Vibrational mode shifts as a measure of local strain in the dilute nitride semiconductor alloy GaN_xAs_{1-x}

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The effect of an applied strain on the frequency of the localized vibrational mode associated with substitutional nitrogen in the dilute nitride GaN_xAs_{1-x} is calculated within first-principles density-functional theory, using a supercell approach. Calculated values of the deformation potentials of frequency of the localized nitrogen vibration mode for each irreducible component of the local strain are as follows: (Γ_1 representation) $a=-1907$ cm^{-1}, (Γ_3 representation) $b=22$ cm^{-1}, (Γ_4 representation) $d=-741$ cm^{-1}.

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I. INTRODUCTION

Dilute nitride alloys have attracted considerable attention in recent years, both because of their unusual physical properties and their potential device applications. When a small fraction of the As atoms in GaAs or InGaAs are replaced by N, the energy gap of the material decreases rapidly; for example by 150 meV when the N concentration is 1%.[1] This makes InGaNAs one of the more promising materials for long wavelength (1.3 and 1.5 μm) telecommunications lasers based on a GaAs substrate,[2] and for extending the wavelength range of GaAs-based solar cells further into the infrared.[3]

Due to the comparatively small mass of N (approximately 1/5 that of As or Ga) and the strength of the Ga-N bond, a highly localized triply degenerate vibrational mode exists about the N atom in the GaAs host lattice. Localized vibrational mode (LVM) spectroscopy is a useful technique for studying local bonding of impurities and impurity complexes in semiconductors.[4–6] The LVM associated with substitutional N in GaAs has been the subject of substantial experimental work,[7–12] using Raman and IR spectroscopy.

Given the low-temperature, nonequilibrium conditions that make the growth of dilute nitride materials possible, phase segregation and inhomogeneous or other unwanted strain are always a concern in relation to the material quality. With regard to strain, one possibility would be to use the nitrogen LVM as a local sensor of strain since the triply-degenerate mode should shift and split under strain. In principle, micro-Raman spectroscopy could be used to analyze inhomogeneous variations in the strain components. However, such measurements of the mode splitting can only be quantitatively translated into local strain if one knows the strain deformation potentials of the nitrogen LVM. In this Brief Report, we present calculations of these deformation potentials.

The hydrostatic pressure dependence of the frequency of the nitrogen LVM has been recently studied in Ref. 13 within first-principles density-functional theory (DFT), using a supercell approach. The same method has been used to study the effect of the substitution of nearest-neighbor gallium atoms with indium on the frequency of the LVM,[14] and also to calculate the phonon spectra of the high-frequency modes associated with substitutional nitrogen atoms in the random alloy for different nitrogen concentrations.[15]

In this Brief Report, we use the same theoretical technique to study the effect of applied strain on the frequency of the LVM. When a strain is applied, the dynamical matrix (DM) of the system changes, with associated changes in the LVM frequency. Within the linear regime, this change in the DM can be expressed in terms of three irreducible strain components,[16] each with a characteristic deformation potential. The deformation potential links a strain of a given symmetry with the change in the same symmetry in the DM. In the present work we calculate the deformation potentials of the nitrogen LVM in GaAs for each irreducible component of the local strain, using a first-principles supercell approach. This extends the work of Ref. 13 to include the two distinct types of uniaxial strain. With the calculated values of the deformation potentials, it is in principle possible to estimate the local strain in a GaN_xAs_{1-x} sample by observing the average shift and splitting of the nitrogen LVM frequency, or conversely to estimate the change in the LVM frequency produced when a known strain is applied.

In Ref. 17 a Raman-scattering study has been performed on GaN_xAs_{1-x} with $x=0-5\%$. A ~ 3 cm^{-1} splitting of the frequency of the Ga-N LO phonon between the (xx) and (xy) configurations (with $x \parallel [100]$ and $y \parallel [010]$) was observed for $x=0.02-0.05$. The authors, using a bond polarization model, attributed this splitting to a trigonal distortion of the lattice, and concluded that the GaN_xAs_{1-x} lattice contains $\{111\}-(GaN)_m(GaAs)_n$ superlattice complexes with $m=n=1$. Since the material is grown on the [001] substrate, it is not immediately clear if uniaxial strain along [001] might also contribute to the observed splitting. We investigate this possibility by simulating epitaxial GaN_xAs_{1-x} with $x=0.03125$, lattice matched on a [001] GaAs substrate, allowing the film dimensions to relax perpendicular to the substrate. We find that the resulting LVM mode splitting is negligible, due to the very small value of the associated deformation potential. This supports the picture in which a substantial [111] uniaxial strain is present in these films.

The remainder of the Brief Report is organized as follows. Details of the calculations are presented in Sec. II. In Sec. III we present and discuss the results of our calculations, and summarize the main points of our study in Sec. IV.

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II. CALCULATIONS

First-principles, pseudopotential, plane-wave, density-functional theory methods allow us to calculate electronic ground-state energies and interatomic forces for a given arrangement of atoms in a periodic structure, without fitting to experimental data. Although systems treated in this approach are formally periodic, supercell methods are used to treat surface and defect structures, such as substitutional N in GaAs.[13,18] Large supercells are required to obtain reliable results within this approach, because the interaction between impurities in neighboring supercells is weak when the supercell is large. However, calculating minimum-energy configurations and interatomic forces in large supercells is computationally demanding, so that a balance must be sought between the size of the supercell and the computational cost. In the present work we use a 64-atom GaAs supercell with one N atom substituting on an As site. In Ref. 13 it is shown that calculations performed on such a supercell under isotropic strain are well converged. (Calculations using an eight-atom supercell yielded LVM frequencies within 5% of those calculated using a 64-atom supercell.)

We find the ground-state electronic energy and Hellmann-Feynman[19] (HF) forces in DFT using the VASP electronic structure theory code,[20,21] which solves the Kohn-Sham equations by an iterative diagonalization scheme in a plane-wave basis set. The local-density approximation (LDA) is used for the exchange-correlation functional, as parametrized by Perdew and Zunger.[22] The calculations have been performed using ultrasoft pseudopotentials[23,24] and the $3d$ states have been included as valence states for Ga atoms. We find that a Γ-centered grid for k-point sampling, due to the underestimated band gap in DFT, introduces a Jahn-Teller distortion when a strain is applied to the system, because the state at the bottom of the conduction band at Γ spuriously lies lower than the top of the valence band. This led to unreliable results. We therefore used a k-point grid shifted off the Γ point by $(\frac{1}{8},\frac{1}{8},\frac{1}{8})$ in our calculations using the eight-atom supercell (with a $4\times4\times4$ mesh), and shifted by $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in our calculations using the 64-atom supercell (with a $2\times2\times2$ mesh). The plane-wave cutoff energy was set at 452 eV, and the structures were optimized until the residual HF forces were less than or equal to 10^{-4} eV/Å.

We calculate the equilibrium structure and DM of the 64-atom supercell containing one substitutional nitrogen, with and without strain, using the approach described in Ref. 13. To save computation time, we employ the perturbation-theory (PT) method[13] to find the LVM frequencies. In this PT method, we first calculate the LVM frequency, assuming that only the nitrogen atom moves, with the surrounding lattice forming a rigid cage. This gives a vibration frequency approximately 3% lower than that obtained with the full DM. Using the forces on all atoms obtained when the nitrogen atom is moved (in the x, y, or z direction), this may then be corrected by second-order perturbation theory to allow for recoil of the other atoms in the lattice, giving a vibration frequency very close to that obtained from the full DM.[13] (Alternately, the PT approach presented in Ref. 13 may be thought of as assuming that the interatomic force constants between Ga and As atoms are unchanged by the substitution of N and only the force constants between the N atom and other atoms in the system need be recalculated. Diagonalizing this approximate DM gives a nitrogen LVM frequency almost identical to that obtained in second-order perturbation theory.) This gives accurate values of the LVM frequency shifts and splitting; for a uniaxial strain of 2% along [111], the eight-atom supercell calculation of the full DM gives a -22.53 cm^{-1} singlet-doublet splitting of the LVM, the eight-atom PT calculation[13] gives the value as -22.48 cm^{-1}, and the 64-atom supercell PT calculation gives the value as -22.78 cm^{-1}.

Thus, the deformation potentials of the nitrogen LVM are calculated by first considering the effect of strain on the reduced 3×3 DM D_{ij}, involving the nitrogen motion only, assuming the other atoms in the lattice remain stationary. The deformation potentials so obtained are then corrected by the small PT shift, which allows for lattice recoil.

We introduce an applied strain by changing the supercell dimensions accordingly (see below) and relaxing the atomic positions to minimize the total energy, keeping the supercell shape and volume constant. We then calculate the required elements of the DM, vibrational mode frequencies and eigenvectors. Adopting the notation used in Ref. 16, we write the strain tensor e_{ij} as

$$e_{ij}=[e_{ij}(\Gamma_1)]+[e_{ij}(\Gamma_3)]+[e_{ij}(\Gamma_4)],$$

and define the deformation potentials, a, b, and d, by writing the change ΔD_{ij} in the DM as

$$\Delta D_{ij}=4\pi\omega_0 a[e_{ij}(\Gamma_1)]+4\pi\omega_0 b[e_{ij}(\Gamma_3)]+4\pi\omega_0 d[e_{ij}(\Gamma_4)],$$

where $\omega_0=2\pi\nu_0$ is the angular frequency of the triply-degenerate nitrogen LVM in the unstrained system. We express ΔD_{ij} in this form so that the deformation potentials link the change in frequency ν (in cycles per unit time), rather than the change in the dynamical matrix, with the irreducible representations of the strain. The coefficients a and b are found by calculating the LVM frequencies for a system strained along the cubic z axis by ϵ (with no change in x and y dimensions). This gives rise to a splitting of the triply-degenerate LVM into a singlet and a doublet of frequencies $\nu_s(\epsilon)$ and $\nu_d(\epsilon)$, respectively. The coefficients a and b are then calculated as

$$a=\frac{d\nu_s}{d\epsilon}+2\frac{d\nu_d}{d\epsilon},\quad b=\frac{d\nu_s}{d\epsilon}-\frac{d\nu_d}{d\epsilon}.$$

The coefficient d is found by applying a volume-conserving uniaxial strain along the [111] axis with the strain tensor, $\epsilon_{xy}=\epsilon_{yz}=\epsilon_{xz}=\epsilon/2$ and $\epsilon_{xx}=\epsilon_{yy}=\epsilon_{zz}=0$. As in the case of the [001] strain, this gives rise to a splitting of the triply-degenerate LVM into a singlet and a doublet of frequencies $\nu_s(\epsilon)$ and $\nu_d(\epsilon)$, respectively. The coefficient associated with Γ_4-type strain is then

$$d=\frac{2}{3}\left[\frac{d\nu_s}{d\epsilon}-\frac{d\nu_d}{d\epsilon}\right].$$

For each type of strain, in order to reduce the effects of numerical noise, we calculate the frequencies for several values of the strain between $\epsilon=-0.02$ and $\epsilon=+0.02$, fit the re-

TABLE I. Values of the deformation potentials of frequency of the nitrogen LVM in GaN_xAs_{1-x}. Each deformation potential corresponds to a different irreducible representation of the strain (see text).

Deformation Potential	Representation	Value (cm^{-1})
a	Γ_1	−1907
b	Γ_3	22
d	Γ_4	−741

sulting functions ν_s and ν_d with third-order polynomials in ϵ and find the derivatives at $\epsilon=0$.

III. RESULTS

We present our results for the values of the deformation potentials of frequency of the nitrogen LVM in GaN_xAs_{1-x} in Table I. The value of the Γ_3 deformation potential b is 2 orders of magnitude smaller than a or d, which implies that a uniaxial strain along the [001] direction will cause very little splitting of the LVM multiplet. The value of the isotropic strain coefficient a is in excellent agreement with the calculations reported in Ref. 13 for the pressure dependence of the LVM frequency, which give a value, $a=-1940$ cm^{-1}. The 2% difference is due to a small difference in the bulk modulus because we have here fitted the range of strains between ±0.02, whereas only positive pressures (negative strain) were included in the calculations of Ref. 13.

We have calculated the relaxation of a thin layer of GaN_xAs_{1-x} (with $x=3.125\%$), grown on a GaAs [001] substrate, by constraining the GaN_xAs_{1-x} 64-atom supercell lattice constant parallel to the surface to match the GaAs lattice constant and minimizing the energy with respect to the perpendicular lattice constant. We find the relaxation of the perpendicular dimensions of the film to corresponds to a Poisson ratio for the material of $\sigma=0.33$, which is in excellent agreement with previous calculations[25] of the elastic constants of the alloy. This gives only Γ_1- and Γ_3-type strains. We find the splitting of the mode to be 0.5 cm^{-1}, significantly smaller than the ~3 cm^{-1} splitting observed by Mintairov *et al.*,[17] thus supporting the conclusion of Mintairov *et al.* that some trigonal [111] Γ_4-type distortion of the lattice is present in the material as grown on the GaAs [001] substrate. A splitting of 3 cm^{-1} corresponds to a uniaxial strain along the [111] axis of 0.4 %.

The relatively small value of the b deformation potential requires some explanation. Figure 1 shows the variation in the Ga-N bond length as a function of the applied strain when strains of different symmetry are applied. For uniaxial Γ_4 tensile strain along [111] the Ga-N bond along the [111] axis is stretched and the other three Ga-N bonds (along the $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$ directions) are compressed. We note that the Ga-N bond length hardly changes at all for Γ_3 strain along [001]. In fact, the first-order change in the bond length is zero by symmetry for Γ_3 strains. It would appear then that the change in bond lengths (rather than bond angles) is the primary factor causing any changes in the LVM frequencies.

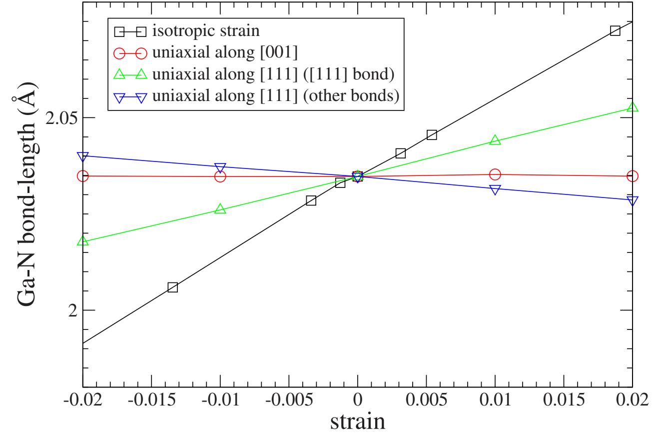

FIG. 1. (Color online) Variation in the Ga-N bond length as a function of the applied strain for the three irreducible components of the strain. For isotropic (Γ_1) strain (black boxes) the abscissa is the fractional change in volume, divided by three. For uniaxial strain along [001] (Γ_3) (red circles) and uniaxial strain along [111] (Γ_4) (green upward-pointing and blue downward-pointing triangles) the abscissa is the fractional change in length along the strain axis (the lines are a guide for the eyes).

In Fig. 2 we have plotted the variation of the bond angles as a function of the applied strain for uniaxial strains along the [001] and [111] directions (the bond angles do not vary in the case of a purely isotropic strain). For [001] tensile strain, the bond angle between [111] and $[\bar{1}\bar{1}1]$ bonds (or equivalent bond angles) decreases and the bond angle between [111] and $[1\bar{1}\bar{1}]$ bonds (or equivalent bond angles) increases. For [111] tensile strain, the bond angle between [111] and $[\bar{1}\bar{1}1]$ bonds (or equivalent bond angles) increases and the bond angle between $[\bar{1}\bar{1}1]$ and $[1\bar{1}\bar{1}]$ bonds (or equivalent bond angles) decreases.

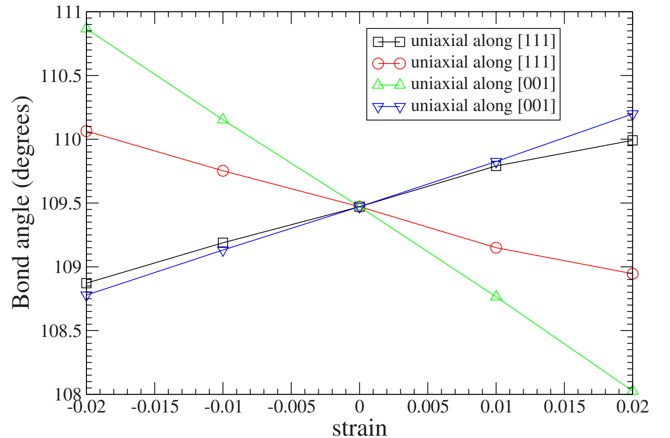

FIG. 2. (Color online) Variation in the Ga-N bond angles for [111] and [001] uniaxial strains. The symbols correspond to bond angles and strains as follows: [111]-$[\bar{1}\bar{1}1]$ bond angle (black boxes) and $[\bar{1}\bar{1}1]$-$[1\bar{1}\bar{1}]$ bond angle (red circles) for [111] (Γ_4) strain; [111]-$[\bar{1}\bar{1}1]$ bond angle (green upward-pointing triangles) and [111]-$[1\bar{1}\bar{1}]$ bond angle (blue downward-pointing triangles) for [001] (Γ_3) strain. The strain is defined as in Fig. 1. The lines are guides to the eyes.

In a previous study[15] we calculated the effect of N-N interactions on the high-frequency phonon spectra associated with substitutional N in GaAs. Our calculated splitting of the mode associated with single substitutional N due to nearest-neighbor N-N pair interactions was of the order of 80 cm^{-1}, substantially larger than those that would be expected from anistropic strain, given our calculated values of the b and d deformation potentials. For second-nearest-neighbor N-N pairs and higher orders the calculated splittings were of similar magnitude as those expected from anistropic strain, but the intensities of these modes were much lower than the intensity of the mode associated with isolated N atoms in the host matrix, and so would be easily distinguishable from that mode. We conclude that the effects on the N localized vibrational mode associated with N-N interactions can be well separated from the effects associated with anistropic strain in the alloy.

IV. CONCLUSION

We have calculated the deformation potentials of frequency of the localized nitrogen vibration mode for each irreducible component of the local strain. We find the Γ_1, Γ_3, and Γ_4 deformation potentials to be $a=-1907$ cm^{-1}, $b=22$ cm^{-1}, and $d=-741$ cm^{-1}, respectively. We have determined that epitaxial strain along the growth axis [001] is insufficient to explain the splitting of the LVM observed by Mintairov *et al.* for GaAsN thin films grown on GaAs [001] substrates, supporting the conclusion that a trigonal distortion of the lattice is present in these films. We have presented a qualitative argument for the difference between b and d, based on the different bond stretching for uniaxial strain along [001] and along [111].

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[1] M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl. Phys., Part 2 **31**, L853 (1992).
[2] H. Riechert, A. Ramakrishnan, and G. Steinle, Semicond. Sci. Technol. **17**, 892 (2002).
[3] J. F. Geisz and D. J. Friedman, Semicond. Sci. Technol. **17**, 769 (2002).
[4] R. C. Newman, Adv. Phys. **18**, 545 (1969).
[5] *Semiconductors and Semimetals*, edited by M. Stavola (Academic, New York, 1999), Vol. 51B, Chap. 4.
[6] M. D. McCluskey, J. Appl. Phys. **87**, 3593 (2000).
[7] T. Prokofyeva, T. Sauncy, M. Seon, M. Holtz, Y. Qiu, S. Nikishin, and H. Temkin, Appl. Phys. Lett. **73**, 1409 (1998).
[8] H. Ch. Alt, A. Yu. Egorov, H. Riechert, B. Wiedemann, J. D. Meyer, R. W. Michelmann, and K. Bethge, Appl. Phys. Lett. **77**, 3331 (2000).
[9] J. Wagner, T. Geppert, K. Köhler, P. Ganser, and N. Herres, J. Appl. Phys. **90**, 5027 (2001).
[10] A. Mascarenhas and M. J. Seong, Semicond. Sci. Technol. **17**, 823 (2002).
[11] H. C. Alt and Y. V. Gomeniuk, Phys. Rev. B **70**, 161314(R) (2004).
[12] M. Güngerich, P. J. Klar, W. Heimbrodt, J. Koch, W. Stolz, M. P. Halsall, and P. Harmer, Phys. Rev. B **71**, 075201 (2005).
[13] A. M. Teweldeberhan and S. Fahy, Phys. Rev. B **72**, 195203 (2005).
[14] A. M. Teweldeberhan and S. Fahy, Phys. Rev. B **73**, 245215 (2006).
[15] A. M. Teweldeberhan and S. Fahy, Phys. Rev. B **77**, 235216 (2008).
[16] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors*, 3rd ed. (Springer, New York, 2005), Chap. 3.
[17] A. M. Mintairov, P. A. Blagnov, V. G. Melehin, N. N. Faleev, J. L. Merz, Y. Qiu, S. A. Nikishin, and H. Temkin, Phys. Rev. B **56**, 15836 (1997).
[18] S. B. Zhang and S.-H. Wei, Phys. Rev. Lett. **86**, 1789 (2001).
[19] R. P. Feynman, Phys. Rev. **56**, 340 (1939).
[20] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[21] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[22] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[23] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[24] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[25] G. Stenuit and S. Fahy, Phys. Rev. B **76**, 035201 (2007).