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Microscopic description of the phase separation process in $\mathrm{Al}_x\mathrm{Ga}_y\mathrm{In}_{1-x-y}\mathrm{N}$ quaternary alloys

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Ab initio total energy electronic structure calculations are combined with Monte Carlo simulations to study the thermodynamic properties of $\mathrm{Al}_x\mathrm{Ga}_y\mathrm{In}_{1-x-y}\mathrm{N}$ quaternary alloys. We provide a microscopic description of the phase separation process by analyzing the thermodynamic behavior of the different atoms with respect to the temperature and cation contents. We obtained, at growth temperatures, the range of compositions for the stable and unstable phases. The presence of Al in InGaN is proven to "catalyze" the phase separation process for the formation of the In-*rich* phase. Based on our results, we propose that the ultraviolet emission currently seen in samples containing AlInGaN quaternaries arises from the matrix of a random alloy, in which composition fluctuations toward InGaN- and AlGaN-like alloys formation may be present, and that a coexisting emission in the green-blue region results from the In-*rich* segregated clusters.

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One important issue in alloy physics is the $T=0$ K lowest energy configurations of the system and its thermodynamic evolution with the temperature. It is important to know how the atoms are distributed in equilibrium, i.e., if they are randomly displayed or if there are nucleations of a certain kind of atom. Equivalently it is important to know whether the individual components will tend on a microscopic scale to attract each other, and on a macroscopic scale to cluster into ordered or disordered phases of particular stoichiometries. The tendency to phase separation in alloys implies there is a repulsive energy between the different alloying species. One example is what happens in nitride alloys, such as, e.g., in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ which are the active media in light emitting diodes and laser diodes operating in the blue-green and ultraviolet (UV) regions of the electromagnetic spectrum.[1] Usually the devices comprise GaN/InGaN or AlGaN/GaN multiple quantum wells, in which GaN and AlGaN act as barrier materials. However, the increase of the Al and/or In compositions in these structures is hindered by the degradation of the interfaces due to the large lattice mismatches. Recently, the $\mathrm{Al}_x\mathrm{Ga}_y\mathrm{In}_{1-x-y}\mathrm{N}$ quaternary alloys emerged as promising materials, especially for the device applications in the UV region.[2] The use of AlInGaN allows one to adjust the lattice constant and the band gap energy, independently, so that lattice-matched materials may be obtained.[3–6]

It is known that the ternary InGaN and InAlN alloys are not fully miscible.[7] In the same way, for the AlGaInN alloys such phenomena as phase separation as well as composition fluctuations are expected to occur considering mainly the In atom. On the other hand, the AlGaInN quaternary has shown to be an effective medium to improve the optical quality for the UV emission over the AlGaN alloys.[8] These facts lead some works to attribute to the presence of localized states in InGaN-*like* clusters, or In-*rich* phases, the observed intense emission in the UV region instead of being due to band-to-band transition in the alloy itself.[9,10] However, other experimental results seem to contradict this explanation. Feng *et al.* observed, together with the usual UV emission a strong green luminescence, which was attributed to the formation of In-rich clusters.[11] Yamaguchi *et al.* have shown that for high content of In and Al, for which there is a great probability of clusters formation, only the green emission is observed.[12] These findings indicate that the luminescence mechanism in the UV region observed in AlGaInN alloys is still a matter of controversy. Therefore, how the In nucleation may take place in the bulk AlGaInN quaternary alloys, in which components is the alloy separated, and whether these compounds are related to the observed radiative emissions are questions whose answers remain unknown.

The thermodynamics of AlGaInN quaternary alloys has been investigated only through the simplified strictly regular solution model.[13,14] A large miscibility gap has been predicted at growth temperatures. However, in order to address the questions raised above one needs a more sophisticated approach. In this paper we use *ab initio* total energy electronic structure calculations, together with a cluster expansion method and Monte Carlo (MC) simulations in order to study the thermodynamics of $\mathrm{Al}_x\mathrm{Ga}_y\mathrm{In}_{1-x-y}\mathrm{N}$ quaternary alloys. We aim at understanding how the simultaneous presence of Al and In leads to a peculiar behavior for the AlGaInN quaternary alloys. A microscopic description of the phase separation process and the emission mechanism taking place in AlGaInN layer samples are analyzed and discussed in the light of the results obtained from the *ab initio* total energy and MC calculations.

Instead of the traditional cluster expansion in *figures*, here we consider an expansion in the energies of *all* the arrangements of the cation atoms in the unit cell. A detailed description of the steps undertaken to obtain the results discussed here will be given elsewhere.[15] We consider a periodic fcc lattice with an unit cell containing 8 fcc sites. There are $3^8=6561$ configurations of the three cations, which are reduced to only 141 configurations by symmetry. The total energies of the 141 independent configurations were calculated by adopting a first principles pseudopotential plane-wave method and the density functional theory within the local density approximation, specifically the "Vienna Ab-Initio Simulation Package."[16] Details of the calculation parameters are described in Ref. 17. The use of the energy expansion in the energies of the 141 clusters allows us to perform a re-

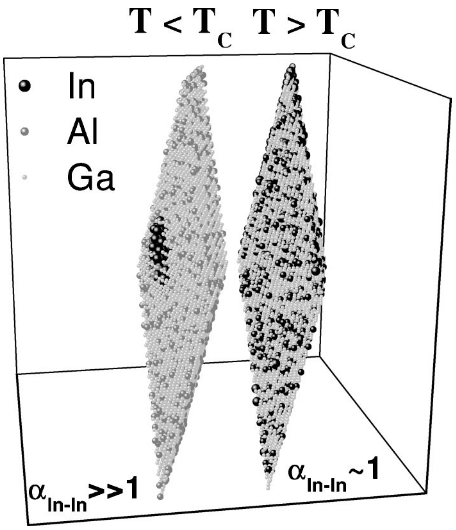

FIG. 1. Schematic representation of the phase separation transition for the $Al_{0.15}Ga_{0.83}In_{0.02}N$ quaternary alloy as obtained from Monte Carlo calculations. Only the Al, Ga and In atoms are shown. The value $T_c = 1100$ K was determined from the annealing simulation process when the In-In affinity $\alpha_{\text{In-In}} \sim 1$.

stricted ground state search, comparing different structures of the same composition.[18] The restricted to 141 ground state search leads to a triangle which connects each binary compound that forms the quaternary alloy, which means that there is no stable ordered phases and the quaternary alloy tends to phase separate. Since we have identified the lower energy structures, we use MC simulations[19] to calculate the temperature and composition ranges for which the random alloy is stable. The MC dynamics was made keeping the concentrations x and y constant (canonical Monte Carlo), by exchanging atoms of neighboring sites only, because of the well-known low diffusion in the nitrides alloys. We used a cell of $23^3 = 12\,167$ fcc sites, and 10^4 atom exchange attempts per site.

In Fig. 1 we show the equilibrium cation distribution in the MC cell for an $Al_xGa_yIn_{1-x-y}N$ quaternary alloy with typical compositions $x = 0.15$ and $y = 0.83$. We clearly see a phase separation of In precipitate for $T < T_c$ (with T_c being the critical temperature) and, as expected, an homogeneous distribution of cations for $T > T_c$. In order to quantify the MC results and to analyze in more detail what is happening in a microscopic scale, similar to previous works we defined an affinity (α) as follows.[20] In an $A_xB_yC_{1-x-y}D$ quaternary alloy, the concentration of atoms A, B, and C in the alloy is x, y, and $(1-x-y)$, respectively, which we will simply call by x_A, x_B, and x_C. In a random distribution, considering a certain atom A, the number of its first cation neighbors of the kind B is on average $12x_B$. We wish to know how much the first neighborhood of A deviates from the one in a random distribution. If, by considering the equilibrium MC cell, we analyze the number of first cation neighbors of each atom and compare with the number it should be in the case of a random alloy, we can conclude on the *tendency* of individual components to attract or repeal each other. Therefore, the affinity between atoms A and B is defined as

$$\alpha_{\text{A-B}} = \frac{\overline{n}_{\text{A-B}}}{12x_{\text{B}}}, \tag{1}$$

where $\overline{n}_{\text{A-B}}$ is, considering atom A, the average number of first neighbors of kind B in the equilibrium MC cell. Observe that the definition of the affinity comprises three interesting situations: (i) if $\alpha_{\text{A-B}} \sim 1$ the distribution is random; (ii) if $\alpha_{\text{A-B}} > 1$ there is a predominance of atoms B in the first neighborhood of atom A, i.e., the atoms A and B tend to attract each other; (iii) if $\alpha_{\text{A-B}} < 1$ there is a lack of atoms B in the first neighborhood of atom A, i.e., the atoms A and B are further away from each other in comparison to the random distribution. Since phase separation here is basically driven by the tendency to form an In-rich phase (see Fig. 1), we first analyze the quantity $\alpha_{\text{In-In}}$. In Fig. 1 we obtained $\alpha_{\text{In-In}} \gg 1$ for $T < T_c$, which reflects the existence of phase separation, and $\alpha_{\text{In-In}} \sim 1$ for $T > T_c$, hence an almost random distribution. Then, to obtain the critical temperature T_c for the alloy at a given composition we use MC dynamics, by varying the temperature, and analyze the resulting value for $\alpha_{\text{In-In}}$. As an example, we start with $Al_{0.15}Ga_{0.83}In_{0.02}N$ at a low temperature ($T = 200$ K) and simulate an annealing process by raising the temperature. T_c is determined when $\alpha_{\text{In-In}} \sim 1$. The phase transition for $Al_{0.15}Ga_{0.83}In_{0.02}N$ taking place at $T_c \sim 1100$ K is schematically shown in Fig. 2. The affinities involving the other atoms are shown in the inset of Fig. 2. We point out that the growth temperatures are very near T_c ($T \sim 1073$ K, shown in the figure by a vertical arrow) in this case. In other words, it is very difficult to ascertain in which regime of stability a sample grown at this temperature will be.

We observe, for $T < T_c$, that contrary to In-In, Al-In and Ga-In have the affinities below 1, which indicate that there is a lack of Al and Ga in the first neighborhood of In. We also note that $\alpha_{\text{Al-In}}$ is even lower than $\alpha_{\text{Ga-In}}$, meaning that the lack of Al atoms in the neighborhood of In is greater than that of Ga atoms. This result is in agreement with the results for the ternary InAlN and InGaN alloys, because InAlN has a wider miscibility gap than InGaN.[7] For $T > T_c$ these affinities become larger and near 1. Another interesting feature to

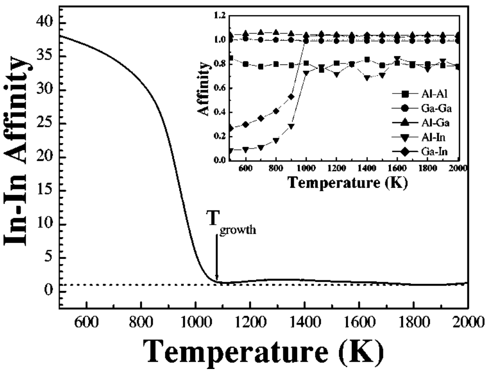

FIG. 2. The In-In affinity as a function of the temperature for the $Al_{0.15}Ga_{0.83}In_{0.02}N$ quaternary alloy. The affinities between the other cations are shown in the inset. The horizontal dashed line indicates the affinity in the random case ($\alpha_{\text{In-In}} \sim 1$). The typical growth temperature, T_{growth} is depicted by a vertical arrow.

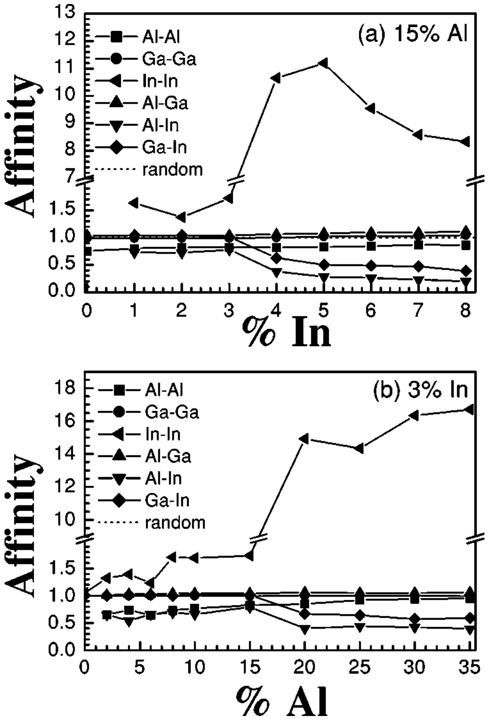

FIG. 3. The affinities between the cations for the $Al_xGa_yIn_{1-x-y}N$ quaternary alloy as a function of the (a) In composition and (b) Al composition. The growth temperature $T=800$ °C was assumed.

be observed is that $\alpha_{\text{Al-In}} \sim 0.8$, still lower than 1 even at high temperatures, and that some affinities remain constant during the heating process as $\alpha_{\text{Al-Ga}}$, $\alpha_{\text{Al-Al}}$ and $\alpha_{\text{Ga-Ga}}$. The behavior obtained for the affinities leads us to two main conclusions. First, the In atom prefers an atom of Ga as first neighbor than an atom of Al, which is reasonable since the In-N bond is longer than the Ga-N bond but it is even longer than the Al-N one. Second, as the AlGaN system has no miscibility gap, i.e., the Gibbs free energy of the alloy is lower than the one of the mixture of the binaries, the Al atom prefers to be with Ga than to form clusters of AlN.

Another interesting study is the behavior of the affinities with the alloy compositions x and y. The results are shown in Fig. 3 for a fixed temperature of $T=800$ °C, which is the growth temperature of AlGaInN alloys. In (a) the Al concentration is fixed (15%) and the In concentration is varied. Then we observe that, as we increase the In content, the In-In affinity changes drastically from ~ 1.5 to ~ 11, meaning that an atom of In has 11 times more first In neighbors than it would have in a random alloy. In other words, there is phase separation and the system turns to be composed of an In-rich phase and another In-poor phase, almost AlGaN. In (b) we observe essentially the same behavior, but now what is being varied is the Al content. That means that the Al atom acts as a "catalyst" for the phase separation process. This behavior is not obvious, since it might be reasonable to think that the Al-N bond-length, as it is smaller than the Ga-N, could "compensate" the largest bond-length In-N. In both pictures (a) and (b), below a certain critical content, $\alpha_{\text{In-In}}$ is around 1.5 and $\alpha_{\text{In-Al}}$ is around 0.7, while $\alpha_{\text{Ga-Ga}}$ and $\alpha_{\text{Ga-In}}$ stay around 1. These results indicate a compositional fluctuation favoring the formation of the two ternary InGaN and AlGaN alloys.

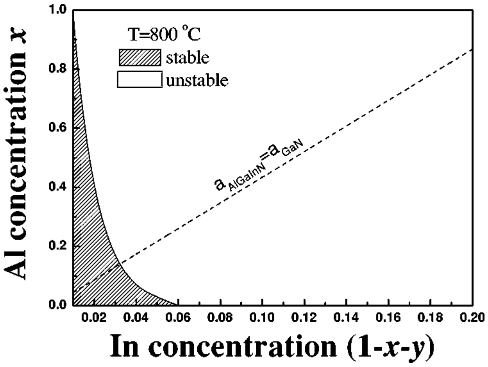

FIG. 4. Diagram of compositions for $Al_xGa_yIn_{1-x-y}N$ quaternary alloys, as constructed from the obtained values of In-In affinities. The dashed straight line corresponds to the situation in which the alloy is lattice matched to GaN.

It is interesting to know, for growth temperatures, the range of compositions, x and y, for which the alloy is stable/unstable. From the knowledge of $\alpha_{\text{In-In}}$, we construct the corresponding phase diagram of compositions, which is depicted in Fig. 4. The line for the transition is obtained when the affinity between In atoms increases abruptly. This result shows clearly the great tendency for compositional instabilities in AlGaInN quaternary alloys.

Based on our results we propose a model for the emission process in the AlGaInN quaternary alloys. (i) For low content of In and/or Al, there is *no phase separation* and the emission channel in the UV region arises from the random quaternary alloy. This conclusion is corroborated by recent *ab initio* calculations carried out for the band gap energy of AlInGaN quaternaries,[17] which show very good agreement with the measured values for the UV emission from these alloys.[10,11] It is worth to point out that, still in this case (low alloy contents) there is already a weak effect of the compositional fluctuation toward the formation of AlGaN and InGaN clusters (see Fig. 3). These fluctuations enhance dramatically the luminescence intensity in the UV region due to quantum confinement effects as observed by Chen *et al.*[10] (ii) As the In and/or Al content increases *there is phase separation*, with the formation of In-*rich* clusters. Now there are two emission channels: one in the blue-green, and another in the UV region of the spectrum, which arise, respectively, from localized states in the In-*rich* clusters and the random matrix. The intensity of the blue-green emission depends on the amount of In in the sample. At the beginning of the phase separation process, for low In content, the intensity of the blue-green emission is lower than the UV one.[11] As the In or Al content is increased, the formation of In-*rich* clusters becomes more and more effective and, as shown by our results, the percentage of In-In neighbors tends to reach the maximum, with a consequent enhancement of the blue-green emission.[12]

In summary, by using state-of-the-art *ab initio* total energy calculations and Monte Carlo simulations we were able to provide a microscopic description of the thermodynamic behavior of AlGaInN quaternary alloys. The phase separation process known to take place in the ternary InGaN alloys is demonstrated here to be "catalyzed" by the presence of Al. From our results we propose that the UV emission observed in the quaternary InGaAlN alloys arises from the matrix of a random alloy, although this emission may also coexist with a green-blue one resulting from the In-*rich* regions. The parameters (critical temperatures and compositions) resulting from the *ab initio* calculations are consistent with what is known experimentally.

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