Ab initio study of elastic constants in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ wurtzite alloys

S. P. Łepkowski and I. Gorczyca

Institute of High Pressure Physics (Unipress), Polish Academy of Sciences, ul. Sokołowska 29/37, PL-01-142 Warszawa, Poland

Dependence of elastic constants on composition and atomic arrangement in wurtzite $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys is studied by self-consistent *ab initio* calculations within a supercell model. It is found that a Vegard's-like law, i.e., linear dependence on the alloy content, x, can be accepted for C_{12}, C_{13}, and C_{44} in $In_xGa_{1-x}N$, and for C_{12}, C_{13}, and C_{33} in $In_xAl_{1-x}N$, whereas significant sublinear deviations are obtained for C_{11} and C_{33} in $In_xGa_{1-x}N$ and for C_{11} and C_{44} in $In_xAl_{1-x}N$. The effect of In atoms clustering, modeled by grouping In atoms in a part of a supercell, leads to a decrease in C_{11}, C_{12}, and C_{44}, and an increase in C_{33}, in both $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys. Therefore, in the alloys with clustered In atoms, C_{11}, C_{12}, and C_{44} show significant sublinear behavior on composition in both $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, whereas the composition dependence of C_{33} is almost linear in $In_xGa_{1-x}N$ and significantly superlinear in $In_xAl_{1-x}N$. The dependence of the bulk modulus on composition is slightly sublinear in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys and changes little due to the In clustering effect.

The group III nitride alloys are strategic materials for optoelectronics and high-power/high-temperature electronics. Despite both experimental and theoretical efforts, many fundamental properties of these materials, including the band gap, the band gap deformation potentials, strain, the macroscopic polarization, and even the structural parameters, are still the subject of vigorous debate.[1–6] The difficulties in determination of the band gap of $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ originate from the specific role of In atoms in these alloys. A decade ago, it was demonstrated that alloying of GaN with In leads to strong localization of the hole wave function and, consequently, the band gap and optical properties of $In_xGa_{1-x}N$ alloys depend on microscopic arrangement of In atoms.[7] Recent calculations of the band gap in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys have shown that the band gap bowing is significantly enlarged when In atoms are grouped in clusters.[1] The knowledge about the deformation potentials of the band gap in nitride alloys is far from being satisfactory and even for binary nitride compounds, the values of these parameters are a subject of intensive research.[2] Regarding $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys, recent study of the pressure coefficient of the band gap has revealed that the effect of In clustering significantly changes the hydrostatic deformation potential of the band gap, whereas it only slightly influences the bulk modulus.[3] It has been suggested that large variations in the band gap and its pressure coefficient, determined on various samples of similar composition are caused by different degree of In clustering.[1,3]

The presence of the macroscopic polarization and strain is a common feature of nitride heterostructures and has a profound impact on their optical and electrical properties. Therefore, description of elastic and polarization related properties of $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys has a decisive influence on the design criteria of nitride nanostructures. It was established that similarly to the behavior of the band gap in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, the spontaneous and piezoelectric polarizations in these alloys depend not only on In content but also on the microscopic distribution of In atoms in the alloys.[8] Particularly, ordering of In atoms in superlattice-like structures alters dramatically the spontaneous polarization

and significantly influences the piezoelectric constants in these alloys.[8–10] For description of the effect of strain in the framework of continuum elasticity theory, the knowledge of the lattice parameters and the elastic constants of $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys is needed. Theoretical calculations show that in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys with a uniform distribution of In atoms, both the a and c lattice parameters follow Vegard's law, i.e., depend linearly on composition.[1,11,12] Small deviations from linear behavior of the lattice parameter c have been found for the alloys with clustered In atoms.[1] Recent x-ray diffraction and Rutherford backscattering spectroscopy experiments performed for strained $In_xAl_{1-x}N$ films have questioned the applicability of Vegard's rule to describe the lattice parameters in these structures.[5,6]

The elastic constants in wurtzite $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys have not been studied thus far. In nanostructure modeling (see, for example, Refs. 4 and 13) or interpretations of experiments,[5,6] it has been assumed that the elastic constants in these alloys would follow a Vegard-like behavior, i.e., interpolate linearly between the corresponding values determined for the binary compounds. On the other hand, sublinear composition dependencies of the elastic constants in random $In_xGa_{1-x}N$ and $Al_yIn_xGa_{1-x-y}N$ alloys of zinc-blende symmetry have recently been calculated using the Keating valence force field model.[14] The experimental determination of the elastic constants in nitride alloys is difficult. Theoretical calculations performed by means of *ab initio* density-functional techniques are the most promising approach to deliver reliable predictions of the elastic constants in nitride alloys.[15–17]

In the present work, we study the dependence of the elastic constants on composition and atomic arrangement in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys using self-consistent *ab initio* calculations with a supercell model. The indium concentrations, $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75,$ and 0.875, have been realized by substituting 2, 4, 6, 8, 10, 12, and 14 Al or Ga atoms by In in a 32-atom supercell. Two extreme atomic arrangements (identical for $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$) have been considered for a given x by
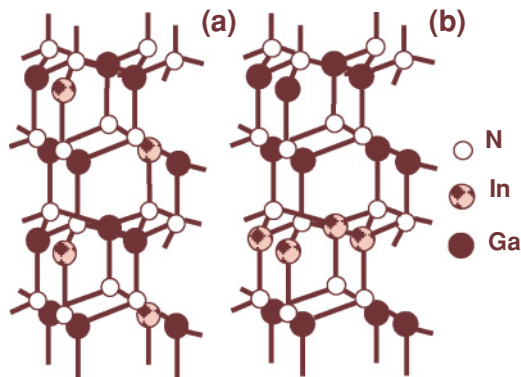
FIG. 1. (Color online) Schematic arrangement of atoms for uniform (a) and clustered (b) $In_{0.25}Ga_{0.75}N$ alloys.

FIG. 2. (Color online) The elastic constants in uniform (a) and clustered (b) $In_xGa_{1-x}N$ alloys, as a function of In molar fraction. The values of the bulk modulus (stars), calculated using Eq. (2), are also presented. Solid lines are linear interpolations between the values obtained for the binary compounds. Dotted lines are added to guide the eye.

either distributing In atoms as uniformly as possible over the supercell (uniform alloys) or by clustering In atoms on cation sites in a part of the supercell (clustered alloys).[1] There is no unique procedure to obtain the most clustered structures, thus for the clustered alloys we choose the structures in which the largest reductions of the band gap have been found in comparison to uniform alloys of the same composition.[1] Take as an example $In_{0.25}Ga_{0.75}N$. In the uniform case, In atoms are distributed in such a way that to each N atom belongs one In and three Ga atoms [Fig. 1(a)], whereas in a clustered $In_{0.25}Ga_{0.75}N$ alloy, every fourth cation hexagonal layer consists entirely of In atoms [Fig. 1(b)].[1] Note that the distribution of In and Ga atoms in the uniform configuration does not correspond to the random distribution of cations in an ideal alloy.

In the linear theory of elasticity, the elastic properties of wurtzite crystals are described in terms of five elastic constants denoted by C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}.[15] We perform the calculations of this set of elastic constants in two steps. In the first step, $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys are optimized by minimization of the total energy with respect to volume and shape of the supercell. In the second step, to every optimized alloy supercell, we apply five types of strains $\varepsilon_{ij} = (\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{zx}, \varepsilon_{zy}, \varepsilon_{yx})$, defined as $\varepsilon_{ij}^{(1)} = (\delta, \delta, 0, 0, 0, 0)$, $\varepsilon_{ij}^{(2)} = (\delta, \delta, \delta, 0, 0, 0)$, $\varepsilon_{ij}^{(3)} = (0, 0, \delta, 0, 0, 0)$, $\varepsilon_{ij}^{(4)} = (\delta, -\delta, 0, 0, 0, 0)$, and $\varepsilon_{ij}^{(5)} = (0, 0, 0, \delta/2, \delta/2, 0)$. For each type of the deformation, the strain variable δ varies between –0.02 and 0.02 in steps of 0.004. When the deformations are applied, new positions of atoms in the supercell are obtained by allowing atomic relaxation and modification of the supercell shape. The elastic constants are determined by comparing the parabolic fits to the calculated values of the total energy vs. parameter δ with expressions derived from the strain-energy relation in the framework of the linear theory of elasticity.[15] For the above types of deformations, the strain-energy expressions are as follows: $U^{(1)} = (C_{11} + C_{12})\delta^2$, $U^{(2)} = (C_{11} + C_{12} + 2C_{13} + C_{33}/2)\delta^2$, $U^{(3)} = C_{33}\delta^2/2$, $U^{(4)} = (C_{11} - C_{12})\delta^2$, and $U^{(5)} = C_{44}\delta^2$.

The total energy calculations have been performed using the VASP, package which is a plane-wave pseudopotential implementation of the density-functional theory.[18] Projector augmented wave pseudopotentials have been used.[19] For the exchange-correlation functional, the local density approxima-
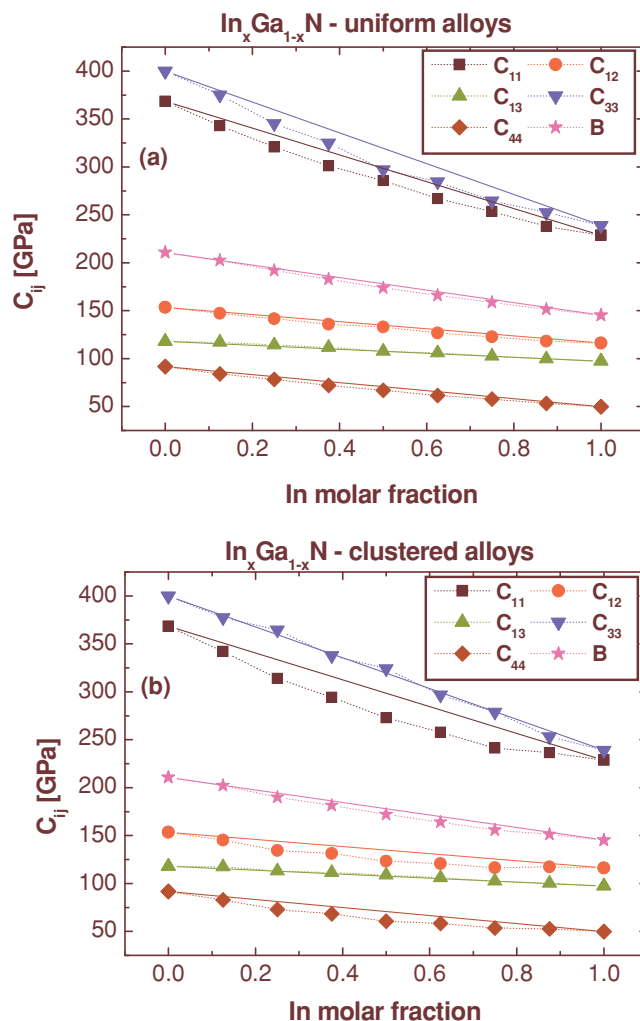
tion with the Perdew-Zunger parametrization of the Ceperley-Alder functional has been applied.[20,21] The semicore $3d$ and $4d$ electrons for Ga and In have been explicitly included in the calculations. The Brillouin-zone integrals have been calculated using a $5 \times 5 \times 5$ Monkhorst-Pack mesh. The cutoff energy for the plane-wave basis set has been chosen to be equal to 600 eV.

The results of calculations are presented in Figs. 2 and 3, where the elastic constants C_{11}, C_{12}, C_{13}, C_{33}, and C_{44} are plotted against composition for $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, respectively. In order to discuss the composition dependencies of the elastic constants quantitatively, we have performed quadratic parametrization of the *ab initio* data shown in Figs. 2 and 3, according to the formula

$$C_{ij}^{MInN}(x) = (1 - x)C_{ij}^{MN} + xC_{ij}^{InN} + bx(1 - x), \quad (1)$$

where the symbol M is used to denote Ga and Al, for $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, respectively, and b is the bowing parameter that accounts for the deviation from the Vegard-like rule. The results of the fitting procedure are listed in
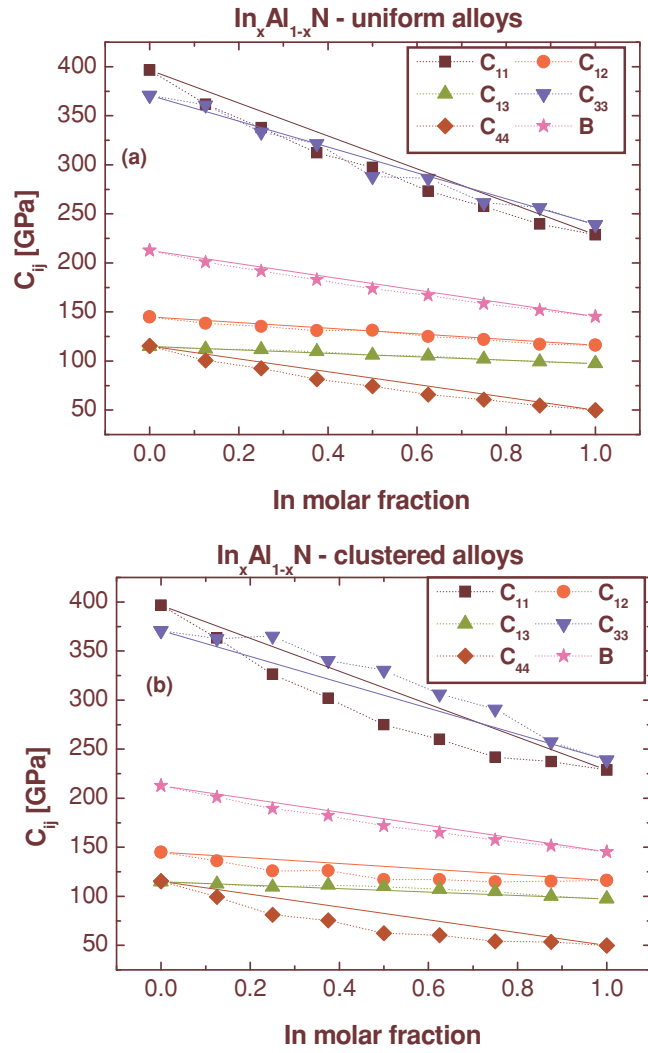
In$_x$Al$_{1-x}$N - uniform alloys

In$_x$Al$_{1-x}$N - clustered alloys

FIG. 3. (Color online) The elastic constants in uniform (a) and clustered (b) In$_x$Al$_{1-x}$N alloys, as a function In of molar fraction. The values of the bulk modulus (stars), calculated using Eq. (2), are also presented. Solid lines are linear interpolations between the values obtained for the binary compounds. Dotted lines are added to guide the eye.

Tables I and II. Additionally, we have included in Tables I and II the values of the average absolute deviations from the parabolic expressions, $\Delta C_{ij}^{\text{par}}$, and from the Vegard-like dependences $\Delta C_{ij}^{\text{Veg}}$. These quantities have been determined according to the standard formula used in statistics, $\Delta C_{ij}^{\text{fit}} = \frac{1}{n}\sum_{i=1}^{n}|C_{ij}^{\text{fit}} - C_{ij}^{ab}|$, where C_{ij}^{fit} denotes the elastic constants found using the parabolic or the Vegard-like dependence on composition, C_{ij}^{ab} are the results of *ab initio* calculations, and n denotes the number of studied In$_x$Ga$_{1-x}$N or In$_x$Al$_{1-x}$N ternary alloys. The $\Delta C_{ij}^{\text{par}}$ and $\Delta C_{ij}^{\text{Veg}}$ indicate the validity of using the parabolic and the Vegard-like approximations to the composition dependencies of the elastic constants.

Discussing the results for In$_x$Ga$_{1-x}$N, one can see that in uniform alloys [Fig. 2(a)], the composition dependences of C_{11} and C_{33} show significant sublinear character, whereas C_{12}, C_{13}, and C_{44} follow the Vegard-like behavior. In the case of clustered In$_x$Ga$_{1-x}$N alloys [Fig. 2(b)], C_{11}, C_{12}, and C_{44}

TABLE I. The results of quadratic parametrization of the composition dependences of the elastic constants in uniform and clustered In$_x$Ga$_{1-x}$N alloys. The average absolute deviations, $\Delta C_{ij}^{\text{par}}$ and $\Delta C_{ij}^{\text{Veg}}$, are also listed. The values for clustered alloys are given in brackets. All data are in GPa.

	C_{ij}^{GaN}	C_{ij}^{InN}	b	$\Delta C_{ij}^{\text{par}}$	$\Delta C_{ij}^{\text{Veg}}$
C_{11}	368	229	60 (100)	1.2 (1.5)	11.4 (18.7)
C_{12}	153	116	14 (43)	0.6 (1.2)	2.8 (7.9)
C_{13}	117	97	−4 (−4.5)	0.7 (0.5)	0.9 (0.9)
C_{33}	400	238	71 (−1)	2.2 (3.2)	13.0 (3.2)
C_{44}	92	50	16 (35)	0.3 (0.9)	3.0 (6.5)

depend sublinearly on In content, whereas the Vegard-like dependences occur for C_{13} and C_{33}. Consequently, the bowing parameters are significant for C_{11} and C_{33} in uniform alloys and for C_{11}, C_{12}, and C_{44} in clustered alloys. In all these cases, the values of $\Delta C_{ij}^{\text{Veg}}$ are considerably larger than the corresponding values of $\Delta C_{ij}^{\text{par}}$ which indicates that the Vegard-like rule is not fulfilled and the quadratic parametrization is reasonably valid. Comparing the results obtained for uniform and clustered alloys, we note that the effect of In clustering in In$_x$Ga$_{1-x}$N decreases the values of C_{11}, C_{12}, and C_{44}, which leads to an increase of the bowing parameters for these elastic constants. On the other hand, In clustering increases significantly C_{33}, decreasing its bowing parameter dramatically.

In the case of In$_x$Al$_{1-x}$N alloys, we observe that for uniform alloys [Fig. 3(a)], the composition dependencies of C_{11} and C_{44} clearly show sublinear character, which correlates with significant values of the bowing parameters and large differences between $\Delta C_{ij}^{\text{par}}$ and $\Delta C_{ij}^{\text{Veg}}$. On the other hand, Vegard-like dependencies are obtained for C_{12} and C_{13} (note small bowing parameters and similar values of $\Delta C_{ij}^{\text{par}}$ and $\Delta C_{ij}^{\text{Veg}}$). For C_{33}, a slightly sublinear deviation is found. For clustered In$_x$Al$_{1-x}$N alloys [Fig. 3(b)], C_{11}, C_{12}, and C_{44} depend sublinearly on composition that results in significant bowing and small values of $\Delta C_{ij}^{\text{par}}$ compared to $\Delta C_{ij}^{\text{Veg}}$. For C_{13}, the Vegard-like dependence can be accepted, whereas significant superlinear dependence on composition occurs for C_{33} giving a large and negative bowing parameter. Comparison of the results obtained for uniform and clustered alloys allows us to note that, similarly to the case of In$_x$Ga$_{1-x}$N, clustering

TABLE II. The results of quadratic parametrization of the composition dependences of the elastic constants in uniform and clustered In$_x$Al$_{1-x}$N alloys. The average absolute deviations, $\Delta C_{ij}^{\text{par}}$ and $\Delta C_{ij}^{\text{Veg}}$, are also listed. The values for clustered alloys are given in brackets. All data are in GPa.

	C_{ij}^{AlN}	C_{ij}^{InN}	b	$\Delta C_{ij}^{\text{par}}$	$\Delta C_{ij}^{\text{Veg}}$
C_{11}	397	229	80 (141)	2.5 (2.2)	15.5 (26.1)
C_{12}	145	116	8.7 (47)	1.2 (1.4)	2.1 (8.8)
C_{13}	115	97	−3 (−11)	0.7 (1.2)	0.7 (2.1)
C_{33}	371	238	25 (−93)	5.6 (4.3)	6.0 (17.0)
C_{44}	115	50	35 (70)	0.9 (2.3)	6.8 (13.0)

of In atoms in $In_xAl_{1-x}N$ alloys decreases C_{11}, C_{12}, and C_{44} and increases C_{33}.

Finally, we discuss the composition dependence of the bulk modulus in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys. The set of elastic constants of a wurtzite material determines its bulk modulus according to the well-known formula[15]

$$B = \frac{C_{33}(C_{11} + C_{12}) - 2(C_{13})^2}{C_{11} + C_{12} - 4C_{13} + 2C_{33}}. \qquad (2)$$

The values of B, calculated via Eq. (2), for $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys are included in Figs. 2 and 3, respectively. One can see that the composition dependence of B shows slightly sublinear character in both uniform and clustered alloys. The bowing parameters are rather small, i.e., 14 and 23 GPa, for uniform and clustered $In_xGa_{1-x}N$, and 19 and 26 GPa, for uniform and clustered $In_xAl_{1-x}N$, respectively. We note that the influence of In clustering on the values of B is small in both materials. The behavior of B with composition is then in agreement with the results presented in Ref. 3, where the values of B were calculated from the dependence of the total energy vs. the supercell volume according to the formal definition of the bulk modulus.

In conclusion, our study reveals that for alloys with a uniform distribution of In atoms, a Vegard-like approximation can describe the composition dependences of C_{12}, C_{13}, and C_{44} in $In_xGa_{1-x}N$ alloys and C_{12}, C_{13}, and C_{33} in $In_xAl_{1-x}N$, whereas significant sublinear deviations are found for C_{11} and C_{33} in $In_xGa_{1-x}N$ and for C_{11} and C_{44} in $In_xAl_{1-x}N$. The effect of In clustering reduces C_{11}, C_{12}, and C_{44} and increases C_{33} in both $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys. Consequently, C_{11}, C_{12}, and C_{44} depend sublinearly on x in clustered $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys, whereas C_{33} shows a linear and superlinear dependence on the composition in clustered $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, respectively. The dependence of the bulk modulus on composition is slightly sublinear in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ alloys and changes little due to the In clustering effect.

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