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Electronic and optical properties of rock-salt aluminum nitride obtained from first principles

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Abstract

We investigated the electronic and optical properties of rock-salt aluminum nitride (AlN) using a first-principles method based on the plane-wave basis set. Analysis of the band structure shows that rock-salt aluminum nitride is a wide gap indirect semiconductor. The band gap is predicted to be 5.82 eV within the screened exchange local density approximation (sX-LDA) but to be reduced to 4.23 eV for strained rock-salt AlN corresponding to the experimental lattice constant 4.24 Å. The optical properties including the dielectric function, reflectivity and energy-loss function are obtained and analyzed together with some features. The pressure coefficients of the indirect band gaps at the Γ, X and L points are also calculated, with the value of the smallest indirect band gap determined as 31 meV GPa^{-1}.

1. Introduction

Aluminum nitride (AlN) is a prospective electronic material particularly for large scale integrated circuit substrates, owing to its excellent mechanical, electronic and thermal properties such as low compressibility, high dielectric constant, high thermal conductivity and high breakdown voltage [1]. In terms of these properties, AlN is also ideal for high power and high temperature devices. All of these applications may be related to the N–Al ionic bonds and induced large band gap which have stimulated research into the other Al–N phases.

To date, there has been increasing interest in the stabilization phases of solids that do not occur in nature, such as the high pressure semiconducting phases, obtained by means of epitaxial growth or nanocrystallites [2]. Under normal conditions, AlN crystallizes in the wurtzite structure with the space group $P6_3mc$ (No. 186), and the phase transition to the rock-salt structure takes place at high pressures (about 22.9 GPa) [3, 4]; however, non-equilibrium

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rock-salt AlN may be retained at ambient conditions as a metastable phase, as has been achieved by many researchers. Especially in AlN/TiN superlattices, AlN can be realized with a much larger lattice constant, which suggests the possibility of band gap engineering [3, 5–8]. Thus, it is of great importance to explore the electronic structure and optical properties of rock-salt AlN, possibly useful in indicating future technological applications of thin film materials. In this paper, we performed a detailed investigation of the electronic and optical properties of rock-salt AlN together with the pressure effects on the band gaps, using the first-principles method.

2. Calculational method

First-principles calculations were performed with the CASTEP code in MS Modeling software [9], with a plane-wave basis set for the electron wavefunction expansion up to a kinetic energy cut-off of 800 eV with periodic boundary conditions. The norm-conserving pseudopotential [10] is used for electron–ion interaction, which can give a more accurate description of optical properties than ultrasoft pseudopotentials, and the local density approximation (LDA) [11] is used for electron–electron interaction. The k point integrations over the Brillouin zone were performed using the Monkhorst and Pack mesh [12]. Here, a $9 \times 9 \times 9$ mesh parameter grid was taken in the irreducible wedge of the Brillouin zone for the rock-salt AlN phase. For optical property calculations, denser k points were generated for accuracy. During the structure optimizations, the total energy was minimized by varying the lattice constants under restriction of the given symmetry, and all forces on atoms were converged to less than 0.001 eV Å^{-1}. The pressure coefficient of an interband transition in a semiconductor is easily calculated: it is given by $\mathrm{d}E_g/\mathrm{d}p$, and is related to the volume deformation potential $\mathrm{d}E/\mathrm{d}\ln V$ and the bulk modulus by the formula $\mathrm{d}E_g/\mathrm{d}p = -(1/B)\mathrm{d}E_g/\mathrm{d}\ln V$ in the cubic structure.

3. Results and discussion

The structural parameters for rock-salt AlN including the lattice constant and bulk modulus are determined as 4.001 Å and 295 GPa, respectively. The calculated equilibrium lattice constant is close to the experimental value 4.045 Å [5], and is about 5.7% smaller than the experimental value 4.241 Å measured for AlN/TiN superlattices where the AlN layer thickness was below the critical value [3].

Band dispersions along high symmetry lines of rock-salt AlN in the Brillouin zone (BZ) obtained from the Kohn–Sham eigenvalues are shown in figure 1. The conduction band minimum is located at the X point, while the valence band maximum is located at the Γ point with threefold degeneracy, leading to an indirect band gap of $E_g = 4.53$ eV. Considering the usual underestimation of energy gaps within the LDA approximation which is known to result from the discontinuity of the exchange–correlation energy [13], screened exchange LDA (sX-LDA) is applied here to obtain more accurate band gaps, which is computationally much less demanding than using the GW quasiparticle method. This has been found to yield band structures, in particular for narrow and medium band gap materials, which are in very good agreement with experimental results [14, 15]. Under sX-LDA correction the band gap for rock-salt AlN could increase to 5.82 eV, slightly smaller than that of wurtzite AlN, 6.2 eV [16]. In the energy band structure, the valence band consists of four energy levels ranging from 0 to −18 eV. The higher three levels exhibit degeneracy, becoming two levels at the L and X points, where the highest one is a doublet, and one level at Γ, which is triplet. For the energy

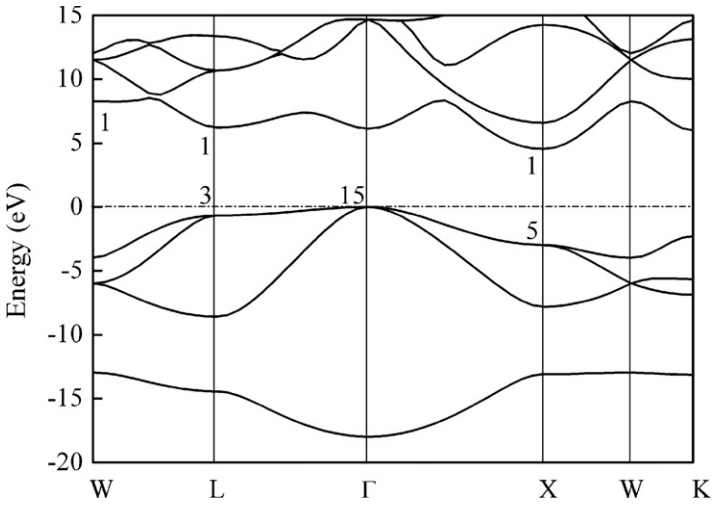

Figure 1. Band structure of rock-salt AlN where the Fermi surface is set to 0 eV.

Table 1. Band gap energies in the sX-LDA approximation and corresponding pressure coefficients.

	Band gaps (eV)	Pressure coefficients (meV GPa^{-1})
Γ–X	5.82	31
Γ–L	7.38	22
Γ–Γ	6.94	49

band, the lowest conduction band energies at the Γ, X and L points relative to the valence band maximum are listed in table 1. These indirect band gaps show a nearly linear increase with applied pressure. The pressure coefficient is determined when we increase the pressure, that is, from the linear region of the energy gap versus pressure plot. Our calculations yield the pressure coefficient of the smallest indirect band gap for rock-salt AlN as 31 meV GPa^{-1}, which compares with the value for wurtzite AlN, 36 meV GPa^{-1} [16]. In the case of rock-salt AlN corresponding to the experimental lattice constant 4.241 Å, the band gap is calculated to be 4.23 eV using the sX-LDA method.

For the energy bands obtained, the directionally averaged effective mass at the conduction band edges is 0.54. The relatively small electron effective mass suggests potential applications as a wide gap semiconductor. In contrast, the uppermost valence bands are flat, suggesting large hole effective masses, which should result in some unusual transport properties for p-type semiconductors. Furthermore, the pressure induced structural phase transition with changes in symmetry may lead to different selection rules, which together with the altered density and band hybridization may lead to some unusual optical properties and potential applications [17]. This is the main reason for us investigating the optical properties of rock-salt AlN in detail.

We now consider the relative functions of optical properties for rock-salt AlN. The dielectric function $\varepsilon(\omega)$ can be used to describe the linear response of the system to electromagnetic radiation, which relates to the interaction of photons with electrons [18]. Its imaginary part $\varepsilon_2(\omega)$ can be given by calculating the momentum matrix elements connecting the occupied and unoccupied wavefunctions within selection rules, and its real part $\varepsilon_1(\omega)$ can be derived from $\varepsilon_2(\omega)$ according to the Kramers–Kronig relationship. The dielectric function

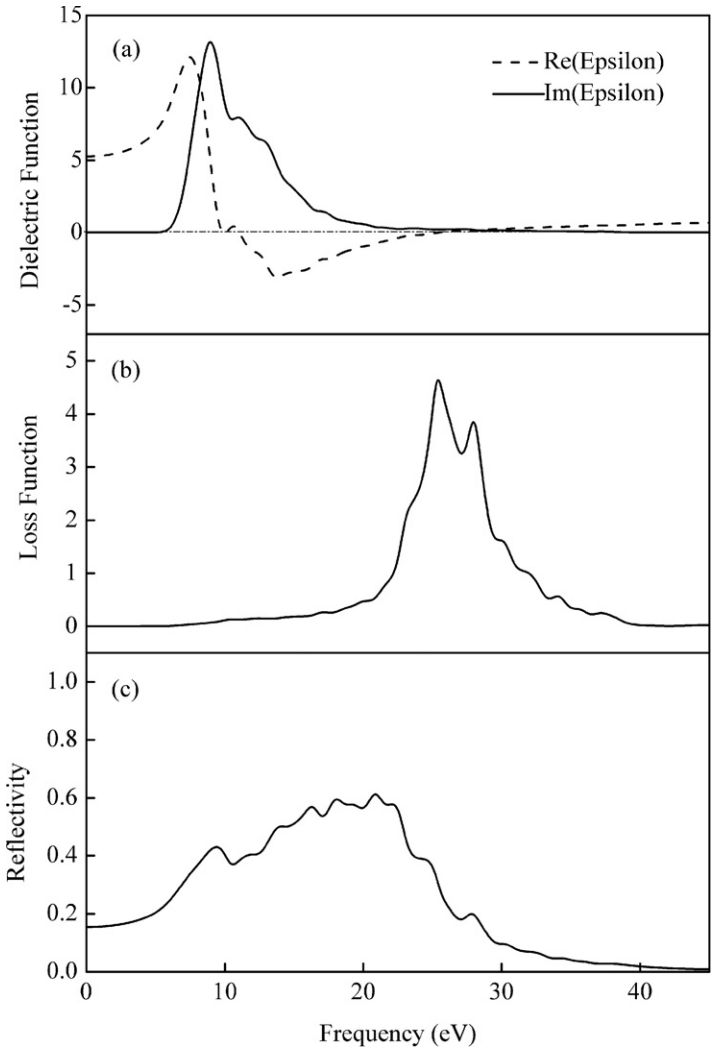

Figure 2. Optical properties of rock-salt AlN: (a) dielectric function: dashed and solid lines represent the real and imaginary parts respectively; (b) energy-loss function; (c) reflectivity.

curves as functions of the photon energy are displayed in figure 2(a) in the range of 0–45 eV, where the solid line and dashed line represent the real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$, respectively. The real part exhibits a peak at 7.5 eV due to interband transitions that originate from the X point at the top of the valence band to the bottom of the conduction band and reduces to a minimum at 10 eV subsequently. For the imaginary part of the dielectric function, the absorption starts at about 4.5 eV, which is related to the minimum band gap at the X point, corresponding to the transition Γ_{15}^{v}–X_1^c. The prominent peak at about 8.9 eV mainly relates to the interband transition L_3^v–W_1^c, and is followed by two weak humps at about 11 and 13 eV.

From the real and imaginary parts of the complex dielectric response function, related functions such as the reflectivity and energy-loss function can easily be obtained. The electron energy-loss function, which is the imaginary part of the reciprocal of the complex dielectric function, is displayed in figure 2(b). This function is usually large at the plasmon

energy position corresponding to $\varepsilon_1(\omega) = 0$, provided $\varepsilon_2(\omega)$ is reasonably smooth in these regions [19]. Therefore rock-salt AlN has a plasmon peak at 28 eV. Finally, we have shown in figure 2(c) the reflectivity spectrum, which drops off to zero at frequencies above the plasma frequency. This probably indicates that the material becomes transparent for frequencies above 28 eV.

4. Conclusion

In conclusion, we present a detailed study on the electronic and optical properties of rock-salt AlN together with the pressure coefficients of its band gaps. The band gap value and small electron effective mass obtained suggest that the rock-salt AlN is a wide gap indirect semiconductor. From the band structure, we calculated the dielectric function, reflectivity and energy-loss function. The relations of the optical properties to the interband transitions are also elucidated. The band gap can be controlled by tuning its lattice constant, which is shown to be feasible in experiments; this makes this material system very suitable for electronics applications.

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