Size effects in band gap bowing in nitride semiconducting alloys

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Chemical and size contributions to the band gap bowing of nitride semiconducting alloys ($In_xGa_{1-x}N$, $In_xAl_{1-x}N$, and $Al_xGa_{1-x}N$) are analyzed. It is shown that the band gap deformation potentials of the binary constituents determine the gap bowing in the ternary alloys. The particularly large gap bowing in In-containing nitride alloys can be explained by specific properties of InN, which do not follow trends observed in several other binaries.

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Semiconducting nitride alloys, such as $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, have attracted great interest in optoelectronic device technology, for example in green-blue-violet light-emitting diodes and laser diodes as well as solar cells operating in the short-wavelength regime. By varying the composition, x, in $In_xAl_{1-x}N$, the band gap, E_g, can be tuned from 0.7 eV (InN) to 6.1 eV (AlN). The variation of the gaps with x differs from Vegards linear "law," i.e., it exhibits *bowing*, and it is characterized by a bowing parameter, b, see Ref. 1. Theoretical studies of the bowing dependence on composition and on atomic arrangements in nitride alloys and detailed comparison between theory and experiments were performed earlier and presented in Refs. 1–4. The calculations[1–4] were performed in two steps: 1) *ab initio* structural optimization by total-energy minimization within the local-density approximation (LDA) and 2) band-structure calculations with semiempirical correction[5] for the "LDA gap error." All details of the calculations are given in Ref. 1. The previously published results and detailed comparison between measured and calculated data are not repeated here, but since the origins of the gap bowing effects are widely discussed (see, for example, Refs. 6–8), we rather focus on simple explanations of the large band gap bowings in ternary semiconducting nitrides. In this context "size" and "chemical" effects, discussed in this work, are shown to be useful concepts in the analyses.

It was found[1–4] that the E_g bowing is larger for the alloys containing In than for $Ga_xAl_{1-x}N$ and it has further been found that the measured gaps of In-containing alloys vs. x exhibit a very large scatter that can be ascribed to formation of In clusters during the sample preparation. The formation of small In clusters leads to variations in In–N bond lengths. In one case, $In_{0.25}Al_{0.75}N$, and for one choice of cluster geometry, see Fig. 1(b) of Ref. 4, it was found that there is a class of N atoms with three In and one Al atoms as neighbors with In–N bonds that are 5% shorter (2.05 Å) than those in pure InN (2.15 Å) and Al-N bond (1.86 Å) slightly shorter than in the host AlN (1.89 Å).

We analyze changes in the band gaps, E_g, caused by substitution of smaller Ga (or Al) cations by the larger In ion in InGaN (InAlN) as well as the effects of replacing the Al cation with the larger Ga in AlGaN. The effects of these modifications of the alloys have two contributions, 1) size and 2) chemical effects. The first includes changes of E_g caused by the change of the unit cell volume, ΔV, (i.e., lattice parameters) following the substitution of cations. This effect can be determined by measurements under hydrostatic pressure or calculated by *ab initio* methods. The change, ΔE_g representing the size effect is related to the volume change, ΔV, via

$$\Delta E_g = a_g(\Delta V/V_0), \quad (1)$$

where V_0 is the equilibrium volume, and a_g is the gap deformation potential. The band-gap pressure coefficient, dE_g/dp, is

$$dE_g/dp = -a_g/B, \quad (2)$$

where B is the bulk modulus.

The second contribution, the chemical effect, carries information about modifications of the character of the chemical bonds, changes due to differences in the free-atom electronic configuration of the exchanged atoms and induced changes in hybridization. The combination of size and chemical effects is often referred to as the "chemical pressure," representing a counterpart of hydrostatic pressure.

In our previous studies[1,2] we found that the particularly strong gap bowing and large scattering in the measured band gaps in ternary In containing nitrides were characteristic for the nitrides. Such effects are not found in III–V alloys containing In, but not nitrogen (InGaAs, for example). Specific properties in the binary InN appear to be responsible for the anomalies. Indeed InN in several senses has properties which do not fit to the trends found for other III–V binaries. For example, it was recently established that InN has a much smaller band gap, about 0.7 eV, than believed earlier (around 1.8 eV).[9] The peculiarities of some of the properties of InN are illustrated in Table I, where common-cation and common-anion trends in E_g, bulk modulus, B, pressure coefficients, dE_g/dp, and the gap-deformation potentials, a_g, are shown for typical III–V semiconductors. Our calculated values are in parentheses, all other values are experimental data.[10–16] The E_g of InN does not follow the trend that within a common-cation group E_g is increasing when the atomic number of the anion is decreasing from antimonides to nitrides, i.e., that the compound with smaller volume has larger E_g. Then, according to the trend, InN

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TABLE I. Values of E_g, bulk moduli, B, band-gap pressure coefficients, dE_g/dp, and the negative of the deformation potentials, $-a_g$, for typical III–V semiconductors. Our calculated values for nitrides are in parentheses, all other values are experimental data (Ref. 10, unless specified otherwise).

Compound	E_g (eV)	B (GPa)	dE_g/dp (meV/GPa)	$-a_g$ (eV)
AlSb	2.32	55.1	-	-
AlAs	3.13	78.1	104	8.1
AlP	4.38	86.0	101	8.7
AlN	6.1 (6.0)	204.4[a] (213)	49.0[c] (48.5)	10.0 (10.3)
GaSb	0.81	56.3	147	8.3
GaAs	1.52	75.6	108[d]	8.3
GaP	2.86	88.2	97	8.6
GaN	3.51 (3.56)	205.4 (210)	40.0[e] (40.6)	8.2 (8.5)
InSb	0.24	48.3	155	7.5
InAs	0.42	57.9	114	6.6
InP	1.46	72.5	92.5[f]	6.7
InN	0.65-0.70 (0.69)	126.0[b], 148.0 (145)	27.3[e] (27.0)	3.4-4.0 (3.9)

[a]Reference 11.
[b]Reference 12.
[c]Reference 13.
[d]Reference 14.
[e]Reference 15.
[f]Reference 16.

should have a gap which is larger than that of InP (1.46 eV), while it in reality is much smaller. A similar trend is observed for bulk moduli: there is a systematic increase of the B values going from antimonides, trough arsenides to phosphides with a sudden, large increase for nitrides. However, for InN this increase is not as large as for AlN and GaN. There is an opposite trend for dE_g/dp, which for the nitrides are smaller. The values of a_g turn out to be quite similar for all members of a common-anion group. For Al compounds $a_g \sim -8$ to -10 eV, for Ga compounds $a_g \sim -8$ eV and for In compounds $a_g \sim -7$ eV, with the exception that for InN a_g is around -4 eV, i.e., considerably smaller in magnitude.

The general trend concerning E_g shown in Table I is related to an interplay of two effects: the chemical and the size contribution to E_g. At fixed volume, due to the chemical factor only, the E_g values of the nitrides should be much lower than the corresponding antimonides, arsenides, and phosphides. This is because the energy of the N 2s orbitals are lower than the energy of the other anion s orbitals, from which the conduction band minimum at the Γ point is made; in the atoms, the N 2s states lie about 4.5 eV lower than the P 3s, As 4s, and Sb 5s orbitals. On the other hand, the size effect, due to the large negative values of a_g, counteracts and exceeds the chemical order, and leads to the generic rule that a smaller volume leads to a larger energy gap. As shown by Carrier and Wei,[17] InN is an exception to this rule because due to the unusually small value of $|a_g|$, the size effect cannot overcome the chemical effect.

In the following, we separate the contributions of size and chemical effects to the gap bowing in ternary nitride alloys. The calculated changes of E_g due to replacement of i) Al ions by In ions in $In_xAl_{1-x}N$ are presented in Fig. 1, ii) Ga by In in $In_xGa_{1-x}N$ are shown in Fig. 2, and iii) Al ions by Ga ions in $Ga_xAl_{1-x}N$ are illustrated in Fig. 3.

The calculations performed for uniform or clustered distribution of cations are marked by filled and open asterisks, respectively. Figure 1(a) contains also experimental points taken from Ref. 1. Dashed lines represent the behavior of E_g for binary alloys (AlN, InN, GaN) induced by change of their volume. These effects are expressed by the corresponding volume deformation potentials of the band gap, a_g. In particular, in Fig. 1(b) it is shown that the large E_g bowing in uniform $In_xAl_{1-x}N$ can be well explained by the difference in a_g values between AlN and InN. The dashed lines represent the change of the AlN (upper line) and InN (lower line) band gap with volume, $E_g^{\rm AlN}(V/V_0)$ and $E_g^{\rm InN}(V/V_0)$, respectively. Open circles correspond to the weighted average between the $E_g^{\rm AlN}(V/V_0)$ and $E_g^{\rm InN}(V/V_0)$ values, evaluated according to

$$E_g(\mathrm{In}_x\mathrm{Al}_{1-x}\mathrm{N}) = (x)E_g^{\rm InN}(V/V_0) + (1-x)E_g^{\rm AlN}(V/V_0), \quad (3)$$

where $V = V(x)$ is the equilibrium volume (measured or calculated) for the alloy with the composition specified by x, and $V_0 = V(0)$ is the AlN equilibrium volume. If $V(x)$ is linear in x (Ref. 1) Eq. (3) is a second-order expression for the E_g variation with x. This implies that if we introduce the difference in specific volume for InN and AlN, $\Delta V = V(1)$-V(0), and assume $V(x) = V(0) + x\Delta V$, the band-gap bowing may be estimated as

$$b_v = a_g(\mathrm{InN})\Delta V/V(1) - a_g(\mathrm{AlN})\Delta V/V_0, \quad (4)$$

The b_v value obtained using Eq. (4) for $In_xAl_{1-x}N$ is equal to 3.6 eV, whereas the value obtained by the *ab initio* calculation for $x = 0.5$ is $b = 4.4$ eV.

A very similar picture is obtained for $In_xGa_{1-x}N$ as illustrated in Fig. 2. Also here the E_g bowing in uniform $In_xGa_{1-x}N$ can be explained mainly by the volume effect. The b_v value obtained for $In_xGa_{1-x}N$ is equal to 2.0 eV and the *ab initio* calculation gave $b = 2.1$ eV for $x = 0.5$.[1]

The same analysis performed for $Ga_xAl_{1-x}N$ shows that in this alloy (see Fig. 3) the gap bowing estimated from the a_g values of the constituents is smaller than the one obtained from

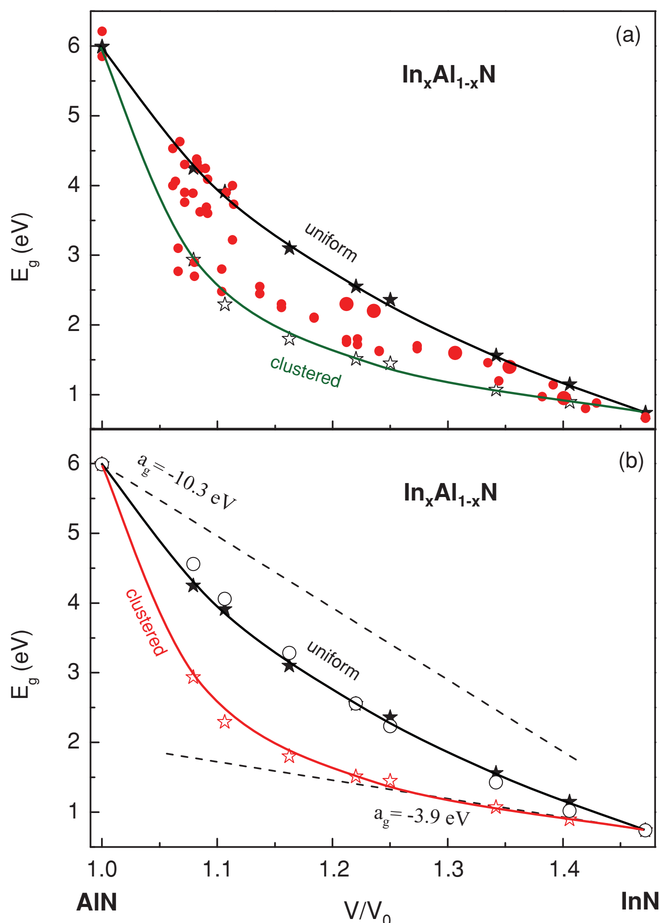

FIG. 1. (Color online) Calculated E_g bowings in $In_xAl_{1-x}N$ (solid lines and asterisks) compared with experimental data[1] (dots) (a) and with the E_g values as predicted from the size effect (open circles), (b) resulting from the size effect only, as described in the text. Full and open asterisks correspond to calculations performed for uniform and clustered distribution of In cations. Solid lines are spline fits to the calculated values. Upper dashed line in Fig. 2(b) represents the change of E_g with volume in AlN, the lower one in InN. $V = V(x)$ and V_0 are defined in the text.

ab initio calculations. The b_v value obtained for $Ga_xAl_{1-x}N$ is equal to 0.24 eV, whereas the *ab initio* calculation gave $b = 0.68$ eV for $x = 0.5$.[2]

Thus, for the nitride alloys with In the gap bowing in the uniform cases is well reproduced by the energy values being weighted averages of the E_g values corresponding to the given relative volumes V/V_0 in the (compressed) InN and (expanded) GaN or AlN. The bowing is well described by its volume part, b_v. Knowledge of the lattice constants and the values of the deformation potentials is sufficient to estimate the bowing in the uniform alloys. On the other hand, the behavior of E_g of $Ga_xAl_{1-x}N$ is mainly determined by the chemical effects.

Considering the case of clustered arrangement of cations an interesting observation can be made related to the alloys with In (see Figs. 1(b) and 2): in the range $x = 0.5$–1 the E_g bowing is almost entirely defined by the E_g behavior of compressed InN, i.e., by the a_g value of InN. In contrast, for $Ga_xAl_{1-x}N$, where

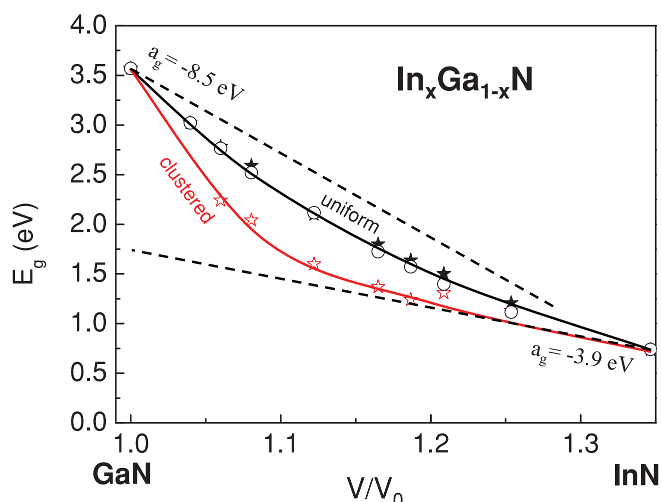

FIG. 2. (Color online) Calculated E_g bowing in uniform $In_xGa_{1-x}N$ (solid line and asterisks) compared with predicted E_g values (open circles) resulting from the size effect only, as described in the text. Upper dashed line represents the change of E_g with volume in GaN, the lower one in InN.

the difference in calculated gap values between the uniform and clustered alloy is small, the behavior of E_g for both AlN and GaN contribute equally to the bowing of the alloy for all x.

In conclusion, the a_g and E_g values in InN are smaller than would be estimated from the chemical trends for semiconductors. The small value of a_g resulting from the high ionicity of InN and relatively large bond lengths, is found to be the main factor determining the anomalies in InN. Large differences in volumes and a_g values between InN-GaN and InN-AlN lead to large gap bowing in the alloys, and it is shown that the values of lattice constants and a_g alone can be used to predict the E_g bowing in these uniform alloys. Whereas

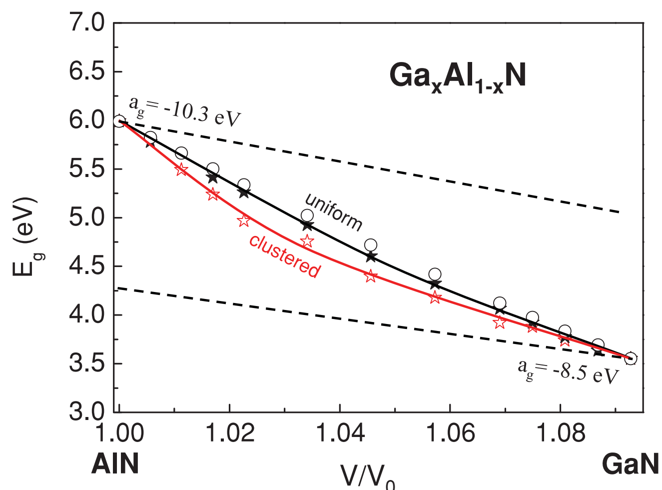

FIG. 3. (Color online) Calculated E_g bowing in uniform $Ga_xAl_{1-x}N$ (solid line and asterisks) compared with the predicted E_g values (open circles) resulting from the size effect only as described in the text. Upper dashed line represents the change of E_g with volume in GaN, the lower one in AlN.

size effects coming from both constituents are responsible for the large E_g bowing in $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ in the uniform case, the increase of E_g bowings caused by In clustering comes from the size behavior of InN itself. The strong interaction between In atoms and neighboring N atoms, reflected in the shortening of the In–N bonds, is responsible for the large E_g bowing. These effects are so strong in the x range from 0.5 to 1 that the E_g bowing in this range is almost entirely determined by the volume dependence of the gap in InN.

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