

## Calculation of the strain-induced shifts in the infrared-absorption peaks of cubic boron nitride

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The effects of strain on the zone-center TO phonon frequencies of cubic BN (and, hence, the positions of the infrared-absorption peaks) are calculated using an *ab initio* pseudopotential linear-combination-of-atomic-orbitals method. The calculated phonon wave number for the unstrained material is  $1063\text{ cm}^{-1}$ , in excellent agreement with the experimental value. The calculated line shift is  $-34\text{ cm}^{-1}$  per 1% isotropic strain, and for uniaxial strain, is  $-61$  and  $10\text{ cm}^{-1}$  per 1% strain for phonon polarizations parallel and perpendicular to the strain axis, respectively. The Poisson ratio of the material is calculated to be 0.316. These results are expected to be useful in the experimental characterization of homogeneous and inhomogeneous strain in cubic BN thin films using infrared spectroscopy.

### I. INTRODUCTION

Cubic boron nitride, a material which has many properties similar to diamond, was first grown<sup>1</sup> by Wentorf in 1957. Its properties of hardness,<sup>1</sup> high thermal conductivity,<sup>2</sup> and chemical inertness make it of considerable technological interest. As a III-V semiconductor, it can be doped *n*- or *p*-type<sup>3</sup> and has a high electrical breakdown strength, making it a promising material for high-power transistor applications.<sup>4</sup> The wide band gaps of the III-V nitrides make them of interest for short-wavelength (blue to ultraviolet) optical devices.<sup>5</sup> Although the first growth<sup>1</sup> of cubic BN was achieved by a high-temperature, high-pressure process using a variety of catalysts, recent growth methods have concentrated on thin-film deposition techniques.<sup>6-12</sup>

In any thin-film growth process, the level of homogeneous or inhomogeneous internal strain of BN thin films is an important measure of the quality of the film and may also provide important clues to the growth mechanisms of the films. It is difficult to measure the strain of BN thin films accurately by x-ray scattering or transmission electron microscopy (TEM). For x-ray methods, the signal from the film can be difficult to resolve from the substrate scattering,<sup>12</sup> and for TEM, the sample must be specially prepared<sup>13</sup> in a structurally invasive way which may alter the internal strains. On the other hand, Fourier transform infrared (FTIR) spectroscopy allows one to measure accurately the zone-center transverse-optical (TO) mode phonon frequencies of the material in the films.<sup>12,13</sup> With FTIR methods, the signal from cubic BN is very clearly distinguished from that of hexagonal BN or of the substrate.<sup>12</sup> However, in order to use this measurement to infer the strain of the films, it is necessary to know how the phonon frequencies vary with material strain. Although the zone-center TO frequency has been measured both for bulk samples<sup>14-16</sup> and for thin films,<sup>12,17-26</sup> and has been calculated<sup>27</sup> for the bulk material, the effect of strain on the frequency has not, to our knowledge, been measured or calculated previously. A reasonably wide range of values ( $1050-1100\text{ cm}^{-1}$ ),<sup>12,17-26</sup> has been reported for the measured IR peak in thin films.

It is therefore of interest in the context of thin-film growth (and in view of the possibilities of strained-layer super-

lattices<sup>28,29</sup> involving BN) to provide accurate calculations of the strain-induced shifts of the zone-center phonon frequencies in boron nitride. Similar calculations have been performed in the past for diamond.<sup>30,31</sup> In general, total-energy band-structure methods can be used in conjunction with the frozen-phonon method to calculate phonon frequencies for semiconductors with a typical accuracy of a few percent or better.<sup>27,30,31</sup> In this approach, the displacement of ions associated with a particular phonon mode is "frozen in" and the total energy of the solid (excluding the classical kinetic energy of the ions) is calculated as a function of the magnitude of the ion displacements. The total energy is then fitted to a polynomial expression in the phonon displacement. The quadratic term of this fit determines the effective "spring-constant" of the mode, and hence, in conjunction with the mass associated with the mode, determines the phonon frequency.

The zone-center TO modes are the modes relevant to the IR activity.<sup>14</sup> Because the present calculations do not include the long-range electric field associated with the macroscopic electric polarization of LO phonons in a polar material, such as cubic BN, the frequencies calculated are for the zone-center TO modes. Thus, the phonon frequencies calculated correspond to the frequencies of the associated IR peaks. Which modes will be observed in a given experiment is determined by the detailed selection rules for coupling of the radiation to the phonon modes and will depend on the angle of incidence and the polarization of the IR beam relative to the strain axis of the film. For example, in a film with a homogeneous uniaxial strain axis normal to the surface, only one peak will be observed at normal incidence although there are two distinct zone-center TO phonon frequencies, whereas, for off-normal beam incidence, two distinct absorption peaks should be observed.

### II. CALCULATIONS

In the case of cubic BN, the cubic symmetry of the material allows us to characterize completely the first-order effects of strain on the zone-center TO mode frequencies by specifying three fundamental types of frequency shift: (1) the shift of all TO modes when the system is subjected to iso-

tropic strain; (2) the shift of modes with polarization parallel to the strain axis in a system subjected to uniaxial strain; and (3) the shift of modes with polarization perpendicular to the strain axis in a system subjected to uniaxial strain. Each of these effects has been calculated by evaluating the change in the phonon frequencies when the system is subjected to strain along high symmetry directions. Although the direction of strain does not affect the linear coefficients for frequency shifts in a cubic material, high symmetry directions were used in order to reduce the computational complexity of the total-energy calculations, where small but finite strains and phonon displacements are imposed.

In order to calculate the frequency shift of type (1) above, the frequencies of phonons with ion displacement along the [111] and [001] directions<sup>32</sup> were calculated for 4 and 0 % isotropic compressive strain. (Strain is specified with reference to the measured lattice constant<sup>33</sup> of cubic BN, 3.615 Å. The equilibrium lattice constant calculated in the present approach by minimization of the energy with respect to lattice constant is 0.82% smaller than the experimental value.) To obtain the coefficient for the frequency shift of type (2) above, the frequency of the phonon with ion displacements along the [111] direction was calculated for 4 and 0 % uniaxial compressive strain along the [111] axis, giving the strain shift for TO modes with polarization parallel to the strain axis. Finally, to obtain the coefficient for the frequency shift of type (3) above, the frequency of the phonon with ion displacements along the [001] direction was calculated for 4 and 0 % uniaxial compressive strain along the [110] axis, giving the strain shift for TO modes with polarization perpendicular to the strain axis. All frequency shifts are assumed to be linear in the strain over the range of 0–4 % strain.

The total energy calculations were performed as follows. The energy of the solid was calculated within the local density approximation<sup>34</sup> using the self-consistent linear-combination-of-atomic-orbitals pseudopotential method of Chan, Vanderbilt, and Louie,<sup>35</sup> as described in detail in Refs. 35–37. The single-particle wave functions for the valence electron states were represented as a linear combination of localized Gaussian orbitals  $f_{\alpha}(\mathbf{r}) = K(\mathbf{r})\exp[-\alpha r^2]$  centered on each atom, where  $K(\mathbf{r}) = 1, x, y,$  or  $z$  are the  $s$  and  $p$  cubic harmonics. Sixteen orbitals on each boron atom (with Gaussian decay constants  $\alpha = 0.17, 0.535, 1.684,$  and  $5.3$  a.u.) and sixteen orbitals on each nitrogen atom (with  $\alpha = 0.23, 0.674, 1.978,$  and  $5.8$  a.u.) were used. The self-consistent potential (Hartree and exchange correlation) was represented in plane waves up to an energy cutoff of 64 Ry. The local exchange-correlation potential was calculated using the form of Hedin and Lundqvist.<sup>38</sup> The ionic pseudopotentials used for boron and nitrogen were of the Hamann, Schlüter, and Chiang type<sup>39</sup> and were identical to those used in Ref. 37. Brillouin-zone integrals were performed using a uniform grid of 125 points in the full zone, with point-group symmetry reducing this to 19 points in the irreducible zone for strain along the [111] axis, 27 points in the irreducible zone for strain along the [110] axis, and 24 points in the irreducible zone for strain along the [001] axis.

Calculations were performed for a system with uniaxial strain axis along the [001] direction in order to find the Poisson ratio for the material. (This is relevant for thin films

TABLE I. Calculated values of the zone-center TO phonon frequency and coefficients of linear strain-induced frequency shifts (in  $\text{cm}^{-1}$  per 1% strain) for cubic BN. The experimental results quoted are for bulk cubic BN. The shift coefficients are for (1) isotropic strain, (2) uniaxial strain with phonon polarization along the strain axis, and (3) uniaxial strain with phonon polarization perpendicular to the strain axis.

	Calc.	Expt.
Unstrained frequency	1063 $\text{cm}^{-1}$ <sup>a</sup> 1004 $\text{cm}^{-1}$ <sup>b</sup>	1065 $\text{cm}^{-1}$ <sup>c</sup> 1055 $\text{cm}^{-1}$ <sup>d</sup> 1054 $\text{cm}^{-1}$ <sup>e</sup>
Strain coefficients:		
Isotropic strain (type 1)	– 34 $\text{cm}^{-1}$ <sup>a</sup>	
Uniaxial strain (type 2)	– 61 $\text{cm}^{-1}$ <sup>a</sup>	
Uniaxial strain (type 3)	+ 10 $\text{cm}^{-1}$ <sup>a</sup>	

<sup>a</sup>Present calculation.

<sup>b</sup>Reference 27.

<sup>c</sup>Reference 14.

<sup>d</sup>Reference 15.

<sup>e</sup>Reference 16.

which may have the lattice constant parallel to the substrate constrained while the lattice constant normal to the substrate is unconstrained.) The energy of the system was minimized with respect to the lattice constant in the [001] direction while the lattice constants in the [100] and [010] directions were held fixed at either 96 or 100 % of the measured lattice constant. The fractional change in the [001] lattice constant divided by the fractional change in the [100] and [010] lattice constants is equal to twice the Poisson ratio.

### III. RESULTS

The results for the calculated equilibrium (unstrained) value and strain shifts of the zone-center TO phonon frequency are given in Table I. The calculated TO zone-center phonon frequency at the calculated equilibrium lattice constant is 1063  $\text{cm}^{-1}$ . This is in perfect agreement with the range of measured values for the bulk material.<sup>14–16</sup> However, this agreement must be considered partly fortuitous since the calculated equilibrium lattice constant is 0.82% smaller than the measured value. The calculated value of the phonon frequency at the experimental lattice constant is 1034  $\text{cm}^{-1}$ . Nevertheless, whether one uses the measured or calculated equilibrium lattice constant, the value of the vibrational frequency is in extremely close agreement with experiment, demonstrating the accuracy of the method as a tool for calculating these quantities without fitting to any experimental data. This accuracy is indeed typical of these calculations for systems of this type. Given the accuracy with which the frequency shifts can be measured with FTIR methods, the present calculations of the strain-induced frequency shifts can be said to be more than accurate enough for the purposes of using the IR peak shift to calibrate the isotropic and uniaxial strain in cubic BN thin films.

In the calculation of the Poisson ratio, it is found that a change of 4% in the  $x$ - $y$  lattice constant causes a change in the relaxed  $z$  dimensions of 2.53%, giving a Poisson ratio of 0.316.

## IV. CONCLUSIONS

In conclusion, the strain-induced shifts of the zone-center transverse-optical phonon frequencies of cubic boron nitride have been calculated using a first-principles total-energy band-structure method. The calculated results for the unstrained material are in excellent agreement with the measured values for bulk cubic BN. The effects of strain have not been measured previously and are calculated for the first time here. In conjunction with FTIR spectroscopy measurements, the calculated results for the effects of strain on the

mode frequencies provide a means of determining homogeneous and inhomogeneous, isotropic and uniaxial strain in cubic boron nitride thin films.

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<sup>32</sup>In principle, because of the cubic symmetry of the system it is necessary to calculate energies for displacements in only one of these directions. Two different directions were calculated as an internal consistency check and the frequencies for small amplitudes of motion were found to be the same for each within the accuracy of the fourth-order polynomial fit to the calculated energies.

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