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First-principles calculations of structure and high pressure phase transition in gallium nitride*

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The phase transitions of semiconductor GaN from the Wurtzite (WZ) structure and the zinc-blende (ZB) structure to the rocksalt (RS) structure are investigated by using the first-principles plane-wave pseudopotential density functional method combined with the ultrasoft pseudopotential scheme in the generalized gradient approximation (GGA) correction. It is found that the phase transitions from the WZ structure and the ZB structure to the RS structure occur at pressures of 46.1 GPa and 45.2 GPa, respectively. The lattice parameters, bulk moduli and their pressure derivatives of these structures of GaN are also calculated. Our results are consistent with available experimental and other theoretical results. The dependence of the normalized formula-unit volume V/V_0 on pressure P is also successfully obtained.

Keywords: transition phase, generalized gradient approximation, GaN
PACC: 6470K, 7115M, 7360L

1. Introduction

As one of the III–V semiconductors, gallium nitride (GaN), which is characterized by high ionicity, short bond length, high thermal conductivity and low compressibility, is an important semiconductor in science and technology. It can be used for wide-band-gap semiconductor materials for optoelectronic applications in the short-wavelength range and also for high-temperature, high-power and high-frequency electronic and optoelectronic devices.[1,2]

Under an ambient pressure, the stable modification of GaN has a hexagonal wurtzite (WZ) structure with space group $P6_3mc$ with mainly covalent, partly ionic tetrahedral bonding and a direct electronic gap of 3.4 eV.[3] The cubic zinc-blende (ZB) structure with space group $F\bar{4}3m$ has technological advantages compared with the WZ structure in that it has the ability to produce cleaved laser cavities and to be doped easily. The ZB structure GaN is still of interest to us partly because of its potential for a higher saturated electron drift velocity and a somewhat lower band gap than the WZ structure GaN.[4] As pressure increases, the WZ structure and the ZB structure experience a phase transition to the RS structure with space group $Fm\bar{3}m$.

Serrano *et al*[5] studied the relative stability of several structural phases for group-III nitride AlN, GaN, and InN by using the density-functional theory in the local-density approximation. They have found that the phase transitions from the WZ structure and the ZB structure to the RS structure occur at 42.9 and 42.1 GPa, respectively. Christensen and Gorczyca[6] applied the self-consistent linear muffin-tin-orbital band-structure calculations to investigating the optical and structural properties of the III-V semiconducting nitrides under a hydrostatic pressure. The calculated transition pressure from the WZ structure to the RS structure is 51.8 GPa. Sun *et al*[7] studied the structural and thermodynamic properties of GaN by using the molecular dynamics method with the Buckingham potential. They have found that the phase transitions from the WZ structure and the ZB structure to the RS structure occur at pressures of 49 GPa and 44 GPa, respectively.

In this work, we also focus on the phase transitions of GaN from the WZ structure and the ZB structure to the RS structure through the first-principles

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calculation. The results obtained are in agreement with the available experimental data and other theoretical results. In Section 2, we make a brief review of the theoretical method. The results and discussion are presented in Section 3. Some conclusions drawn for the present study are given in Section 4.

2. Theoretical method

Our calculation is performed by using the plane-wave pseudopotential density functional method combined with the non-local ultrasoft pseudopotential introduced by Vanderbilt,[8] in the generalized gradient approximation (GGA) for exchange-correlation functional in the scheme of Perdew–Burke–Ernzerhof (PBE).[9] In the structure calculation, the electronic wave functions are expanded in a plane-wave basis set with an energy cut-off of 350.00 eV. Pseudo atomic calculations are performed for N $2s^2 2p^3$ and Ga $3d^{10} 4s^2 4p^1$. As for the Brillouin-zone k-points sampling, 9×9×6 and 11×11×11 Monkhorst-Pack meshes[10] are employed for the hexangular WZ structure and the cubic ZB and RS structures, respectively, which is enough to achieve the self-consistent convergence of total energy to 10^{-6} eV/Atom. All the total-energy electronic-structure calculations are implemented through the Cambridge Serial Total Energy Package (CASTEP) scheme.[11]

3. Results and discussion

For the WZ structure with space group $P6_3mc$, there are two independent atoms (one Ga atom and one N atom). The initial structural model is built according to a typical wurtzite structure, with the Ga atom arbitrarily set at (1/3, 2/3, 0) and the N atom at (1/3, 2/3, u). We are calculate total energy E for a unit cell which has four atoms (two Ga atom and two N atom) in it after the symmetry operation. The independent structural parameters for the WZ structure needed determining are the primitive cell volume V_0, axial ratio c/a, and cell-internal dimensionless parameter u. For the ideal WZ structure, the axial ratio $c/a = \sqrt{8/3} \approx 1.633$, and the internal parameter $u = 3/8$. We take the following steps to achieve the optimized WZ structure GaN. In the first step, for a given u, we fix the ratio c/a, and take a series of different values of a and c to calculate total energy E. No constraints are imposed on the c/a ratio, that is, lattice parameters a and c both are optimized simultaneously. The second step is to repeat the above procedure over a wide range of ratio c/a. By obtaining a minimum of total energy for each fixed c/a, a minimum of total energy is also obtained for the given u. In the third step, we repeat the above procedures for several values of u, and then find a minimum of total energy for each values of u. By fitting the $E-u$ data to a third-order polynomial, we find the optimized internal parameter $u = 0.3769$.

From the optimized internal parameter $u = 0.3769$, we can find that the most stable structure of the WZ structure GaN occurs at an axial ratio $c/a = 1.628$, corresponding to the equilibrium lattice parameters $a = 3.204$ Å and $c = 5.216$ Å. By fitting the corresponding $E-V$ data to the Birch–Murnaghan equation of state (EOS)[12] we have

$$P = 3B_0 f_E (1+f_E)^{5/2}\Big(1+\frac{3}{2}(B'-4)f_E + \frac{3}{2}\Big(B_0 B'' + (B'-4)(B'-3) + \frac{35}{9}\Big)f_E^2\Big), \quad (1)$$

where f_E is written as

$$f_E = [(V_0/V)^{2/3} - 1]/2. \quad (2)$$

We can obtain the isothermal bulk modulus B_0 and its pressure derivative B_0' for the WZ structure GaN at zero pressure.

For the face-centred cubic ZB structure and RS structures with space groups $F\bar{4}3m$ and $Fm\bar{3}m$, respectively, there are eight atoms (four Ga atoms and four N atoms) in a unit cell, and only two independent atoms (one Ga atom and one N atom) left in a primitive cell after the symmetry operation. The initial structural model for the ZB structure is built according to a typical zinc-blende structure, with the Ga atom arbitrarily set at (0, 0, 0) and the N atom at (1/4, 1/4, 1/4). And the initial structural model for the RS structure is built according to a typical rock-salt structure, with the Ga atom arbitrarily set at (0, 0, 0) and the N atom at (1/2, 1/2, 1/2). For both the cubic ZB and RS structures of GaN, only the lattice constant a needs optimizing. Here, we calculate the total energy E for a primitive cell. The total-energy electronic-structure calculations are carried out over a series of different values of lattice constant a. Through this method, we obtain a series of total energies and the values of corresponding primitive cell volume V, and then fit the calculated total energy-volume data to the Birch–Murnaghan EOS.[12] Thus we can obtain the values of lattice constant a and bulk modulus B_0,

and the pressure derivatives of bulk modulus B_0' for both the ZB structure and RS structure of GaN at zero pressure.

All the results are listed in Table 1. It is obvious that for the WZ, ZB and RS structures of GaN, the differences among our lattice parameters and the experimental data and other calculated results are less than 1.7%, 1.5 % and 3%, respectively. The calculated energies per formula unit in the WZ, ZB and RS structures as functions of volume for GaN are shown in Fig.1(a). In order to see the difference in energy between the WZ structure and the ZB structure of GaN, we illustrate the energies per formula unit in the WZ structure and ZB structure as functions of volume in Fig.1(b). It is found that at low pressures the WZ structure has the lowest energy, which indicates that the WZ structure GaN is more stable than the ZB structure GaN.

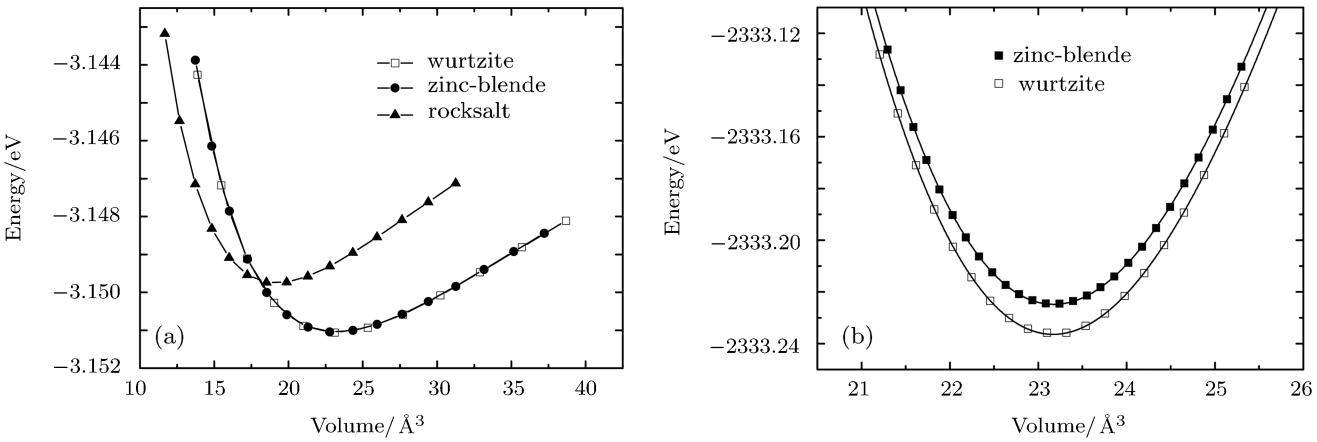


Fig.1. The calculated energies per formula unit in the WZ, ZB and RS structures of GaN as functions of volume (a) and the calculated energies per formula unit in the WZ and ZB structures of GaN as functions of volume (b).

Table 1. Lattice constants (Å), bulk moduli (GPa) and their pressure derivatives of the WZ, ZB and RS structures of GaN at zero pressure.

	Present Calculation	Other Calculation	Measurement
WZ structure			
a	3.204	3.215 (3.199)[a], 3.17[b], 3.193 (3.245)[c], 3.180[d], 3.203[e]	3.189[f], 3.190[g], 3.19[h]
c	5.216	5.13[b], 5.218 (5.296)[c], 5.217[e]	5.185[f], 5.189[g], 5.19[h]
c/a	1.628	1.614 (1.618)[a], 1.62[b], 1.634 (1.632)[c], 1.632[d]	1.626[f], 1.627[g] 1.626[h]
u	0.3769	0.38[a], 0.379[b], 0.376 (0.3762)[c], 0.376[d]	0.377[g], 0.377[i]
B_0	178.5	210.6 (251.0)[a], 207[b], 1.72[c], 196[d]	245[g], 188[h], 237 (±31)[i]
B_0'	4.502	3.75 (2.70)[a], 4.5[b], 5.11[c], 4.3[d]	3.2 [h], 4.3 (±2.0)[i]
ZB structure			
a	4.525	4.528[j], 4.497[d], 4.46[b]	4.50[k], 4.52[l]
B_0	177.6	186[j], 196[d], 201[b],	190.0[m]
B_0'	4.444	3.87[j], 4.2[d], 3.9[b]	
RS structure			
a	4.248	4.268 (4.219)[a], 4.225[d], 4.117[j]	4.234[h]
B_0	217.3	236 (287)[a], 240[d], 190[j]	248.0[h], 323 (±27)[n]
B_0'	4.710	4.23 (4.3)[a], 4.5[d], 5.14[j]	5.5[h], 3.5 (±0.8)[n]

[a]GGA(HF)-LCAO[13]; [b]LDA-FP-LMTO[14]; [c]LDA(GGA)-PPPW[15]; [d]DFT-LDA[5]; [e]DFT-GGA-PWPP[16]; [f]Ref.[17]; [g]Ref.[18]; [h]Ref.[19]; [i]Ref.[20]; [j]Ref.[21]; [k]Ref.[22]; [l]Ref.[23]; [m]Ref.[24]; [n]Ref.[25].

One method to obtain the zero-temperature transition pressures of GaN from the WZ and ZB structures to the RS structure is developed from the usual condition of equal enthalpies, i.e. at the transition pressure P, the values of enthalpy, $H = E + PV$, of both the WZ (ZB) structure and the RS structure are the same. The values of enthalpy H as functions of pressure P for the WZ, ZB and RS structures are illustrated in Fig.2. It is found that the transition pressure from the WZ structure to the RS structure is about 46.1 GPa, and the transition pressure from the ZB structure to the RS structure is about 45.2 GPa. The obtained results are presented in Table 2. It is obvious that our results are in good agreement with the experimental data[18−20] and other theoretical results.[5−7,21,26]

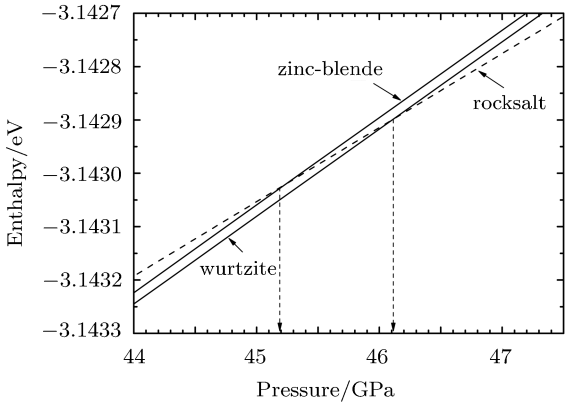


Fig.2. The enthalpies as functions of pressure for the WZ, ZB and RS structures of GaN.

Table 2. Transition pressures (GPa) of GaN from the WZ and ZB structures to the RS structure.

	Transition pressure	Theoretical methods	References
WZ - RS			
	46.1	PWPP-GGA	Present work
	47	x-ray absorption spectroscopy	[18]
	37	x-ray diffraction	[19]
	52.2±3.0	x-ray diffraction	[20]
	42.9	PWPP-LDA	[5]
	51.8	LMTO-LDA	[6]
	47	MD- empirical potential	[7]
	55.1	pseudoptential	[26]
ZB - RS			
	45.2	PWPP-GGA	Present work
	42.1	DFT-LDA	[5]
	44	MD- empirical potential	[7]
	42	MD-empirical potential	[21]

We finally investigate the EOS of GaN by using the quasi-harmonic Debye model,[27] in which the phononic effect is considered. Applying this model, we have successfully investigated the thermodynamic properties of GaAs,[28] c-BN[29] and ZnS.[30] Considering that the transition pressure from the WZ structure to the RS structure occurs at 46.1 GPa, and the transition pressure from the ZB structure to the RS structure occurs at 45.2 GPa, we present the diagrams of normalized volume-pressure V/V_0 (V_0 is the zero-pressure formula-unit volume) of the WZ structure and the RS structure of GaN at $T = 0$ and 1600 K in Fig.3(a), the ZB structure and the RS structure of GaN at $T = 0$ and 1600 K in Fig.3(b), respectively. Obviously, as temperature increases, the V/V_0-P curve becomes steeper, indicating that GaN is compressed much easier at higher temperatures.

4. Conclusions

We use the *ab initio* plane-wave pseudopotential density functional theory in the GGA-PBE generalized gradient approximation to investigate the structural properties and the high pressure phase transition in GaN. The lattice parameters, bulk moduli and their pressure derivatives for the WZ, ZB and RS structures of GaN are obtained. The phase transitions from the WZ structure and the ZB structure to the RS struc-

ture occur at 46.1 and 45.2 GPa, respectively. All the results are consistent with the available experimental data and other theoretical results. Moreover, the dependences of the normalized formula-unit volume on pressure at several temperatures are also successfully obtained.

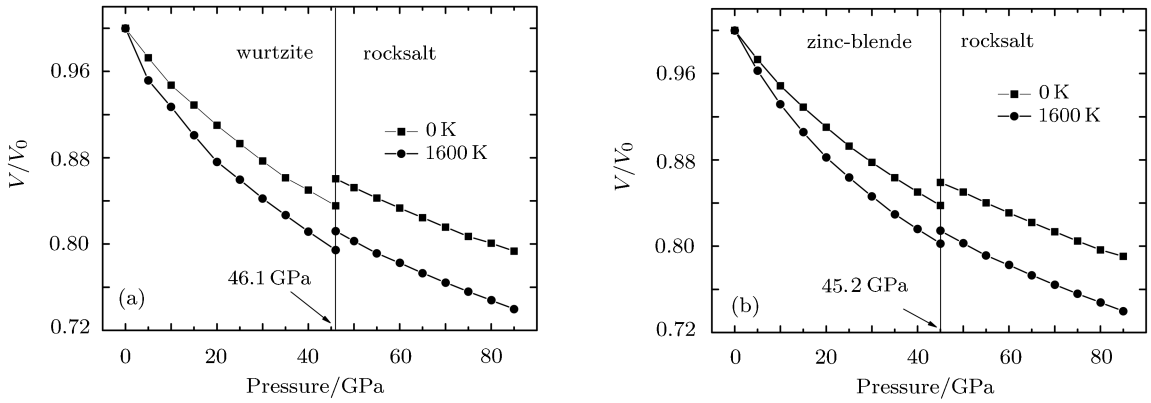


Fig.3. The normalized volumeV/V_0-P diagrams of the WZ and the RS structures of GaN at T=0 and 1600 K, respectively (a) and the normalized volume V/V_0-P diagrams of the ZB and the RS structures of GaN at T = 0 and 1600 K, respectively (b).

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