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Citation: Applied Physics Letters **82**, 4274 (2003); doi: 10.1063/1.1583854

View online: http://dx.doi.org/10.1063/1.1583854

View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/82/24?ver=pdfcov

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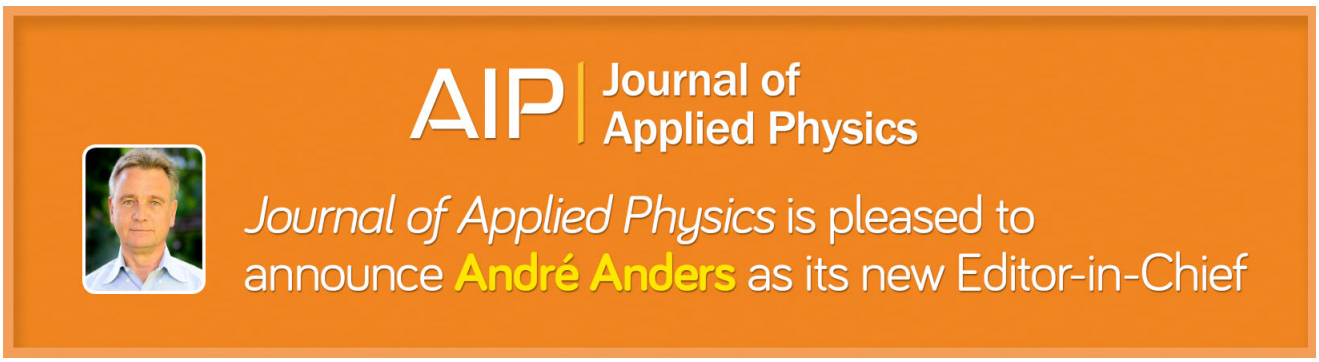

Strain-induced ordering in $In_xGa_{1-x}N$ alloys

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(Received 2 December 2002; accepted 16 April 2003)

The energetics and thermodynamic properties of cubic (c-)$In_xGa_{1-x}N$ alloys are investigated by combining first-principles total energy calculations, a concentration-dependent cluster-based model, and Monte Carlo simulations. The search for the ground-state energies leads to the conclusion that biaxial strain suppresses phase separation, and acts as a driving force for chemical ordering in c-$In_xGa_{1-x}N$ alloys. Ordered superlattice structures, with composition $x \cong 0.5$ and stable up to $T=1000$ K, arises as the relevant thermodynamic property of the strained alloy. We suggest that the In-rich phases recently observed by us in c-GaN/$In_xGa_{1-x}N$/GaN double heterostructures are ordered domains formed in the alloy layers due to biaxial strain. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1583854]

Considerable effort has been devoted in recent years to the study of the structural and optical properties of hexagonal (h-) and cubic (c-)$In_xGa_{1-x}N$ epitaxial layers.[1,2] The motivation behind these investigations is the fact that the $In_xGa_{1-x}N$ ternary alloy is the active medium in the highly efficient quantum-well structure light-emitting diodes and laser diodes operating in the short-wavelength visible and UV regions of the spectrum. One important issue that has attracted considerable attention is the origin of the light-emission process in these devices. It has been argued that self-organized nanometer-scale In-rich quantum dots (QDs), originated from In segregation taking place in the $In_xGa_{1-x}N$ alloys, are the source of a radiative recombination channel emitting in the blue-green region of the spectrum.[2–5] The effect of biaxial strain induced by a pseudomorphic growth process in $In_xGa_{1-x}N$ layers has also been investigated and its relation with phase separation suppression effects has been established.[6,7]

Recently, it has been reported that the ternary $In_xGa_{1-x}N$ alloy can also be chemically ordered.[8–11] The effect was detected on h-$In_xGa_{1-x}N$ epitaxial layers grown on (0001) sapphire substrates. Transmission electron microscopy (TEM) experiments were carried out on 0.2-μm layers with alloy composition varying from 10% to 60% grown on top of thick GaN buffers.[8] The diffraction patterns from the InGaN films show superlattice spots, allowing the identification of the ordered $In_{0.5}Ga_{0.5}N$ phase. Ordered $In_{0.5}Ga_{0.5}N$ domains of approximately 20 nm were observed by TEM in 0.3–0.5-μm h-$In_xGa_{1-x}N$ layers with $x=0.25$ and $x=0.49$.[10] Ordered $In_{0.25}Ga_{0.75}N$ domains were also observed in these films.

We recently investigated the structural and optical properties of c-GaN/$In_xGa_{1-x}N$/GaN double heterostructures (DHs) with In content varying from $x=0.09$ to $x=0.33$ and alloy layer thicknesses of about 0.03 μm.[5] The DHs were grown by plasma-assisted molecular-beam epitaxy on top of thick GaN buffer layers previously grown on GaAs(001) substrates. High-resolution x-ray diffraction (HRXRD) and photoluminescence experiments were combined to show the presence of strained nanometer scale In-rich phases (QDs) in the c-$In_xGa_{1-x}N$ layers. Figure 1 shows the distribution of the scattered x-ray intensities in reciprocal space (reciprocal space maps) of the asymmetric $(\bar{1}13)$ Bragg reflexes of c-GaN/$In_xGa_{1-x}N$/GaN DHs with alloy layer compositions $x=0.33$ and $x=0.09$.[12] Strained In-rich phases with $x=0.55$ and $x=0.57$, respectively, are clearly observed in the maps.[13] The striking feature of the HRXRD reflexes is the fact that all the samples comprise In-rich phases with In content between 0.55 and 0.58. Although HRXRD is not sensitive enough to detect ordering from the small diffracted volume of the QDs, we show here that the In-rich domains in our DHs are probably ordered phases, as detected in the h-InGaN layers.

In this letter, we show from theory that ordered phases with composition of about $x=0.5$ arise from the thermodynamic properties of the $In_xGa_{1-x}N$ alloy under external biaxial strain. The alloy energetics and thermodynamics are investigated by combining *ab initio* total energy calculations, a concentration-dependent cluster-based expansion method, and Monte Carlo (MC) simulations.[14–19] Total energy and electronic structure calculations of each basic configuration required by the cluster expansions are carried out by using a pseudopotential method (Vienna *Ab-initio* Simulation Package—VASP code) within the framework of the density functional theory and the local density approximation.[15] Two structures are assumed: zinc-blende, to describe the fully relaxed alloy, and tetragonal, to simulate the pseudomorphically grown alloy on rigid c-GaN (001) buffer layers. The tetragonal configurations are suitable to simulate the $In_xGa_{1-x}N$ alloy lattice matched to c-GaN in the (001) plane, therefore under external biaxial strain. The five (six) basic configurations used for the zinc-blende (tetragonal) structures and how their energies are determined are de-

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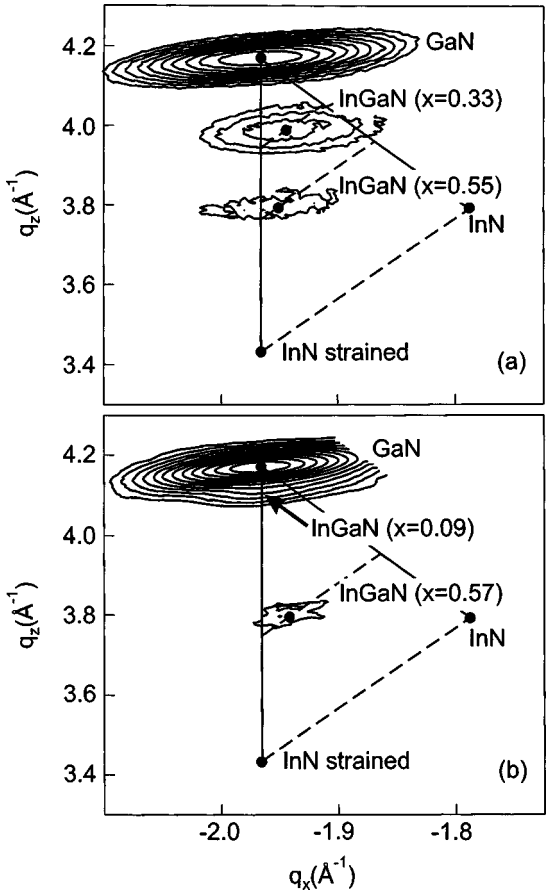

FIG. 1. Distribution of the scattered x-ray intensity in reciprocal space (reciprocal space maps) of the asymmetric $(\bar{1}13)$ Bragg reflexes of c-GaN/$In_xGa_{1-x}N$/GaN DHs. The measured alloy layer composition is (a) $x=0.33$ and (b) $x=0.09$. The In content in the separated phase is (a) $x=0.55$ and (b) $x=0.57$. The position of the maximum intensity of the GaN and InGaN Bragg reflexes of strained and relaxed InGaN layers of varying In content are indicated by full lines. The position of the Bragg reflexes of a partially relaxed InGaN layer of a given composition is shown by dashed lines.

scribed in Refs. 16 and 17. Once the energies of the basic configurations are obtained, the cluster expansion, expressed as a generalized Ising Hamiltonian, is used to calculate the alloy energies.[18] This procedure allows us to readily determine the $In_xGa_{1-x}N$ ground-state structures and, by using the MC statistical mechanics technique and the Metropolis algorithm, to access the $In_xGa_{1-x}N$ thermodynamic properties.[19] The six basic configurations were calculated with the VASP code for a lattice parameter in the plane (001), $a_{\parallel}$, equal to that of GaN on which the alloy is pseudomorphically grown. Contrary to what is usually done in the standard cluster expansion method, where the lattice parameter c is equilibrated for each basic configuration, in our procedure we generate a table of energies for each configuration at a fine net of parameters c. A cluster expansion was fit to the VASP results with the feature of having the interactions dependent on the local concentration at the sites. This feature leads to the exact results for the long-period superlattices.[20] A detailed description of the steps undertaken to obtain the results discussed in this letter will be given elsewhere.[21] The generalized Ising Hamiltonian, or the energy expansion in terms of multisite interaction energies, allows us to search for the $In_xGa_{1-x}N$ ground state by comparing the energies of

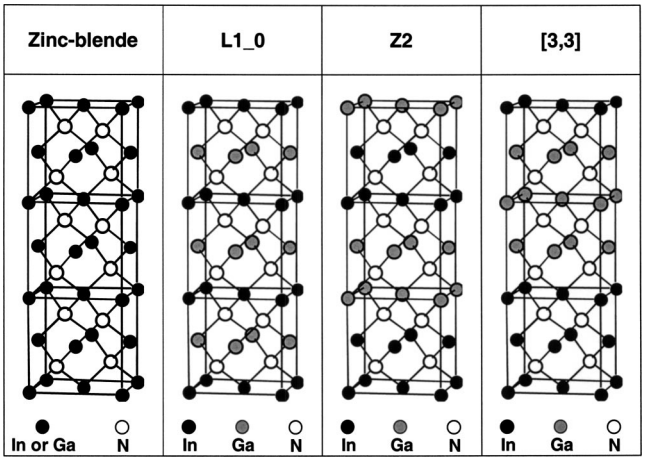

FIG. 2. Schematic representation of some relevant structures for the c-$In_xGa_{1-x}N$ alloy showing the zinc-blende, the CuAu-I-like layered tetragonal, the Z2 $(GaN)_2(InN)_2$ superlattice and the [3,3] $(GaN)_3(InN)_3$ superlattice structures.

different structures at the same alloy composition x. Typical ordered structures are shown in Fig. 2 labeled according to Ref. 22. We use the notation $[n,m]$ to represent a tetragonal ordered $(InN)_n(GaN)_m$ superlattice with axis in the $\langle 001\rangle$ direction.

We address first the results for the unstrained or fully relaxed alloy considering ordered structures with full tetrahedral symmetries. It is found that for all the alloy compositions, there are no stable ordered structures, showing the tendency of the unstrained $In_xGa_{1-x}N$ alloy to undergo phase separation as previously reported.[2–5]

We proceed now with the ground state search for the coherently grown $In_xGa_{1-x}N$ alloy on GaN by considering the tetragonal structures in the energy expansion. The results are summarized in Fig. 3, where the alloy excess energy ΔE is shown as a function of the In content for some relevant ordered structures. The straight-line pieces connecting points corresponding to the stable ordered structures define the alloy ground-state line (GSL). For the unstrained alloy, the

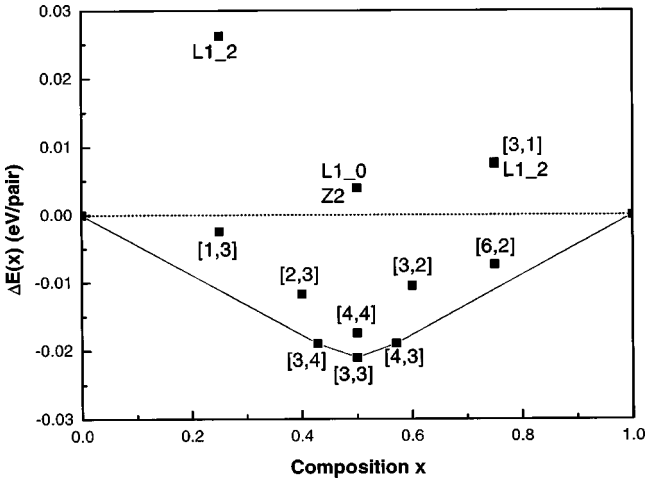

FIG. 3. Excess energy ΔE for some relevant ordered structures for the $In_xGa_{1-x}N$ alloy pseudomorphically grown on rigid GaN (001) buffer layers. The solid curve gives the alloy GSL and the dashed line connects the two binary GaN and InN constituents taken as the reference to calculate ΔE. $[n,m]$ notation represents a tetragonal order $(InN)_n(GaN)_m$ superlattice with axis in the $\langle 001\rangle$ direction.

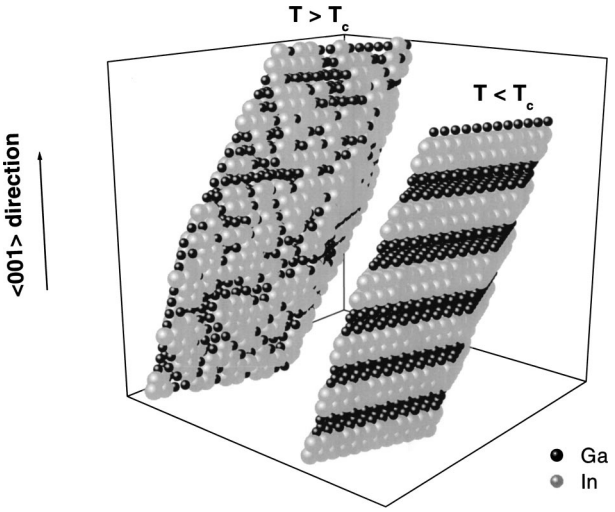

FIG. 4. Schematic representation of a disordered/ordered phase transition for the Z2 structure as calculated from MC simulations. Only the Ga and In atoms are schematically shown. The value $T_c = 1400$ K was determined from the annealing simulation process.

GSL coalesces into a straight line connecting the two pure binary compounds. The results shown in Fig. 3 comprise interesting features: (i) there are several ordered structures with energies close to those of the GSL, implying that a mixture of ordered phases or domains of ordered phases with different In content may arise depending on the growth conditions; (ii) the lowest excess energies for the strained alloys occur at the neighborhood of the [3,3] ordered superlattice, implying that the composition $x \cong 0.5$ is the most favorable ordered phase; and (iii) the biaxial strain induced by the GaN buffer suppresses the tendency of the alloy to phase separate and acts as the driving force to form ordered structures at certain stoichiometric compositions.

The difference in energy between the ordered phase [1,3] $In_{0.25}Ga_{0.75}N$ and the lowest energy phase [3,3] $In_{0.5}Ga_{0.5}N$ is only 18 meV/pair. Figure 3 shows that several ordered structures, with even smaller energy differences, are predicted to occur. The possibility for mixing ordered structures, with competing energies, may explain why In contents measured by HRXRD in our DHs are about 0.55 instead of 0.5.

Ordering in the alloy takes place only below a critical temperature, the stability limit temperature T_c. Temperatures higher than T_c drive the alloy to a disordered phase. One important task here is the determination of T_c for the ground-state ordered structures identified for the strained $In_xGa_{1-x}N$ alloy. To obtain T_c for a given ordered structure, we use MC thermodynamics. As an example, we start with $(GaN)_2(InN)_2$ (Z2) ordered superlattice at a low temperature ($T = 200$ K) and simulate an annealing process by raising the temperature. T_c is determined when the disappearance of the ordered phase is observed. The ordered/disordered phase transition for Z2 taking place at $T_c = 1400$ K is schematically shown in Fig. 4. MC calculations lead to the values 1487, 1149, and 1086 K for the [3,3], [3,4], and [4,3] ordered phases, respectively. The values of T_c calculated by us for the ground-state ordered phases are above the reported growth temperatures of the $In_xGa_{1-x}N$ layers, consistent with the presence of ordered structures as observed.[5,10]

In summary, we found that the ground states of the *unstrained* $In_xGa_{1-x}N$ alloy are formed by the mixture of the two binary constituents, implying the absence of stable ordered phases and the tendency of the alloy to undergo phase separation. The coherence with the relaxed GaN buffer layers suppresses the tendency of the alloy to separate into their pure-component ''endpoint'' phases, and at the same time greatly enhances its tendency to form ordered compounds at certain stoichiometric compositions. Our study shows that the *strained* $In_xGa_{1-x}N$ alloy comprises ordered structures, or $[n,m]$ superlattices formed by n planes of In followed by m planes of Ga, which are stable up to 1000 K. The alloy ground-state line shows that the composition $x \cong 0.5$, around [3,3], is favored, which suggests that the In-rich phases observed in our c-$In_xGa_{1-x}N$ layers are ordered structures.

This work was supported by FAPESP and CNPq, Brazilian funding agencies, and Deutsche Forschungsgemeinschaft (DFG).

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