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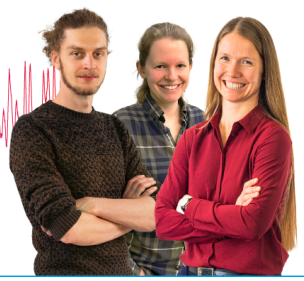

Lattice parameter and energy band gap of cubic $Al_xGa_yIn_{1-x-y}N$ quaternary alloys

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First-principles total energy calculations, combined with a generalized quasichemical approach to disorder and compositional effects, are used to obtain the lattice parameter and the energy band gap of cubic $Al_xGa_yIn_{1-x-y}N$ quaternary alloys. It is found that the lattice parameter $a(x,y)$ fulfills a Vegard's-like law; that is, it shows a linear dependence on the alloy contents x and y. The range of compositions for which the alloy is lattice-matched to GaN is obtained. The energy band gap $E_g(x,y)$ of the quaternary alloy deviates from a planar behavior displaying a two-dimensional gap bowing in the $x-y$ plane. Analytical expressions that fit the calculated $a(x,y)$ and $E_g(x,y)$ surfaces are derived in order to provide ready access to the lattice parameter and energy band gap of the alloy for the entire range of compositions. The results are compared with data for the wurtzite phase alloys. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1597986]

The wide-band-gap group-III nitride semiconductors AlN, GaN, InN, and their AlGaN, InGaN, AlInN ternary alloys have been extensively investigated due to their importance for the electronic and optoelectronic device technology.[1–3] Recently, the $Al_xGa_yIn_{1-x-y}N$ quaternary alloy has also emerged as an interesting material for device applications. It permits the independent control of the band gap and of the lattice parameter, so that GaN-based lattice-matched structures can be obtained.[4] Another interesting property that is verified in $Al_xGa_yIn_{1-x-y}N$ alloys concerns their emission intensity which can be much higher than that of AlGaN with comparable Al composition. These features make the quaternary $Al_xGa_yIn_{1-x-y}N$ alloy a better choice over AlGaN for many UV optoelectronic applications. Recently, efficient UV-light-emitting diodes and laser diodes comprising quaternary AlGaInN/AlGaInN multiple quantum wells have been demonstrated.[5–8] Although, from the experimental point of view, considerable progress has been already achieved in the study of the nitride quaternaries, very few attempts have been reported on theoretical predictions of their physical properties.

In this letter, we present a theoretical study of the lattice parameter and of the energy band gap as function of the alloy composition in quaternary $Al_xGa_yIn_{1-x-y}N$ nitride alloys. The calculations are based on a first-principles total energy method and an extension of the generalized quasichemical approach to treat disorder and compositional fluctuations. The zinc-blende (zb) polytype is considered as a model system. However, the results can also be applied to the wurtzite (w) modification. So far, only phase diagrams for these quaternary alloys have been calculated by adopting the simplified regular solid solution model.[9]

The calculations were carried out by combining the cluster expansion method within the framework of the generalized quasichemical approximation (GQCA) and *ab initio* density functional theory local density approximation (DFT-LDA). We extended the GQCA expressions previously used for ternary,[10] to the quaternary alloys. The $Al_xGa_yIn_{1-x-y}N$ alloy is divided into an ensemble of clusters, each independent statistically and energetically of the surrounding atomic configuration. Each cluster j with a certain number n_j, m_j, and $(n-n_j-m_j)$ of Al, Ga, and In atoms, respectively, occurs with a certain probability x_j. The total energy of each cluster is calculated by adopting a pseudopotential plane-wave DFT-LDA code, the so-called "Vienna Ab-initio Simulation Package" (VASP).[10] Any configurationally averaged quantity describing a structural or electronic property P of the alloy is given by a summation over the quantities being characteristic for each cluster P_j, and weighted by the probability x_j:

$$P(x,y,T)=\sum_{j=0}^{J} x_j(x,y,T)P_j. \tag{1}$$

Supercells with sixteen atoms are used as basic clusters to describe the fully relaxed alloys. The structure of each cluster is optimized by minimizing its total energy with respect to the lattice constant. A detailed description of the GQCA expressions used to obtain the results presented here will be given elsewhere.[11]

We start by analyzing the results for the configurationally averaged lattice constant $a(x,y)$, which are depicted in Fig. 1. We observed a very small variation of $a(x,y)$ with the growth temperature considered in the thermodynamic calculations; thus, in the results discussed here, the temperature was fixed at $T=1000$ K. The main feature of the results shown in Fig. 1 is the linear behavior of the lattice parameter as a function of the compositions x, y. The maximum deviation of $a(x,y)$ from a plane is 0.03%. Thus, the fulfillment of

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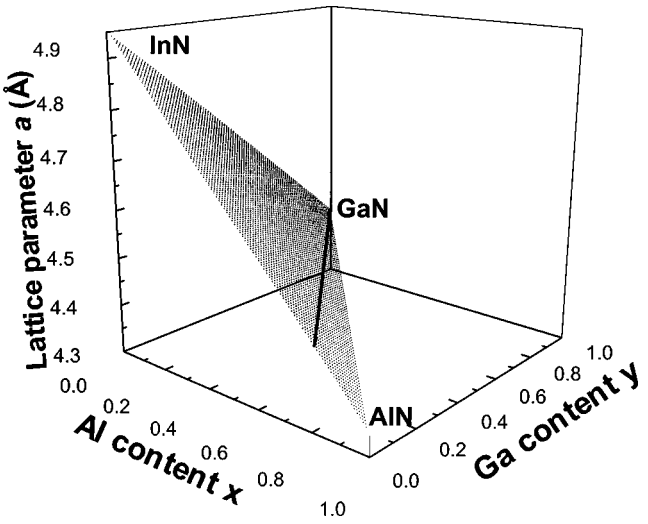

FIG. 1. Configurationally averaged lattice parameter a versus compositions x,y for the $Al_xGa_yIn_{1-x-y}N$ alloy. The calculated values for the binary compounds are $a^{AlN}=4.34$ Å, $a^{GaN}=4.46$ Å, and $a^{InN}=4.95$ Å. The solid line, corresponding to the values of compositions for which the alloy is lattice-matched to GaN, is given by the relation $y=1-1.23x$.

a Vegard's-like law for the quaternary alloys allows us to write:

$$a(x,y)=xa_{AlN}+ya_{GaN}+(1-x-y)a_{InN}, \tag{2}$$

with $a_{AlN}=4.34$ Å, $a_{GaN}=4.46$ Å, and $a_{InN}=4.95$ Å being the calculated binary lattice parameters. Another interesting quantity that can be extracted from our results is the composition range for which the lattice constant of $Al_xGa_yIn_{1-x-y}N$ alloys is lattice-matched to, say, GaN, which is represented by the solid line in Fig. 1. We found that it should occur for $y=1-1.23x$. In other words, the quaternary $Al_xGa_yIn_{1-x-y}N$ alloy with an Al/In mole fraction ratio of 4.3 will be lattice-matched to GaN. It is typical to consider an Al/In mole fraction ratio of five for the hexagonal alloy.[12]

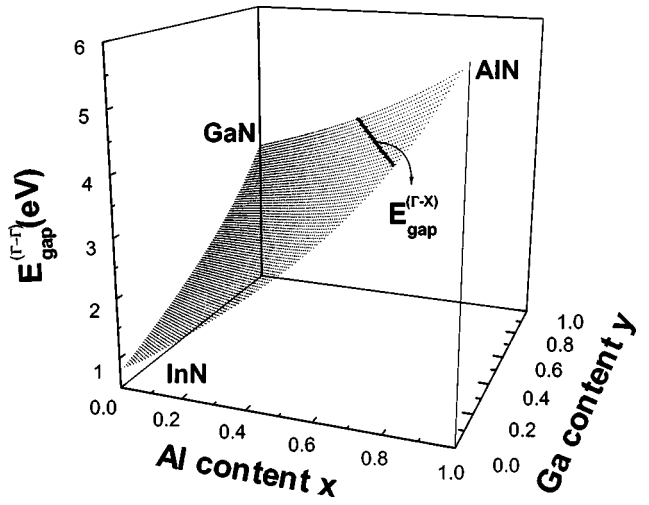

FIG. 2. Calculated direct (Γ–Γ) energy band gap of zb-$Al_xGa_yIn_{1-x-y}N$. For the binaries, the experimental values corresponding to the zinc blende phase have been assumed [$E_g^{AlN}=5.94$ eV, $E_g^{GaN}=3.3$ eV, and $E_g^{InN}=0.9$ eV (Refs. 15–17)]. The thick solid line delimits the direct-to-indirect gap regions, and is given by $E_g^{AlGaInN}(x,y=1.4-1.7x)$, with $x+y\leqslant 1$ in Eq. (3).

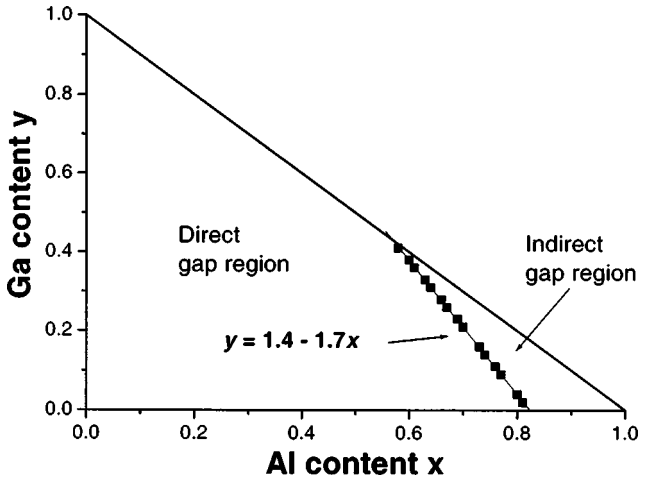

FIG. 3. Direct-to-indirect gap transition projected in the $x-y$ plane (see Fig. 2) for zb-$Al_xGa_yIn_{1-x-y}N$. Squares correspond to calculated points along the solid line depicted in Fig.2 delimiting the two regions.

We discuss now the results for the averaged energy band gap E_g of zb-$Al_xGa_yIn_{1-x-y}N$ for the transitions from the valence-band maximum (Γ-point) to the conduction-band Γ and X points minima. In order to correct the LDA results, which underestimate the band gap, we proceed accordingly with what was done for the ternary alloys.[13] A plane shift[14] in the band gap of the alloy is applied in order to have the values for the energy gap of the binary compounds AlN, GaN, and InN comparable with the experimental ones [$E_g^{AlN}=5.94(6.2)$ eV, $E_g^{GaN}=3.3(3.4)$ eV and $E_g^{InN}=0.9(0.9)$ eV for zb (w) phase].[15–17] The direct energy band gap is shown in Fig. 2. It is clearly seen that $E_g(x,y)$ deviates from a planar behavior, displaying a two-dimensional gap bowing in the $x-y$ plane. The direct-to-indirect band-gap transition is represented by the solid line in Fig. 2, and is predicted to occur at $y=1.4-1.7x$, as is emphasized in Fig. 3. It is worth mentioning that this direct-to-indirect gap transition is not expected to occur for the wurtzite phase of the alloy, since W-AlGaN is known to be a direct semiconductor alloy. In Table I, we compare our results for the energy band gap E_g with experimental data as obtained from photoluminescence (PL) measurements by Aumer *et al.*[18] A very good agreement is seen between the theoretical and experimental values.

In order to provide an analytical expression for the fundamental energy band gap of the $Al_xGa_yIn_{1-x-y}N$ quater-

TABLE I. Direct energy band gaps for the $Al_xGa_yIn_{1-x-y}N$ alloy (in eV). The calculated values were shifted by a constant plane surface, defined by fixing to the experimental values the band-gap energy for zincblende (zb) and wurtzite (w) binaries (Refs. 15–17).

(x,y)	Expt	E_g^{zb}	E_g^{w}
(0,0.9)	3.05,[a] 2.85[b]	2.90	2.99
(0.03,0.87)	2.98[b]	2.98	3.07
(0.16,0.74)	3.23[a]	3.24	3.36
(0.18,0.72)	3.37[a]	3.29	3.41
(0.22,0.68)	3.42,[a] 3.20[b]	3.37	3.49
(0.25,0.65)	3.35[b]	3.44	3.57

[a]Reference 18. PL for thick w-films (~430 nm).
[b]Reference 18. PL for thin w-films (~60 nm).

TABLE II. Constant ($b_{ABN}=b$) and linear composition-dependent ($b_{ABN}=\alpha+\beta x+\gamma y$) bowing parameters for the ternary ABN alloys, with $A,B=$In,Al,Ga (in eV). The alloy compositions obey the constraints $1-x-y=0$, $x=0$, and $y=0$, for AlGaN, InGaN, and InAlN, respectively.

Alloy	b	α	β	γ
Al_xGa_yN	0.632	0.500	0.368	−0.119
$Ga_yIn_{1-y}N$	1.370	0.928	0	0.879
$Al_xIn_{1-x}N$	2.914	1.786	2.155	0

nary alloy which could be of practical use and of easy access, we write $E_g(x,y)$ as

$$E_g(x,y)=xE_g^{\mathrm{AlN}}+yE_g^{\mathrm{GaN}}+(1-x-y)E_g^{\mathrm{InN}} - b_{\mathrm{InGaN}}y(1-y)-b_{\mathrm{InAlN}}x(1-x)-b_{\mathrm{AlGaN}}xy + (b_{\mathrm{InGaN}}+b_{\mathrm{InAlN}})xy-Cxy(1-x-y), \quad (3)$$

where b_{ABN}, $(A,B=\mathrm{In,Al,Ga})$ are the respective ternary bowing parameters, C is a constant multiplying the product of the Al, Ga, and In contents in the alloy. Equation (3) reduces to the standard expressions for the energy band gap of the ternary alloys. As clearly seen in Fig. 2, the values of E_g deviate from a planar behavior. This deviation is characterized by the bowing parameters and the C parameter [Eq. (3)]. For the ternary alloys, the constant and composition-dependent values for the bowing parameter are given in Table II. By substituting the composition-dependent values for the bowing parameters, and adjusting the surface equation for the energy gap, given by Eq. (3), to the calculated values for $Al_xGa_yIn_{1-x-y}N$, over the entire range of composition (x,y), we found the value of 2.59 eV for the C parameter. The maximum deviation of $E_g(x,y)$ in Eq. (3) from the calculated value was 0.04 eV. For practical use, we point out that if one makes $C=0$, and the bowing parameters constant (b) in Eq. (3), the maximum deviation is 0.1 eV.

We can also extract from our results the direct energy gap of the $Al_xGa_yIn_{1-x-y}N$ alloy when it is lattice-matched to GaN, by substituting the relation $y=1-1.23x$ in Eq. (3). It ranges from 3.30 eV $(x=0,\ y=1)$ to 4.40 eV $(x=0.81,\ y=0)$.

In conclusion, we studied the composition dependence of the lattice parameter $a(x,y)$ and energy band gap $E_g(x,y)$ of $Al_xGa_yIn_{1-x-y}N$ quaternary alloys, by combining *ab initio* total energy calculations and a cluster expansion method. We observed the fulfillment of a Vegard's-like law for the lattice parameter. From the calculated lattice constants, we predicted the range of compositions for which AlGaInN is lattice-matched to GaN. The energy band gap of the quaternary alloy displays a two-dimensional bowing, which is described by an analytical surface equation. The expressions derived for $a(x,y)$ and $E_g(x,y)$ are useful for tailoring electronic and optoelectronic devices based on either cubic and wurtzite $Al_xGa_yIn_{1-x-y}N$ quaternary alloys.

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