Microscopic description of the phase separation process in Al\textsubscript{x}Ga\textsubscript{1−x}In\textsubscript{1−y}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 Al\textsubscript{x}Ga\textsubscript{1−x}In\textsubscript{1−y}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\textsubscript{x}Ga\textsubscript{1−x}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. 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 Al\textsubscript{x}Ga\textsubscript{1−x}In\textsubscript{1−y}N quaternary alloys emerged as promising materials, especially for the device applications in the UV region. 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.

It is known that the ternary InGaN and InAlN alloys are not fully miscible. In the same way, for the AlGaN 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 AlGaN quaternary has shown to be an effective medium to improve the optical quality for the UV emission over the AlGaN alloys. These facts lead to be an effective medium to improve the optical quality for the UV emission over the AlGaN alloys. These findings indicate that the luminescence mechanism in the UV region observed in AlGaN alloys is still a matter of controversy. Therefore, how the In nucleation may take place in the bulk AlGaN 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 AlGaN quaternary alloys has been investigated only through the simplified strictly regular solution model. 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 Al\textsubscript{x}Ga\textsubscript{1−x}In\textsubscript{1−y}N quaternary alloys. We aim at understanding how the simultaneous presence of Al and In leads to a peculiar behavior for the AlGaNN quaternary alloys. A microscopic description of the phase separation process and the emission mechanism taking place in AlGaNN 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. We consider a periodic fcc lattice with an unit cell containing 8 fcc sites. There are 3\textsuperscript{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.” 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 $\alpha_{\text{In-In}} \sim 1$.

Restricted 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 forms the quaternary alloy, which means that a search leads to a triangle which connects each binary composition.

$$\alpha_{A-B} = \frac{n_{A:B}}{12x_B},$$

where $n_{A:B}$ 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 $\alpha_{A-B} \sim 1$ the distribution is random; (ii) if $\alpha_{A-B} > 1$ 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 $\alpha_{A-B} < 1$ 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 $\alpha_{\text{In-In}} \sim 1$ 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, $T_{\text{growth}}$, is depicted by a vertical arrow.
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 Al-N one.

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 AlGaN 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 $\sim 1.5$ to $\sim 11$, meaning that an atom of In has 11 times more first In neighbors than the Al-N bond. In other words, there is a compositional fluctuation due to the metal atom that is lattice matched to GaN.

For low In content, the In-In affinity changes from $\sim 1.5$ to $\sim 11$, meaning that an atom of In has 11 times more first In neighbors than the Al-N bond. In other words, there is a compositional fluctuation due to the metal atom that is lattice matched to GaN.
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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