

Influence of miscibility on the energy-gap dispersion in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys: First-principles calculations

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We present first-principles calculations of the electronic properties of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys. Resulting from a low spinodal decomposition temperature, the miscibility of AlN and GaN at the growth temperatures is very high. Due to a likely low diffusion rate it is possible to prepare the alloy at different configurations with different properties and energy band gaps. The calculated band gaps are found to be mostly dependent on the local order and composition rather than dependent on the global composition. The different gaps investigated here provide an explanation for the discrepancies of the experimental values of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ bowing parameter found in the literature.

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The ternary AlGaIn alloy has become an important topic of investigation in optoelectronic and electronic devices, due to their wide band-gap energies, with a potential wavelength variation of 200–360 nm depending on Al concentration. AlGaIn is one of the most promising materials for ultraviolet (UV) devices as light-emitting diodes (LED) and laser diodes (LDs).¹ In the electronic field, AlGaIn is a promising material for high-power, high-temperature, and high-frequency operation devices.² AlGaIn/GaN heterojunctions with two-dimensional electron gas (2DEG) have been widely used to fabricate structures for scientific investigation and semiconductor devices as field-effect transistors (FETs). Also, much attention is being given to AlGaIn/GaN high-electron mobility transistors (HEMTs) as a key device for future high-power and high-voltage applications in microwave and millimeter-wave frequency regions.

A fundamental property to the development of any device is the energy-gap dependence with the composition. The deviation from the linear behavior of the fundamental energy gap $E_g(x)$ is characterized by the bowing parameter b . However, for the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy there is a variety of values of b in the literature that are inconsistent. In Ref. 3 the authors reported a variation of the bowing parameter from -0.8 eV (upward bowing) to $+2.6$ eV (downward bowing) most likely resulting from $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy samples prepared by different techniques. These huge discrepancies require a deeper understanding. The attempt to obtain a unique good value for the bowing parameter of AlGaIn seems to be misleading. Moreover, experimental results suggest that the AlGaIn alloy samples are partially ordered and that the material consists of a mixture of ordered and disordered domains.^{4–6} This spontaneous ordering may significantly modify the band gap and other electronic properties. Thus, we propose here a new interpretation and explanation for the variety of values obtained for the AlGaIn bowing parameter. Our argument is

based on the high miscibility of AlN and GaN, on a low rate of diffusion of Al and Ga in the lattice, and the band-gap dependence on the arrangement of atoms (configuration) in the alloy sample.

In this Brief Report, we present theoretical first-principles studies of the electronic structure of wurtzite-based $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys in a large set of different configurations. The systematic generation of configurations is made as in Ref. 7 and 8. The total-energy and electronic-structure calculations for each configuration are based on the density-functional theory (DFT) within the generalized-gradient approximation (GGA) for exchange-correlation potential, proposed by Wang and Perdew.⁹ We use the frozen-core projector-augmented wave method as implemented in the “Vienna *ab initio* simulation package” (VASP-PAW code).^{10,11} The k -space integrals are approximated by sums over special point mesh of the Monkhorst-Pack type within the irreducible part of the Brillouin zone (BZ). The lattice constants, external parameters of the supercell, were relaxed only for the two binary wurtzite compounds GaN and AlN, while for the alloy configurations we used the Vegard law. We performed first-principles calculations on a set of 327 configurations, those whose unit cell had at most eight cations (and eight anions).^{7,8} The atomic coordinates, that is, the internal parameters in the supercell, were relaxed by the first-principles code for the binaries only. For the alloy configurations we used a force field with reliability proved for the 63 most symmetric configurations.¹²

For most nitride alloy systems there are strong indications of a miscibility gap. AlGaIn alloys are an exception because of the small lattice mismatch between AlN and GaN. The lattice mismatch between GaN and AlN is 2.5% and 4.1% for the hexagonal a and c lattice constants, respectively, while between InN and GaN, for example, it increases to 10.7% and 15%. Due to the smaller difference

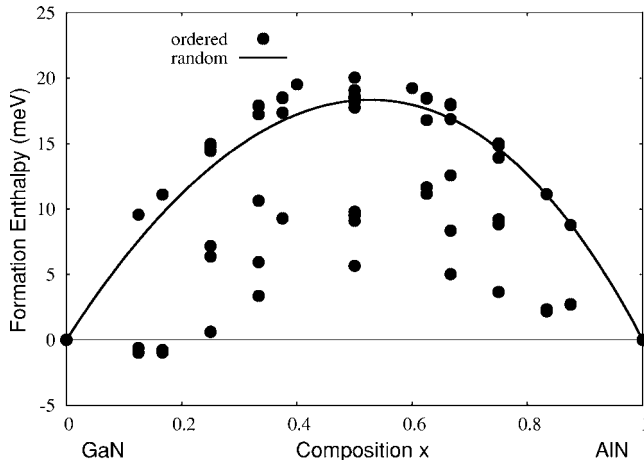


FIG. 1. First-principles enthalpies of formation of the 63 most symmetric configurations. The line is the enthalpy of formation for the random alloy, calculated with a cluster expansion optimized to the first-principles results.

n bond lengths, there is no considerable internal strain leading to phase separation and resulting in a lower spinodal decomposition temperature.

We fitted a cluster expansion (CE) to the total energies of a set of the 63 most symmetric relaxed configurations. The CE was chosen to have the most predictive power. The larger set of 327 configurations was used to monitor the quality of the CE.¹² Having the CE, it was possible to determine the statistical energy average $\langle E(\sigma) \rangle$ and the enthalpy of alloy formation for a random alloy,

$$H(x) = \langle E(\sigma) \rangle - xE(\text{AlN}) - (1-x)E(\text{GaN}). \quad (1)$$

At high temperatures we obtain the Bragg-Williams free energy per site,

$$G = H(x) + kTx \ln(x) + kT(1-x)\ln(1-x). \quad (2)$$

An estimate of the spinodal decomposition temperature is obtained from the second derivative

$$\frac{\partial^2 G}{\partial x^2} = 0,$$

which gave 405 K at $x=0.5$ for the AlGaIn system. This means that, at the practical growth temperatures, AlN and GaN are very miscible. This result is in agreement with several studies in the literature about the thermodynamic stability of AlGaIn, which also indicates very low spinodal decomposition temperatures.¹³

In Fig. 1 we plot the enthalpies of formation for the 63 most symmetric configurations σ ,

$$\Delta E(\sigma) = E(\sigma) - (1-x)E(\text{GaN}) - xE(\text{AlN}). \quad (3)$$

There we also plot the enthalpy for the random alloy. We can observe there are many ordered configurations with lower enthalpy than the random alloy. We can observe also that the dispersion of the many enthalpies of the various configurations is around 20 meV, which means that, at growth temperatures, any configuration can be obtained, the resulting

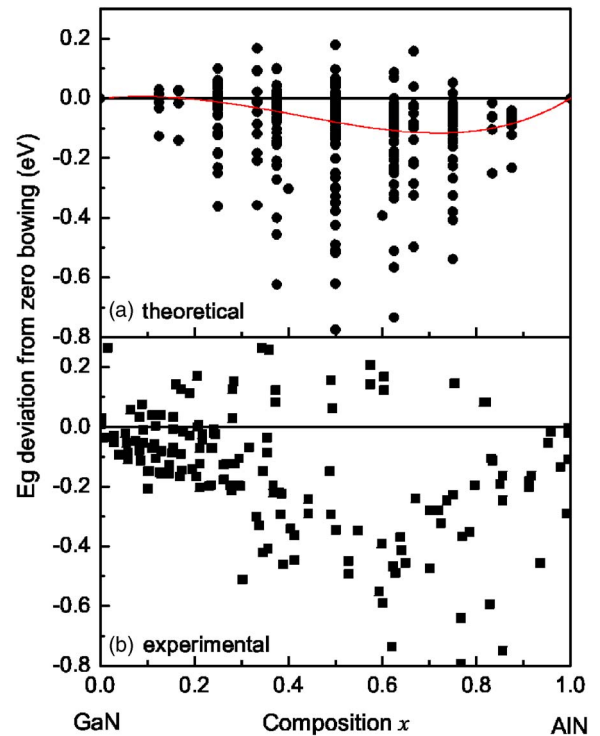


FIG. 2. (Color online) Energy-gap deviations from zero bowing. (a) First-principles calculated values for 327 configurations. The solid line is the value for a random alloy obtained from an optimal cluster expansion. (b) Compilation of several experimental results extracted from Ref. 3.

structure being extremely dependent on the growth conditions. Consequently, it would be possible to obtain any gap value corresponding to the many configurations.

In order to see how the energy gap values are dispersed, we tabulated the energy gaps of each configuration calculated by first principles. Figure 2(a) shows the energy gaps for all the 327 calculated configurations, plotted as the difference between the energy gap and the corresponding linear-composition dependent, i.e., zero bowing. Fortunately, the quasiparticle corrections vary almost linearly with the composition, as shown previously,¹⁴ and we do not need to include it in the plotting we are presenting. From the results obtained on Fig. 2(a) we can observe a dispersion in the energy-gap values, reflecting the great dispersion on the bowing values reported by various researchers. Still, from the results we can observe that the dispersion is greater toward negative values, meaning a greater chance of a downward bowing. Recently, a compilation of several experimental results indicates a wide scatter in the data as shown Fig. 2(b).³ We observe that there is a good agreement between the scatter of our results and of experiment, and that in the compilation of experiments the positive values of b are also observed. Further, from our theoretical results we observe that compositions near 50% are the ones that present the greater dispersion in the E_g values and, consequently, affect the bowing parameter most. This result was also experimentally observed in Ref. 3.

We also used the calculated gaps of the smaller set of 63 configurations to generate an optimal gap CE. Again the

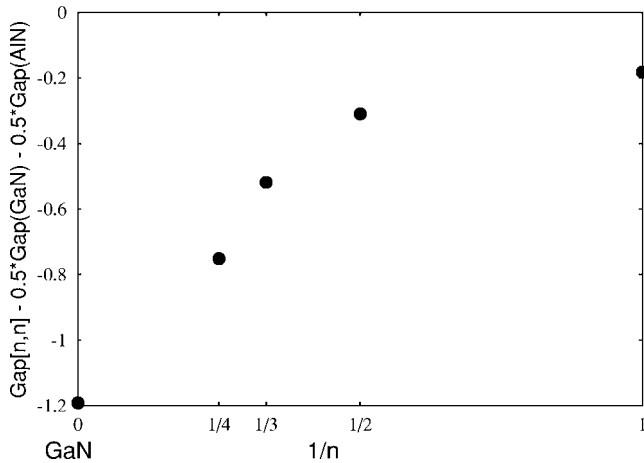


FIG. 3. Energy gaps of $[n, n]$ superlattices in the c direction, with n consecutive planes of Al and n of Ga. As n increases the gap has to approach that of GaN, which has the smallest gap between the two binaries.

larger set of 327 configurations was used to monitor the quality of the gap CE. With the gap CE it is possible to obtain the energy gap for a random alloy, which is shown by the solid line in Fig. 2(a). The first thing to observe is that the bowing for the random alloy is much smaller than that of the many experimental results, meaning that experiment is dealing with ordered samples, not random. The behavior of the random alloy is more complex than the behavior obtained by the other theoretical works.^{15,16} It is necessary a fourth order polynomial¹² in order to correctly describe this curve. Alternatively the function may be approached by a straight line from $x=0$ to $x=0.2$ and a quadratic with bowing parameter $b=0.72$ eV from to $x=1.0$.

A fundamental question is why the energy gap varies so much for configurations of same alloy composition. We found that the gap depends more on the local order and composition than on the global composition. Since the electron-hole pair is likely to combine in space regions with smallest electron-hole pair energies, the characteristic transition energies in, e.g., photoluminescence experiments are roughly given by a minimum local gap energy. The same gap may be relevant in photoreflection spectroscopy, where mainly space regions with excited electron-hole pairs contribute to the signal. The local composition effect to the gap of the whole alloy can be clearly observed when we take a superlattice $[n, n]$ along the c axis, with n from 1 to 4, meaning n layers of Ga and n of Al, and increase the value of n . For instance, if we take the superlattices $[n, n]$ (in this case the composition of the whole structure is $x=0.5$), with $n=2$ and increase n to $n=4$, the energy gap tends to a lower value, and as n increases, $[n, n] \rightarrow [\infty, \infty]$, we will tend to obtain the energy

gap of GaN, which has the smallest gap of the two binaries. The results are presented in Fig. 3 for $2 \leq n \leq 4$, considering the superlattices in the direction c . We can observe that in fact, the energy gap tends to be smaller as n increases.

The importance of the c -axis superlattices was also verified in Fig. 2. The configurations with the largest E_g deviation were all alternations of Al and Ga planes along the c axis. The record-breaking configurations were as follows: For $x=1/8$ and $x=7/8$ the alternation $[7,1]$, for $x=1/6$ and $x=5/6$ the alternation $[5,1]$, for $x=1/4$ and $x=3/4$ the alternations $[6,2]$, $[5,1,1,1]$, and $[4,1,2,1]$, for $x=3/8$ and $x=5/8$ the alternations $[5,3]$ and $[4,2,1,1]$, and for $x=1/2$ the alternations $[4,4]$ and $[3,3,1,1]$.

Compared with other high-miscibility ternary systems, such as AlGaAs, the nitride is unique in two respects. First, the band-gap dispersion is much larger in the nitride system; for instance, for the AlGaAs system the experimentally observed bowing parameter ranges only from 0.14 to 0.66 eV.¹⁷ Analogous to our nitride $[4,4]$ c -axis superlattice, which has a record-breaking deviation from zero bowing of 0.8 eV, for the zinc-blende arsenide $[4,4]$ (111) superlattice we calculated a deviation of only 0.33 eV. Secondly, unlike the arsenides, the nitrides appear in many states of order that do not randomize easily. Comparing with the arsenide we can think of two reasons for the nitride feature: (i) the formation enthalpies are smaller in the arsenides (for the arsenide superlattice we calculated an enthalpy of 1.46 meV/cation while for the nitride we found 5 meV/cation), which favors randomization. (ii) while N is a small atom, leading to a close packing of Ga and Al, As is not as small and leads to a looser arrangement of atoms with many vacant spaces, such as a diamond structure, which favors diffusion and randomization.

In conclusion, we calculated the band-gap energies of wurtzite-based $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys for a large set of configurations of different Al concentrations. The results were used to develop a comprehensive picture of the dispersion of energy gaps observed in the literature. We found a large dispersion of the E_g values in the calculated results. In order to analyze the probability of obtaining these different configurations and gaps we performed total energy calculations to obtain their formation enthalpies. We observed that the many configurations were almost degenerate, meaning that growing them could be extremely dependent on the growth conditions. Thus, the different gaps observed in the literature seem to result from different growth techniques.

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