Optical and vibrational properties of $2H$-, $4H$-, and $6H$-AlN: First-principle calculations

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The optical and vibrational properties of $2H$-, $4H$-, and $6H$-AlN are studied based on the ab initio pseudopotential density functional theory. Three polymorphs have similar electronic and optical properties implying that $4H$- and $6H$-AlN are also of importance to optoelectronics. Infrared spectra of the three polymorphs show two main modes at 660 and 690 cm$^{-1}$ and an additional mode at 570 cm$^{-1}$ can only be observed from $4H$- and $6H$-AlN. The Raman spectra of $4H$- and $6H$-AlN show more active modes than that of $2H$-AlN. These infrared and Raman features can be used as the fingerprints to distinguish the three polymorphs. © 2009 American Institute of Physics.

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I. INTRODUCTION

Recently, group-III nitride semiconductors (GaN, AlN) with nonpolar growth have attracted much attention from the perspective of high-efficiency light-emitting devices (LEDs) due to elimination of unfavorable effects in heterostructures.¹ In particular, AlN and related alloys are being developed for devices that emit at deep-ultraviolet wavelengths.² In order to eliminate unfavorable defects in high-quality AlN, several groups have paid their attention on nonpolar growth of AlN on various substrates. In typical chemical vapor deposition, the produced AlN has a polycrystalline structure which is not suitable for LEDs. Recently, Horita et al.³,⁴ synthesized high-quality nonpolar 4H-AlN on 4H-SiC by molecular beam epitaxy (MBE). 6H-AlN has also been produced on the $M$-plane of SiC by plasma-assisted MBE.⁵ Since 4H- and 6H-AlN are two new materials, their optical properties have not been investigated in details. The optical properties of high pressure phases of AlN (zinc blende and rocksalt) have been reported.⁶,⁷ Liu and Ni⁸ and Kobayashi and Komatsu⁹ calculated the electronic properties of $4H$- and $6H$-AlN and revealed that they belong to wide band gap semiconductors (band gap >4 eV). However, the optical properties of $4H$- and $6H$-AlN have not been determined in detailed either by experiments or theory.

In experiments,³⁻⁵ x-ray diffraction (XRD) is frequently used to distinguish different phases in $4H$- and $6H$-AlN. However, due to similar structures in the three AlN polymorphs, the XRD patterns of $4H$- and $6H$-AlN are quite similar to that of $2H$-AlN with the exception of only a small difference in the full width at half maximum (FWHM).³⁻⁵ Therefore, XRD is not a good means to clearly discern the three polymorphs of AlN. As standard and sensitive techniques in the identification of phase structures, infrared (IR) and Raman scattering have been widely used to distinguish SiC polymorphs which have more than 150 different structures. On account of the similar structural features between AlN and SiC, we believe that IR and Raman scattering can be effective in identifying $2H$-, $4H$-, and $6H$-AlN. In fact, the IR and Raman properties of $2H$-AlN have been previously studied¹⁰⁻¹² but both experimental and theoretical studies on $4H$-, and $6H$-AlN have not been carried out so far.

In this work, we theoretically study the optical properties including the dielectric function and absorption spectra, together with the IR and Raman properties of $2H$-, $4H$-, and $6H$-AlN, by first principle calculations. The Perdew–Burke–Eruzerhof generalized gradient approximation method¹³ implanted in the CASTEP code¹⁴ is employed to describe the exchange and correlation potentials. The ionic potentials are calculated with PWSCF (Ref. 15) code within the framework of the density functional perturbation theory.¹⁶,¹⁷ Vibrational frequencies can be efficiently calculated by the first-order response.¹⁷ IR absorption intensities are described in terms of a dynamical matrix and Born effective charges,¹⁷ and peak intensity of the nonresonant Stocks Raman spectrum can be predicted under the Placzek approximation.¹⁸

II. RESULTS AND DISCUSSIONS

The optimized lattice constants of $a$ and $c$ of $2H$- (3.07 and 4.94 Å), $4H$- (3.07 and 9.95 Å), and $6H$-AlN (3.07 and 14.89 Å) are consistent with the calculated and experimental results in Ref. 9 and references therein (within approximately 2%). The larger lattice constants, $c$, of $4H$- and $6H$-AlN compared to that of the $2H$ phase result in additional XRD reflections responsible to the widened FWHM observed in experiments.³⁻⁵ Our calculated band gap of $6H$-AlN...
(ABCBCB) is direct (Γ–Γ) with a value of 4.26 eV which is different from the calculated indirect (Γ–L) band gap of about 4.06 eV. The inconsistence in the band gap of 6H-AlN may be due to differences in the optimized structures and the pseudopotential used in the calculation. The calculated indirect (Γ–M) band gap, 4.15 eV, of 4H-AlN is a bit larger than 3.95 eV reported previously. The calculated band gaps of 4H- and 6H-AlN are close to that of 2H-AlN. The band gaps of 4H- and 6H-AlN are determined to be about 6 eV.

The imaginary part of the dielectric function \( \varepsilon_2(\omega) \) is a pendent of the optical properties for any material. The real part \( \varepsilon_1(\omega) \) can be derived from \( \varepsilon_2(\omega) \) by the Kramer–Kronig relationship. All the other optical constants such as absorption coefficient \( \alpha(\omega) \), reflectivity \( R(\omega) \), and electron energy loss \( \Im[\varepsilon(\omega)] \) can be deduced from \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \). Figure 1 shows that \( \varepsilon_2(\omega) \) of 2H-, 4H-, and 6H-AlN have linear polarization along the [001] and [110] directions ranging from 0 to 20 eV, respectively. It can be seen that the spectra of the three polymorphs are almost identical and can be attributed to their similar electronic structure. In the case of [110] polarization, the \( \varepsilon_2 \) spectra have two main peaks at 8.0 and 12.4 eV, whereas those of [001] polarizations have three main peaks at 7.4, 10.4, and 12.4 eV. In addition, the intensities of \( \varepsilon_2 \) along [001] polarization are almost half of those along [110] polarization.

Figure 2 shows \( \varepsilon_1(\omega) \) and \( \alpha(\omega) \) of 4H-AlN with polarizations along the [001] and [110] directions. The dielectric constants \( \varepsilon_1(\infty) \) along [001] and [110] polarizations are \(~5.0\) and 8.0, respectively. According to \( \varepsilon_1(\omega) \), it can be found that 4H-AlN will become metal-like when the photon energy is larger than 12 eV. The absorption spectrum \( \alpha(\omega) \) shows a main peak at 13.3 eV and its left shoulder has a peak at 8.4 eV for photon with [110] polarization and has two peaks at 8.4 and 10.2 eV for photon with [001] polarization. These results are consistent with our previous studies on 2H-AlN. The calculated optical properties \( \varepsilon_2(\omega), \varepsilon_1(\omega), \) and \( \alpha(\omega) \) suggest that the three polymorphs are anisotropic crystals and exhibit some differences in the low energy region.

Because the primitive cell of 2H-AlN (P6\(_{3}mc, \ C_{6v}, \ Z = 2\) contains four atoms, there are 12 phonon modes at Γ point, including three acoustic modes (\( A_{1}+E_{1} \)) and nine optical modes (\( A_{1}+2B+2E_{2} \)). The optical modes 2\( B \) are Raman active, optical modes 2\( E_{2} \) are Raman active (unpolarized), and \( A_{1}+E_{1} \) are both IR and Raman active (polarized). In 4H-AlN (P\(_{6}mnc, \ C_{6v}, \ Z = 4\) ), there are 24 phonon modes, including acoustic modes (\( A_{1}+E_{1} \)). Raman inactive optical modes 4\( B \), Raman active unpolarized optical modes 4\( E_{2} \), and both IR and Raman active polarized modes 3\( A_{1}+3E_{1} \). Since 6H-AlN (ABCBCB) belongs to the P\(_{3}m1\) group (\( C_{3v}, \ Z = 6\) ), there are 33 optical modes (11\( E_{1}+11A_{1} \)), which are all IR and Raman active. Figure 3 depicts the experimental and calculated IR spectra of 2H-, 4H-, and 6H-AlN. Previous experiments have shown that the IR spectrum of 2H-AlN has two main modes at 616 (\( A_{1} \)) and 676 cm\(^{-1} \) (\( E_{1} \)). The calculated IR spectrum of 2H-AlN has two modes at 589 (\( A_{1} \)) and 645 cm\(^{-1} \) (\( E_{1} \)), which are very close to the experimental values. The calculated IR spectra of 4H- and 6H-AlN show two main modes, (618, 648 cm\(^{-1} \))\(_{4H} \) and (398, 612 cm\(^{-1} \))\(_{6H} \). The \( A_{1} \) mode frequency of 4H-AlN has a blueshift of \(~20\) cm\(^{-1} \) compared to those of 2H-AlN, while the \( E_{1} \) mode has almost the same frequency. The circle with

FIG. 1. Imaginary parts of the dielectric functions \( \varepsilon_2(\omega) \) of 2H-, 4H-, and 6H-AlN.

FIG. 2. Real parts of the dielectric function \( \varepsilon_1(\omega) \) and absorption coefficient \( \alpha(\omega) \) of 4H-AlN with the linear polarization along the [001] and [110] directions.

FIG. 3. The experimental IR spectrum (a) of 2H-AlN, together with the calculated IR spectra of 2H- (b), 4H- (c), and 6H-AlN (d). The circle with arrow indicates IR active mode with small intensity.
arrow in Fig. 3 indicates another small vibration mode ($A_1$) at ~522 cm$^{-1}$ that is absent in the IR spectrum of 2H-AIN. Similar to 4H-AIN, 6H-AIN has an additional $A_1$ mode at 537 cm$^{-1}$.

The calculated and experimental Raman active mode frequencies of 2H-, 4H-, and 6H-AIN are listed in Table I. It is known that the LO mode is different from the TO mode because the dipole moment originating from the former can induce a macroscopic electric field parallel to the wave vector resulting in LO/TO splitting. In our calculation, we impose LO/TO splitting in the Raman polarized active modes of the three polymorphs, and so we can compare the modes with the experimental results. The Raman active polarized modes ($A_1, E_1$) of 2H-AIN are split in the experiments. The calculated Raman modes of 2H-AIN are consistent with the theoretical Raman modes $[A_1(\text{TO}), E_1(\text{TO}), E_2]$. 4H-AIN has 10 Raman active modes (3$A_1+3E_1+4E_2$) and 6H-AIN ($P3m1$) has 22 Raman active modes ($11E_1,11A_1$).

The calculated Raman spectra of 2H-, 4H-, and 6H-AIN together with the experimental Raman spectrum of 2H-AIN are shown in Fig. 4. The peak intensities and locations of calculated and experimental Raman active modes are similar except for the $E_2$ mode at 250 cm$^{-1}$. Though 4H-AIN has two unpolarized modes ($2E_2$) below 190 cm$^{-1}$, their intensities are so feeble that they cannot be seen in Fig. 4. Comparing with 2H-AIN, there are two additional $A_1$ modes at 522 and 729 cm$^{-1}$ for 4H-AIN, and another $A_1$ and $E_1$ modes with large LO/TO splitting have a little blue shift. In 6H-AIN, the $E_2(\text{TO})$ mode at 612 cm$^{-1}$ and $E_2(\text{LO})$ mode at 870 cm$^{-1}$ have strong intensities and the $A_1$ mode splits in the range of 400–725 cm$^{-1}$. From Fig. 4(d) we can find that there are two modes ($A_1:110$ cm$^{-1}$, and $E:165$ cm$^{-1}$) below 200 cm$^{-1}$ these Raman spectral features obtained above provide a possibility to distinguish the three polymorphs. Here, we should stress that when comparing our results directly with the experimental values, it should be done carefully because our calculation is carried out in the absence of taking account of temperature influence to the Raman intensity.

III. CONCLUSION

We have theoretically investigated the optical and vibrational properties of 2H-, 4H-, and 6H-AIN based on density functional calculation. The electronic and optical properties of the three polymorphs present similar features, implying that 4H- and 6H-AIN have the same importance as 2H-AIN in optoelectronics. IR transmittance spectra of the three polymorphs indicate that the two main vibrational modes of 4H-AIN have a blue shift compared to that of 2H-AIN, and the $A_1$ mode of 6H-AIN has a red shift to 398 cm$^{-1}$ compared with that of 2H-AIN. In addition, 4H- and 6H-AIN have another $A_1$ mode located at around 530 cm$^{-1}$ with feeble intensity. The calculated Raman active modes of the three polymorphs show different features below 200 cm$^{-1}$ and in the range of 300–600 cm$^{-1}$, suggesting that Raman scattering is a sensitive technique to distinguish different polymorphs observed in experiments.

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