Electronic and elastic properties of BN, AlN and GaN

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We have carried out first-principles total energy calculations to investigate electronic and elastic properties of both zinc-blende and wurtzite BN, AlN, and GaN. We have calculated lattice parameters, elastic constants, deformation potential constants, phonon frequencies at **r** point, Born effective charges, and piezoelectric constants. Lattice parameters are fully relaxed by using the first-principles molecular dynamics method with variable cell shape. The internal strain in a strained crystal is also relaxed by the first-principles molecular dynamics method. The internal strain influences the elastic constants, the deformation potential constants, and the piezoelectric constants effectively. We have calculated the wurtzite deformation potential constants $D_1 - D_5$ considering the internal strain correction. The piezoelectric constants of wurtzite and also zinc-blende crystals have been calculated using the Berry phase approach and we have found from first principles that those of BN have an inverse sign in contrast to AlN and GaN. Discussions will be given in comparison with results obtained herein with the previous ones. © *1998 American Institute of Physics.* [S0021-8979(98)07921-3]

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1. INTRODUCTION

AlN and GaN are promising materials for applications in optoelectronics in the short wavelength range, light emit- ting diode and laser diode, and BN is for the extreme hardness and high thermal conductivity electronics devices. Re- cently there has been much interest in III nitrides and their alloys because of the potential for fabrication of a light emitter [1,2]. These materials grown on sapphire suffer a biaxial strain because of the lattice mismatch. In modeling these electronics devices, knowledge of their elastic constants, de- formation potential constants, and energy band information depending on a strain is indispensable. However, there is little information on these properties, especially deformation potential constants, in spite of the fact that there have been many theoretical [3-5] and experimental [6-8] results on them.

In recent work by Wright, all the elastic constants of AlN, GaN, and InN for both zinc-blende (ZB) and wurtzite (WZ) structures were obtained from first-principles calculations based on the pseudopotential method. Kim *et al.* reported all the elastic constants of BN, AlN, GaN, and InN using the full potential linear muffin tin orbital (FP-LMTO) method. Kato and Hama reported their work on elastic con stants of WZ–AlN using the pseudopotential method [9-12]. Majewski *et al.* and Kim *et al.* have obtained the de- formation potential constants for WZ crystal D_3 and D_4 in the Bir–Pikus notation by using the FP-LMTO and pseudo-potential methods within the local density approximation, respectively. Among recent calculations for deformation potential constants, only Suzuki and Uenoyama[3] have obtained all of the deformation potential constants $D_1 - D_6$ at the Brillouin zone center based on the linearized augmented plane wave method together with a cubic approximation. However, their calculation has not relaxed the internal strain which plays an important role in determining the deformation potential constants and the elastic constants. Their results are not satisfactory in comparison with experimental values by Shikanai *et al.* and by Yamaguchi *et al.*

It has been pointed out that the piezoelectric field, arising from the residual strain due to lattice mismatch, plays an important role in InGaN quantum wells [13]. However, there are only a few reports on the WZ piezoelectric constants [14,15] and those of ZB [16-19], and there is still no work which calculated many physical quantities of ZB and WZ BN, AlN, and GaN systematically, including piezoelectric constants with the same accuracy by using the pseudopotential-plane-wave method. It has been known that the physical parameters of them with the WZ structure sensitively depend on the cell shape and the atomic geometry. Thus, in calculating the above-mentioned values of their various physical parameters, the optimization of the crystal structure is indispensable. In this article, we report on the systematic study of the electronic and elastic properties of BN, AlN, and GaN in both ZB and WZ structures. We have performed first- principles calculations using the molecular dynamics method with variable cell shapes [20] to optimize their unit cell structures. To find the equilibrium positions of atoms in a strained crystal, we have carried out first-principles molecular dynamics calculation. Discussions on calculated results are given in comparison with the previous computational and memory. For each pseudopotential, the logarithmic derivatives are examined by using the criteria developed by Gonze, Stumpf, and Scheffler to eliminate the appearance of unphysical states well known as the ''ghost states.'' For exchange–correlation potential we have used the Ceperley–Alder type parametrized by Perdew and Zunger. The Kohn–Sham equation is solved iteratively with the eigenvalue

minimization scheme. The Brillouin zone **k** integration has been performed by the special-points method of Chadi and Cohen. We have used ten special **k** points for zinc blende-structure and six special **k** points for WZ structure in the irreducible wedge of the Brillouin zone. To treat the deep N $2p$ and Ga $3d$ potential, we have to take large energy cutoffs (90 Ry for BN and GaN, 80 Ry for AlN) to eliminate computational uncertainties. These cutoff energies give good convergence of both total energy and
pressure.

2. RESULTS AND DISCUSSION

The calculations were first carried out assuming ideal ZB and WZ structures. For WZ structures, the axis ratio c/a =1.633 and the internal parameter u=0.375 were used. The calculated total energies and pressures for several lattice con- stants were fitted with the empirical Murnaghan equation of state[31] to obtain equilibrium lattice constants. For ZB struc- tures, the forces acting on atoms and the elements of the stress tensor have converged within 10^{-5} and 10^{-6} Ry/a.u.^{3}, respectively. For WZ structures, the values of the various physical parameters depend sensitively on the shape of the unit cell and the atomic geometry, and, thus, structural optimization is needed as mentioned before. Starting from the resulting ideal atomic geometry, the crystal structure optimization has been iterated using the first-principles molecular dynamics method with variable cell shape until the forces acting on atoms and the elements of the stress tensor have converged within 10^{-4} and 10^{-6} Ry/a.u.^{3}, respectively.

Tables I and II summarize the results of our calculations for lattice parameters. Because there are so many results for ZB structure, we only show the range of the results. For WZ structure, only fully relaxed calculations are listed in Table II. Our results agree very well with the experimental data. The lattice constants of GaN are overestimated by about 1%. This comes from the fact that we have considered Ga $3d$ electrons as valence states. If these electrons are considered as core states, lattice constants are underestimated by a few percent as that of C_{11} and C_{12}. For a dilation along the [111] axis, the atomic positions in the unit cell are no longer determined by symmetry, and one has to find the atomic positions where the forces acting on atoms vanish. Following Nielsen and C_{66}. The results are listed in Table IV. The values in parentheses are obtained without internal strain correction. It is shown that the internal strain corrects the values of the elastic constants explicitly. The bulk moduli of ZB crystals are determined by the Murnaghan equation fitting for total energies and pressures of several lattice constants, and those of WZ are calculated using the following relation:

Experimental data of the elastic constants for the ZB structure are available only for BN and our results are in good agreement with the experimental data to within a few %. The other calculations predict nearly the same value within a few percent compared with ours except for Sokolovskii's results. Our value of internal strain parameter of ZB–BN is larger than the others by about 50%. For ZB–AlN and ZB–GaN, there are no experimental data and there are several other calculations. Our calculations are all. For WZ structure, there is only one result calculated from first principles for all elastic constants. Kim *et al.* have calculated only C_{33} directly from first principles, and other elastic constants are obtained by using Martin's trans- formation method. For BN and AlN, our results indicate

The values of the deformation potential constants are obtained in a way similar to the calculation of the elastic constants. We have used the Bir–Pikus notation to compute the values of the deformation potential constants, and spin orbit interaction has been neglected. For ZB structure, a dilation along the [001] axis results in a splitting of the results are listed in Tables V and VI. Experimental data are only available for WZ–GaN to our knowledge. The values in parentheses are obtained without internal strain correction. It can be found that the internal strain plays a significant role in calculating the deformation potential constants. Especially for the ZB shear deformation potential constant *d*, the WZ deformation potential constants D_3 , and D_4 , the values are nearly twice as large as the values calculated without internal strain correction. If we apply our results for elastic constants to the above equation using the relation $D_3=-2D_4$ we obtain D_3=8.40 (eV) and D_4=-4.20 (eV). The differences with the experimental data are reduced to 31% and 23%, respectively. In comparison with the results of Yamaguchi *et al.*[7] for D_4 and D_5, the discrepancies with our results are 4% and 14%, respectively, and with the other results of Yamaguchi *et al.*[8] for D_3 and D_4, they are 19% and 9.7%. Yamaguchi *et al.*[8] use C_{33}/C_{13}=3.34 to calculate D_3 and D_4. If we apply our result C_{33}/C_{13}=3.615 to Eq. (9), we obtain D_3=6.77 and D_4=-3.38 (eV). Then the differences with our results are 14.3% and 3.9%, respectively. In determining the values of deformation potential constants from the experimental results, the relation D_3=-$2D_4$ is generally used. However it is inconclusive to use it to obtain D_3 and D_4 , because our results and some other computational results[4,3] indicate that this relation does not hold. Thus, a relatively large difference between the computational results and experimental data is acceptable.

Piezoelectric constants and Born effective charges are calculated with Berry phase approach.[14,39–42] We have used the Monkhorst–Pack equivalent mesh (4,4,10) for Brillouin zone **k** integration to calculate the polarization of the *z* direction for both ZB and WZ structures. The unit cell shape of ZB structure is the cubic one in which there are eight atoms and that of WZ structure is ordinary one in which there are four atoms. In this approach, only the polarization Brillouin zone. Phonon frequencies are determined by calculating the forces acting on atoms which are displaced from their equilibrium positions according to the symmetry of each mode. The magnitudes of atomic displacements are 0.1%–0.5% of lattice constants. Tables VII, VIII, IX, and X show the calculated results. Experimental data for the ZB structure are obtained for BN and GaN, and our results agree well with the experimental data within a few %. For AlN, the difference with other calculations is within 5%. The results for the WZ structure are presented in Tables VIII, IX, and X. While a few experimental results and calculations exist for BN, there are much data for AlN and GaN. Good results are obtained for BN compared with experimental data and/or other calculations. For AlN, our results agree well with the experimental data and/or other calculations except for B_1 difference between the initial state and the final state is significant where the initial state means the equilibrium state and the final state means the atomic displaced or strained state. The atomic displacements are 0.1% of the ZB lattice constants and 1% of the WZ lattice constant and the induced strains are 0.1% for both ZB and WZ structures transformed from −0.64 with the above transformation equations. This table indicates that the transformation equa- tion is not meaningful for AlN because these equations assume the ideal WZ structure. We have obtained only $Z^*_{WZ, 1}$ for WZ Born effective charges where 1 indicates the (0001) direction. For those of ZB–BN there is about a 5% difference with the experimental result. The agreement with other calculations is excellent for the other values of the Born effective charges.

Table XII shows the results of the piezoelectric constants. The piezoelectric constants of BN have an inverse sign in contrast to AlN and GaN and have the same one with ordinary III–V semiconductors such as GaAs. This is because the value of the internal strain parameter and the Born effective charges of BN are small compared to AlN and GaN, whereas the piezoelectric constants of BN calculated without the internal strain correction are close to the ones of GaN. There are a few experimental results for the piezoelectric constants and they are for ZB–GaN and WZ–AlN and there is only one calculated result for the ZB–BN piezoelectric constant. For BN the discrepancy is very large compared to our result.

3. CONCLUSIONS

We have carried out first-principles total energy calculations for BN, AlN, and GaN within LDA to the DFT and optimized the unit cell shape and the atomic geometry using the first-principles molecular dynamics method with variable cell shape. Our results of lattice constants and the elastic constants are in good agreement with experimental data and/or other calculations. For the deformation potential constants, the difference with experimental data is still large, but in comparison with other calculations good agreement is obtained. The split of the B_1 mode optical phonon frequency is smaller than the other results. Calculated frequencies of the lower branch of the E_2 mode phonon of GaN are large compared to other results. The reason for those discrepancies is not known yet. A further investigation will be needed. We have also calculated piezoelectric constants and the Born effective charges with the Berry phase approach. Our results of the Born effective charges agree very well with other calculations and experimental results. For the piezoelectric con- stants the differences between the data are large. This is because they are very sensitive to the Born effective charge and the internal strain parameter.

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