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Electronic distribution and elastic properties of zinc-blende AlN and GaN

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Abstract. The density-functional theory (DFT) and density-functional perturbation theory (DFPT) are employed to study the electronic distributions and elastic properties of zinc-blende AlN and GaN. The linear charge density distributions along the [111] direction and charge density distribution of (001) planes for zinc-blende AlN and GaN are calculated. The total state of density and partial state of density of AlN and GaN are also calculated. Based on the optimized lattice parameters, the elastic constants and the internal strain parameters of zinc-blende AlN and GaN are calculated. The elastic tensors and compliance tensors are used to calculate Young's modulus of (101) planes.

1. Introduction

AlN and GaN are promising materials for applications in optoelectronics in the short wavelength range, light emitting diode and laser diode. All these materials also have potential for high temperature, high-power, and high-frequency electronics. These properties are closely related to their wide band gaps and strong (mixed ionic and covalent) bonding. Virtually all epitaxial AlN and GaN films are expected to contain some amount of residual strain due to differences in the film and substrate lattice constants and in their thermal expansion coefficients. This unintentional strain can modify the film's electronic structure, and accounting for this effect is important when interpreting optical spectra.[1, 2] Regardless of whether strain is introduced intentionally or unintentionally, predicting its effect on electronic properties requires knowledge of the material's elastic properties, and specifically the elastic constants which describe the response to an applied macroscopic stress. A knowledge of their elastic constants and strain deformation potentials is indispensable. For example, the elastic constants allow one to determine by continuum elasticity theory [3] the precise strain state of a pseudomorphic epitaxial thin film. In recent work, [4, 5] all the elastic constants of AlN and GaN for zinc-blende structures were obtained from first-principles calculations based on the pseudopotential method. Kim et al. [6, 7] reported all the elastic constants of AlN and GaN using the full potential linear muffin tin orbital (FP-LMTO) method. While general information on the properties of group III nitrides is available in a recent compilation [8]. In this article, we report on the systematic study of the electronic and elastic properties of zinc-blende AlN and GaN.



2. Theoretical method

Based on the density functional theory and the first-principle pseudopotential plane wave method, the pseudopotentials for all atoms are generated according to scheme of Troullier and Martins [9], because this pseudopotential can generate the correct charge density, and suitable for self-consistent calculation. The theoretical calculation is performed by using the local density approximation of the exchange-correlation Hamiltonian as implemented in ABINIT package [10]. Based on the density function perturbation theory (DFPT), the complete relaxation of the structure is completed first, then the response function is calculated, and the first order differential of occupied state wave function with respect to atomic displacement and strain is obtained, finally, the second order differential response function tensor is calculated with these values. The Monhorst-Pack scheme [11] was adopted in the calculation of k space integral, and the brillouin region was divided in the form of $8 \times 8 \times 8$. The charge density are calculated by tetrahedral integral method, and the calculation step is 5×10^{-5} Hartree.

3. Results and discussions

3.1 Lattice parameter optimization and electron distribution

The electronic structures of Al, Ga and N are $\text{Ne}3s^23p^1$, $\text{Ar}4s^24p^1$ and $\text{He}2s^22p^3$ respectively. The valence electrons of Al and Ga involved in this calculation are the three outermost electrons, and the valence electrons of N are the five outermost electrons. The space group of zinc-blended AlN and GaN is F-43M (216). The anions and cations are constructed with a face-centered cubic structure along a quarter of the diagonal line, respectively. In this paper, the lattice constant is firstly optimized. Since there is only one lattice constant, the convergence of monkhorst-pack lattice and truncation energy is tested by using the minimum energy principle. By calculation, their lattice constants are $4.337 \text{ \AA}$ and $4.47 \text{ \AA}$ respectively. Compared with the experimental values of 4.38 [12] and 4.50 [6], the optimized values are very close to those of other experimental values, with an error of less than 1%.

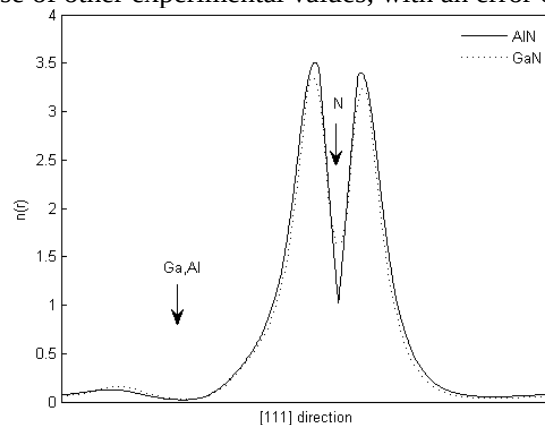


Figure 1. The linear charge density distributions of zinc-blende AlN and GaN in the [111] direction.

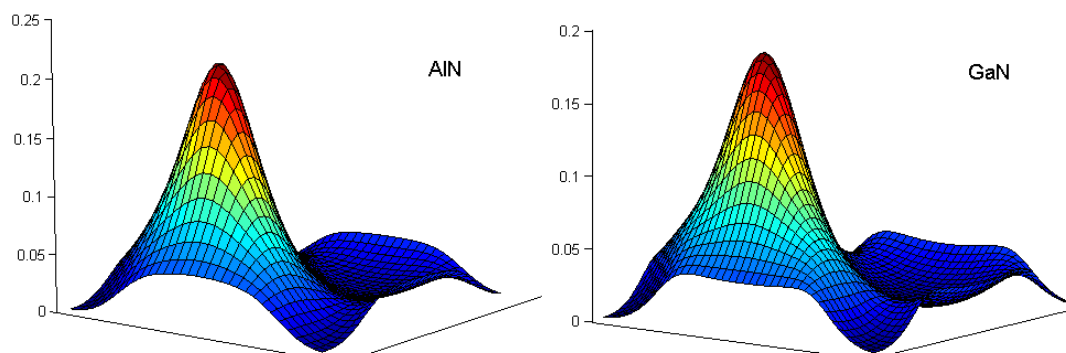


Figure 2. Charge density distribution of (001) planes for zinc-blende AlN and GaN. (online colour)

Based on the calculated lattice constant, the valence charge density distributions of AlN and GaN are calculated. Figure 1 shows the linear charge density distribution of zinc-blende AlN and GaN along [111] direction. As can be seen from the figure, there is almost no charge density in the center of the nucleus. This is because the density visualization is obtained by pseudopotential calculation, and the nuclear charge is not included. Due to the charge transfer from cations to anions, the positive and negative charges are redistributed. The covalent properties of bonds can be determined from the spherical symmetry deviation of charge density. The strength of the covalent bond between two ions can be determined from the height of the density peak between positive and negative ions. It can be seen from the figure that the strength of the covalent bond of AlN is stronger than that of GaN. The strength of covalent bonds directly affects other physical properties such as elastic properties and dielectric properties. Figure 2 shows the charge density distribution on the (001) surface of zinc-blende AlN and GaN. The surface charge density distribution of zinc blende structure is different from that of general face-centered cubic structure and body-centered cubic structure, which has no symmetry distribution. This is because the zinc-blende structure is tetrahedral structure. The cation is at the four corners and the center. The peak value of surface charge distribution does not appear at the symmetry center because the charge distribution is affected by the anions at the quarter of the diagonal. In addition, it can be seen from the figure that the peak value of AlN is higher than that of GaN, which is also a criterion that the covalent bond of AlN is stronger than that of GaN.

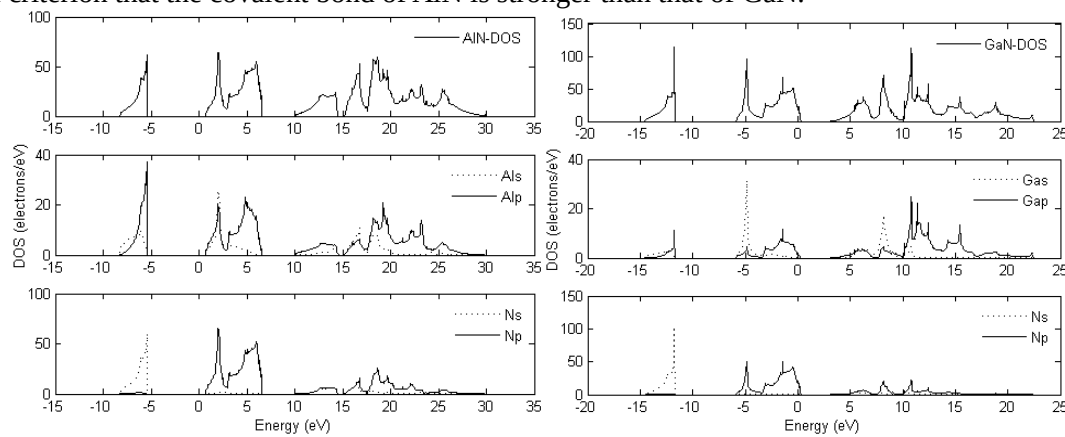


Figure 3. Total and partial density of state of the zinc-blende AlN and GaN.

Figure 3 shows the calculated total state of density (DOS) and partial DOS of AlN and GaN. It can be seen from Fig. 3 that the total density of states of AlN and GaN can be divided into three main groups/structures. From the partial DOS, we are able to identify the angular momentum character. The lowest energy group have mainly Al-3p states and N-2s states for AlN, and have mainly N-2s states for GaN. The second groups are mainly composed of Al-3p (Ga-4p) states, N-2p states as well as Al-3s states. From the partial DOS, we note a strong hybridization between Al-3s and Al-3p states in low energy portion of the second group. The last group mainly has contributions from Al-3p (Ga-4p), N-2s and N-2p.

3.2 Elastic properties

Based on the optimized lattice parameters, the elastic constants and the internal strain parameters of zinc-blende AlN and GaN are calculated. Because the calculation of elastic constant $C_{11} = \frac{\sigma_1}{\eta_1}$ and

$C_{12} = \frac{\sigma_2}{\eta_2}$ of zinc-blende AlN and GaN is not as simple as that of C_{44} , the internal strain parameters

ξ should be calculated. If there is an expansion along the [111] axis, the position of the atom in the cell is no longer determined by symmetry, but must be found where the force on the atom is zero, so that the relaxation is no longer equal to the non-relaxation, according to Nielsen and Martin relations [13],

$$C_{44} = C_{44}^{(0)} - \frac{1}{4a} \mu \omega_{TO}^2(\Gamma) \xi^2 \quad (1)$$

Here C_{44} and $C_{44}^{(0)}$ are relaxed and non-relaxed elastic tensors, respectively. the μ is the reduced atomic mass. $\omega_{TO}(\Gamma)$ is the central phonon frequency in the transverse Brillouin region, and ξ is the internal strain parameter. ξ is used to describe the sublattice displacement due to macroscopic strain. The internal strain can be obtained by the differential of the strain of an atom in a cell with respect to the displacement μ [14]

$$\xi = \frac{a}{\mu \omega_{TO}^2(\Gamma)} \left(\frac{\partial \varepsilon_{yz}}{\partial u_x} \right)_{\eta=0} \quad (2)$$

The calculated elastic constants of zinc-blende AlN and GaN are listed in tables 1 respectively, and the theoretical and experimental values of other literatures are also listed in the table. As far as we know, few experimental values are available for comparison because it is difficult to produce single crystals with high quality and large volume by chemical and physical vapor deposition and high pressure synthesis. In general, the calculated results are in good agreement with the theoretical values in other literatures. The calculated values are very close to those of the recent pseudopotential plane wave method (PP-PW) [5,15], and linear muffin-tin orbital (LMTO) method [6].

According to the Born stability criterion [16], the strain energy of the crystal must be positive, otherwise the crystal will be unstable. This means that there is a certain limit on the elastic constant of the stable crystal, and the limit on the cubic crystal system is:

$$C_{44} > 0 \quad C_{11} > |C_{12}| \quad C_{11} + C_{12} > 0 \quad (3)$$

By calculation and comparison, the calculated value satisfies the Born stability criterion, which shows that zinc-blende AlN and GaN are stable phases under the ground state. According to the so-called Cauchy relationship, the cubic crystals have $C_{11} = C_{44}$. As seen from table 1, they obviously do not satisfy such a relation.

Table 1. Elastic constants (GPa) and internal strain parameters of zinc-blende AlN and GaN.

		C_{11}	C_{12}	C_{44}	$C_{44}^{(0)}$	ξ
3C-AlN	Present	306	173	189	234	0.59
	Calc ^[15]	294	160	189	233	0.57
	Calc ^[6]	304	152	199	230	0.60
	Calc ^[17]	348	168	135		
3C-GaN	Present	288	158	158	219	0.68
	Calc ^[6]	296	154	206	225	
	Calc ^[5]	285	161	149		

^[15, 5] PP-PW; ^[6] LMTO. ^[17] Hartree-Fock

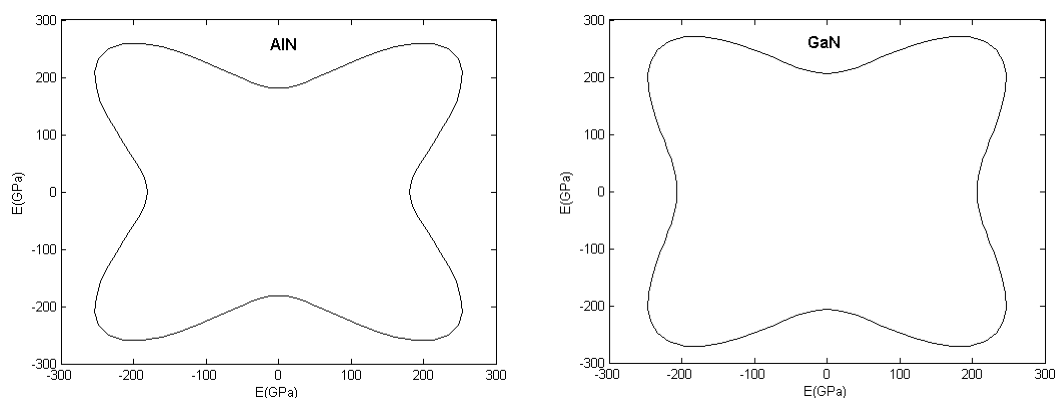


Figure 4. Young's modulus of (101) planes for zinc-blende AlN and GaN.

In engineering applications, it is usually necessary to know the Young's modulus, shear modulus and Poisson's ratio of the material. In fact, no single surface can fully express the elastic properties of the crystal. In practice, a very useful surface is one that represents the change of young's modulus in different directions. In general, tension produces not only longitudinal and transverse strains, but also shear strains. For the direction of tension, young's modulus is defined as the ratio of longitudinal stress to longitudinal strain, i.e. $\frac{\sigma}{\varepsilon}$. According to the following formula [13], the elastic tensors and compliance tensors of zinc-blende AlN and GaN obtained from the above calculation are used to calculate Young's modulus of (101) planes for zinc-blende AlN and GaN,

$$E = S_{11} - 2(S_{11} - S_{12} - \frac{1}{2}S_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2) \quad (4)$$

Here, S_{11} , S_{12} and S_{44} are the reciprocal of C_{11} , C_{12} and C_{44} , and l_1 , l_2 and l_3 are cosines of azimuth respectively. As seen from figure 4, even for cubic crystal systems, young's modulus is not isotropic, and its change with the direction depends on $l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2$. This quantity is zero in the $\langle 100 \rangle$ direction but has a maximum 1/3 along the $[111]$ direction. If it is positive, Young's modulus is the largest in the $[111]$ direction and the smallest in the $[100]$ direction. Therefore, the Young's modulus characteristic surface is uplifted along the cubic axis. As far as we know, there is no calculation of Young's modulus on the characteristic surface of these materials so far. It is hoped that the research results given in this paper can provide reference for future research.

4. Conclusion

In this paper, the first-principle is used to optimize the structure of zinc-blende AlN and GaN. The results show that the lattice constants calculated by pseudopotential plane wave method under local density approximation are slightly smaller than the experimental values at room temperature. Based on the optimized lattice constants, the electron distribution of zinc-blende structure are discussed. AlN and GaN are both mixed bond compound semiconductors, but the covalence of AlN is greater than that of GaN, which can be confirmed by their line charge density distribution along $[111]$ direction and surface charge density distribution in (001) plane. Based on the optimized lattice parameters, the elastic constants of these materials are calculated by density function perturbation theory. Compared with the theoretical values provided by other literatures, the calculated values are high or low, which shows the reliability of the calculation. Based on the calculated elastic constants, the young's modulus planes of the characteristic plane (101) of these materials are drawn for the first time.

Acknowledgments

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