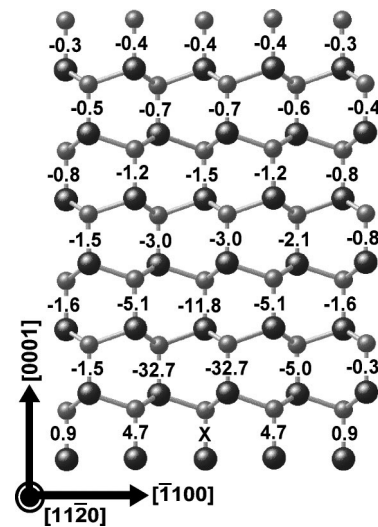


FIG. 2. Schematic $[11\bar{2}0]$ view of the wurtzite crystal structure with labels corresponding to the dipole interaction energy (in millielectron volts) between an In–N dipole located at the position marked X and another In–N dipole located at the position in the lattice where the label is placed. The interaction energy is calculated for each dipole pair isolated from the rest of the crystal.

about the $[0001]$ direction, sites located below the dipole at the origin are not included in Fig. 2.

It is possible to make a number of important observations from Fig. 2. Foremost among these is that when the central site is occupied by an In atom, occupation of the central site’s vertical nearest neighbor (VNN) positions by In atoms is strongly favored, whereas occupation by In of the horizontal nearest neighbor (HNN) sites is energetically unfavorable. It is also apparent that the interaction energy decreases quickly as the dipole separation increases. These as well as further calculations show that beyond three unit cells, the interaction energy is relatively small. The dipole interaction between two sites occupied by Ga atoms is qualitatively the same as the In–In interactions, but smaller in magnitude due to the dipole moment of a Ga site being much smaller than the dipole moment of an In site. Calculations also show that occupation of VNN sites by different types of atoms is unfavorable, but that HNN site occupation by unlike atoms is favorable. For an In atom located at the center site, replacing a Ga atom with In in a VNN position decreases the energy of the configuration by $\sim 37 \text{ meV}$, while the same substitution in a HNN site increases the energy by $\sim 5 \text{ meV}$. For a Ga atom located at the center site, the replacement of an In atom by a Ga atom in a VNN position decreases the energy of the configuration by $\sim 5 \text{ meV}$, whereas the same substitution in a HNN site increases the energy of the configuration by $\sim 1 \text{ meV}$. These results reinforce the two main points that like atoms favor vertical clustering, and unlike atoms favor horizontal anticlustering.

A limitation of the calculations presented before is that they only include interactions between two dipoles at specific positions, and do not take into account the interactions of the dipoles with the rest of the crystal. Thus, we have also calculated the energy arising from the interactions between all the dipoles in a fixed volume to determine whether vertical clustering is still favorable. In calculating the energy for one site (referred to as the site energy U_{site}), the interactions

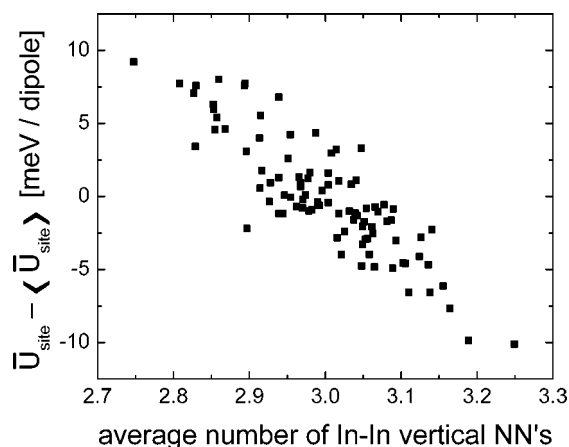


FIG. 3. Average dipole interaction energy per site for 100 randomly generated $\text{In}_{0.50}\text{Ga}_{0.50}\text{N}$ configurations referenced to average energy per site for all configurations. Plotted vs the average number of In vertical nearest-neighbors of each In site, this shows that a greater number of In sites aligned along the growth direction on average decreases the dipole interaction energy for the volume.

between the dipole at that site and the dipoles within 20 sites in each direction were summed; more extensive calculations indicated that the interactions with the rest of the crystal could be approximated by a constant. The constant term, however, depends on whether the dipole at the center is an In–N or Ga–N dipole, and, therefore, only differences in energy for sites with an In–N dipole or differences in energy for sites with a Ga–N dipole are meaningful.

Calculating the average site energy for a fixed volume, \bar{U}_{site} , gives a good measure of whether the configuration in that volume is energetically favorable. From the calculations before, the configuration that should exert the largest influence on the site energy is two In atoms occupying VNN sites. Figure 3 shows \bar{U}_{site} for 100 randomly generated $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy configurations with $x=0.50$, referenced to the average value of \bar{U}_{site} for all configurations, $\langle \bar{U}_{\text{site}} \rangle$. \bar{U}_{site} decreases as the average number of In–In VNNs increases, showing that when including all the dipole interactions, it is still favorable to have In atoms aligned along the growth direction. Calculations for other compositions yielded similar results.

We have also compared energies associated with other mechanisms which can influence the local configuration to the dipole interaction energy in an effort to assess its relative significance. The vertical In clustering suggested by our calculations is a nonrandom configuration which will increase the mixing energy due to the substantial decrease in entropy. Our estimates of the energy arising from this entropy decrease indicate that at low In concentrations, this energy is greater than the dipole interaction energy for typical growth temperatures, but for higher In concentrations where the decrease in entropy is not as great, the dipole interaction energy is the more important term. By substituting an In atom for a Ga atom in a VNN position of an In atom, the energy reduction arising from the dipole interaction is roughly equal to the increase in energy associated with the decrease in entropy for a temperature of 1000 K and an In concentration of $\sim 30\%$. Strain energy minimization will also affect the local composition of a semiconductor. We have calculated the strain energy for the entire range of In composition and

found that the magnitude of the dipole interaction energy is larger than that of the strain energy for In concentrations below $\sim 25\%$. Because we have most likely overestimated the relevant dielectric constant in our calculations, the influence of the dipole interaction energy may be even greater than just stated.

From the present work, it appears that minimization of the dipole interaction energy could be a major factor leading to clustering. Formation of In clusters aligned along the [0001] direction is especially favorable and is most likely to occur at midrange In compositions where the energy associated with the decrease in entropy and the energy due to strain in the material are less significant than the dipole interaction energy. Recent work has shown that strain-induced ordering in InGaN can also have important effects for both electronic and optical properties of the material.¹⁴ A study which incorporates the strain energy and dipole interaction energy simultaneously would therefore be useful. Ordering in AlGaN has also been detected,¹⁰ however, our calculations indicate that the dipole interaction energy for this material system is significantly lower, suggesting that other mechanisms may contribute to clustering or ordering in $\text{Al}_x\text{Ga}_{1-x}\text{N}$.

In summary, analytic calculations of the electrostatic interaction energy between the fixed dipoles that exist at each unit cell in $\text{In}_x\text{Ga}_{1-x}\text{N}$ have been performed to assess the possible influence of the dipole interaction energy on local material composition. Calculations of the dipole interaction energy have shown that In clustering in the [0001] direction and In anticlustering in the (0001) plane are energetically favorable. By calculating the energy associated with the decreased entropy of the In cluster, it was found that the dipole interaction is more likely to have an influence at higher In concentrations. The dipole interaction energy should also be an important factor relative to the strain energy, especially for low In concentrations.

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- ¹S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, *Appl. Phys. Lett.* **69**, 4188 (1996).
- ²J. L. Sanchez-Rojas, J. A. Garrido, and E. Munoz, *Phys. Rev. B* **61**, 2773 (2000).
- ³F. A. Ponce, D. Chems, W. Goetz, and R. S. Kern, *Mater. Res. Soc. Symp. Proc.* **482**, 453 (1998).
- ⁴N. Duxbury, U. Bangert, P. Dawson, E. J. Thrush, W. Van der Stricht, K. Jacobs, and I. Moerman, *Appl. Phys. Lett.* **76**, 1600 (2000).
- ⁵M. Benamara, Z. Liliental-Weber, W. Swider, J. Washburn, R. D. Dupuis, P. A. Grudowski, C. J. Eiting, J. W. Yang, and M. A. Khan, *Mater. Res. Soc. Symp. Proc.* **572**, 357 (1999).
- ⁶S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997).
- ⁷F. Bernardini, V. Fiorentini, and D. Vanderbilt, *Phys. Rev. B* **56**, R10024 (1997).
- ⁸D. Jena, A. C. Gossard, and U. K. Mishra, *J. Appl. Phys.* **88**, 4734 (2000).
- ⁹A. Krost, J. Bläsing, H. Protzmann, M. Lünenburger, and M. Heuken, *Appl. Phys. Lett.* **76**, 1395 (2000).
- ¹⁰B. Neubauer, A. Rosenauer, D. Gerthsen, O. Ambacher, M. Stutzmann, M. Albrecht, and H. P. Strunk, *Mater. Sci. Eng., B* **59**, 182 (1999).
- ¹¹A. Zunger, *Mater. Res. Bull.* **22**, 20 (1997).
- ¹²R. M. Feenstra, H. Chen, V. Ramachandran, A. R. Smith, and D. W. Greve, *Appl. Surf. Sci.* **166**, 165 (2000).
- ¹³A. F. Wright, *J. Appl. Phys.* **82**, 2833 (1997).
- ¹⁴L. Bellaiche and A. Zunger, *Phys. Rev. B* **57**, 4425 (1998).