Raman tensor of AlN bulk single crystal

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Received October 28, 2014; revised December 17, 2014; accepted December 17, 2014; posted January 7, 2015 (Doc. ID 225675); published March 17, 2015

The angle dependence of optical phonon modes of an AlN bulk single crystal from the m-plane (1100) and c-plane (0001) surfaces, respectively, is investigated by polarized Raman spectroscopy in a backscattering configuration at room temperature. Corresponding Raman selection rules are derived according to measured scattering geometries to illustrate the angle dependence. The angle-dependent intensities of phonon modes are discussed and compared to theoretical scattering intensities, yielding the Raman tensor elements of A1(LO), E1(LO), and A1(TO) phonon modes and the relative phase difference between the two complex elements of A1(TO). Furthermore, the Raman tensor of wurtzite AlN is compared with that of wurtzite ZnO reported in previous work, revealing the intrinsic differences of lattice vibration dynamics between AlN and ZnO.

1. INTRODUCTION

AlN is a promising semiconductor for vacuum- and deep-ultraviolet application [1–2], due to its remarkable physical properties, including an ultrawide band gap of 6.2 eV, superior radiation resistance, high chemical and thermal stability, and high melting temperature [4,5]. Investigating the vibration properties of phonons in AlN is very important for AlN-based devices, because AlN is a polar semiconductor, which will cause substantial joule heating under high current densities [6,7], mainly resulting from the Fröhlich electron–phonon interaction [8]. Raman spectroscopy is a powerful technique to probe the vibrational mode behavior of materials, providing information about the symmetry of the vibrational mode, the crystal structure and quality, and the lattice defect. The earliest study on Raman spectra of wurtzite AlN was published in the 1960s and determined the fundamental vibrational modes of AlN crystals [9]. Since then, Raman spectra of AlN have been studied intensively [10–19]. However, some problems remain unsolved, such as the determination of the Raman tensor.

In this work, we present the angle-dependent polarized Raman spectra by parameterizing the incoming and scattered polarization vectors from a hexagonal AlN bulk single crystal and compare them with calculated Raman intensities extracted from Raman selection rules. Such a process gives a full mode assignment and determines the Raman tensor elements of wurtzite AlN. Moreover, the differences between the Raman tensor of wurtzite AlN and that of ZnO are particularized and discussed in detail.

Typically, AlN and ZnO single crystals both have wurtzite symmetry, which belongs to the space group C6v (P63mc). The differences between AlN and ZnO in spontaneous polarization, piezoelectric constants [20], radiation anisotropy [21–24], etc., lead them to different applications in the field of optoelectronics. This work provides new insight into the intrinsic difference of lattice vibration dynamics between AlN and ZnO materials.

2. EXPERIMENTAL DETAILS

A hexagonal prismatic AlN bulk single crystal (see inset in Fig. 1) was grown by the physical vapor transport (PVT) method at 2150°C in a nitrogen environment using a tungsten crucible [25]. The crystal structure was analyzed by high-resolution x-ray diffractometry (HR-XRD) (Rigaku, TTRAX III, Cu Kα, 18 W). All diffraction peaks can be indexed to a relaxed wurtzite-type AlN structure. Micro-Raman measurements were carried out via a Renishaw Raman spectrometer (inVia Reflex) with spectral resolution of 1.5 cm⁻¹, using a 532 nm laser (Samba CW DPS) with a power of 3 mW for exciting light. The 532 nm laser was focused on the m- and c-plane surfaces of the AlN crystal, respectively, via a 50× objective. Raman scattered light was collected in backscattering geometry, and was then dispersed by a spectrometer with a 250 mm focal length, and finely detected by a CCD detector.

To enable the measurement part of the scattered light with polarization parallel (or perpendicular) to that of incoming light, a rotatable polarizer was inserted in the scattering light path. A microscope stage rotated around the axis along the direction of the incoming laser was used to observe angle-dependent Raman spectra. The configuration of our experiment is presented in Fig. 1. zy=xz is congruous with the crystal axes of AlN crystal where the z axis is parallel to the c axis. As
incident light is set along the $z$ axis, the AlN sample can be rotated around the $z$ axis, and the rotation angle $\omega$ is between the polarization vector of incident light and the $x$ axis; as incident light is set along the $x$ axis, the AlN sample can be rotated around the $x$ axis and the rotation angle $\theta$ is between the polarization vector of incident light and the $z$ axis.

3. RAMAN SELECTION RULES

In a wurtzite AlN crystal structure in which a per primitive unit cell contains four atoms, there are nine optical phonon modes that reduce to 1 $A_1$, 2 $B_1$, 1 $E_1$, and 2 $E_2$ modes at the center of the Brillouin zone. According to group theory, both $A_1$ and $E_1$ modes are Raman- and infrared-active, where $A_1$ is polarized along the $z$ direction, while $E_1$ is polarized in the $xy$ plane. Due to bond polarity, Raman phonons with $A_1$ and $E_1$ symmetry exhibit frequency shifts. The $E_2$ mode, being twofold degenerate, is only Raman-active. The two $B_1$ modes are silent modes [26].

For the Raman-active optical phonon modes, the intensity $I$ of Raman scattering is given by [27,28]

$$I \sim |e_s \cdot R \cdot e_i|^2,$$

where $e_i$ and $e_s$ represent the unit polarization vectors of incident and scattered light, respectively. $R$ is the complex second-rank Raman tensor [29], which is represented by a complex $3 \times 3$ matrix. This matrix describes the properties of a phonon mode with respect to Raman scattering. The Raman tensor of Raman-active $A_1$, $E_1$, and $E_2$ modes in a wurtzite material is given by [27,28]

$$R[A_1] = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},$$

$$R[E_1] = \begin{bmatrix} 0 & 0 & -c \\ 0 & c & 0 \\ -c & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & -|e|e^{i\phi_c} \\ 0 & |e|e^{i\phi_c} & 0 \\ -|e|e^{i\phi_c} & 0 & 0 \end{bmatrix},$$

$$R[E_2] = \begin{bmatrix} d & d & 0 \\ d & -d & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} |d|e^{i\phi_d} & |d|e^{i\phi_d} & 0 \\ |d|e^{i\phi_d} & -|d|e^{i\phi_d} & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

where $a, b, c,$ and $d$ denote the Raman tensor elements, and $\phi_a, \phi_c, \phi_d,$ and $\phi_b$ denote the complex phase of the Raman tensor elements. For Raman backscattering measurements on the $m$-plane surface, the polarization vectors of incident and scattering light referred to the hexagonal axes can be written as

$$e_i = \begin{bmatrix} 0 \\ \sin(\theta) \\ \cos(\theta) \end{bmatrix} \quad \text{and} \quad e_s = \begin{bmatrix} 0 \\ \cos(\omega_\theta) \\ \sin(\omega_\theta) \end{bmatrix},$$

where $\omega_\theta$ represents the angle between the $x$ axis of the sample and the polarization vector of the incident (scattered) light. For Raman backscattering measurements on the $c$-plane surface, the polarization vectors of incident and scattering light referred to the hexagonal axes can be written as

$$e_i = \begin{bmatrix} \cos(\omega) \\ \sin(\omega) \\ 0 \end{bmatrix} \quad \text{and} \quad e_s = \begin{bmatrix} \cos(\omega_\theta) \\ \sin(\omega_\theta) \\ 0 \end{bmatrix},$$

where $\omega_\omega(\omega_\theta)$ represents the angle between the $x$ axis of the sample and the polarization vector of the incident (scattered) light. Here, we have discussed the parallel ($e_i \parallel e_s$, e.g., $\theta_s = \omega$) and perpendicular ($e_i \perp e_s$, e.g., $\theta_s = \omega + \pi/2$) scattering configurations. For these configurations, according to Eq. (1), the Raman intensity can be expressed in the following cases.

A. Raman Backscattering Measurements on $m$-Plane Surface

For $e_i \parallel e_s$ scattering configurations,

$$I^{\parallel}_{A_1}(\theta) \sim |a|^2 \sin^4 \theta + |b|^2 \cos^4 \theta + \frac{1}{2} |a||b| \sin^2(2\theta) \cos(\phi_{a-b}).$$

(7)

$$I^{\parallel}_{E_1}(\theta) \sim \frac{|c|^2}{2} \sin^2(2\theta),$$

(8)

$$I^{\parallel}_{E_2}(\theta) \sim |d|^2 \cos^4 \theta$$

(9)

with $\phi_{a-b} = \phi_a - \phi_b$.

For $e_i \perp e_s$ scattering configurations,

$$I^{\perp}_{A_1}(\theta) \sim \frac{1}{4} |a|^2 + |b|^2 - 2|a||b| \cos(\phi_{a-b}) \sin^2(2\theta).$$

(10)

$$I^{\perp}_{E_1}(\theta) \sim |c|^2 \cos^2(2\theta).$$

(11)
$$I_{E_2}^1(\theta) \sim \frac{|d|^2}{4} \sin^2(2\theta).$$  \hfill (12) 

B. Raman Backscattering Measurements on c-Plane Surface

For $e||e_t$ scattering configurations,

$$I_{E_{11}}^1(\theta) \sim |a|^2.$$  \hfill (13)

$$I_{E_{12}}^1(\theta) \sim 0.$$  \hfill (14)

$$I_{E_{13}}^1(\theta) \sim |d|^2.$$  \hfill (15)

For $e_t||e_t$ scattering configurations,

$$I_{E_{11}}^2(\theta) \sim 0,$$  \hfill (16)

$$I_{E_{12}}^2(\theta) \sim 0,$$  \hfill (17)

$$I_{E_{13}}^2(\theta) \sim |d|^2.$$  \hfill (18)

It should be noted that the phase difference $\theta_{a-b}$ between the Raman tensor elements $a$ and $b$ has a significant influence on the Raman scattering intensities of the $A_1$ mode. Figure 2 displays $I_{E_1}^1(\theta)$ for one particular choice of values $|a|$ and $|c|$ and several different phase angles $\theta_{a-b}$. It should be noted that the function $I_{E_1}^1(\theta)$ is unique for any particular value of $|a|$, $|b|$, and $\theta_{a-b}$ and allows an unambiguous value of these three parameters, for instance, when the value of $I_{E_1}^1(\theta)$ at $\theta = 0^\circ$ and $90^\circ$ is given by $|a|$ and $|b|$, respectively. This is not true for $I_{E_1}^1(\theta)$, by which different choices of $|a|$, $|b|$, and $\theta_{a-b}$ may produce identical line shapes. Nevertheless, $I_{E_1}^1(\theta)$ is still useful to check the parameters obtained from a determination of $I_{E_1}^1(\theta)$.

4. RESULTS AND DISCUSSION

A. Angle-Dependent Polarized Raman Spectra of AlN

In Fig. 3(a), the Raman spectra from the $m$-plane surface of the AlN sample in a range of 560–720 cm$^{-1}$ are shown for different rotation angles $\theta$ increasing from $0^\circ$ to $180^\circ$ with a step of $5^\circ$ for parallel polarization vectors of the incoming laser and the scattered light $|x|z) |x|y) |z|z)$ and perpendicular $|x|z) |x|y) |z|z)$ polarization vectors of the incoming laser and the scattered light, respectively. (c) and (d) record the angle-dependent Raman spectra from the $c$-plane of the AlN sample for parallel $|z|z) |y) |z|z)$ and perpendicular $|z|z) |y) |z|z)$ polarization vectors, respectively. For clarity, the ordinates in (b) and (d) have been magnified eight and four times, respectively, compared to those in (c) and (d).

Fig. 3. (a) and (b) show the Raman spectra from the $m$-plane surface of the AlN sample for different rotation angles, shifted by a constant amount on the $x$ and $y$ axes, for parallel $|x|z) |x|y) |z|z)$ and perpendicular $|x|z) |x|y) |z|z)$ polarization vectors of the incoming laser and the scattered light, respectively. (c) and (d) record the angle-dependent Raman spectra from the $c$-plane of the AlN sample for parallel $|z|z) |y) |z|z)$ and perpendicular $|z|z) |y) |z|z)$ polarization vectors, respectively.

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than 3.8 cm\(^{-1}\) located at around 657, and 891 cm\(^{-1}\), which are constant angle dependent, are ascribed to phonon modes E\(_{2}^{\gamma}\) and A\(_{1}^{\gamma}\) (LO), respectively. The constant angle dependence of two such allowed phonon modes is in agreement with the calculated selection rules as Eqs. (13) and (15). The low intensity of the A\(_{1}^{\gamma}\) (LO) signal observable in Fig. 3(c), according to Callender et al., is due to suppression caused by destructive interference of the deformation potential with the Fröhlich contributions [30]. The constant angle-dependent vibration behavior of such Raman spectra scattering from the c-plane surface shown in Figs. 3(c) and 3(d) is obviously different from that scattering from the m-plane surface shown in Figs. 3(a) and 3(b), which is attributed to the isotropic arrangement of atoms in the c-plane. In Fig. 3(d), only the E\(_{2}^{\gamma}\) mode with FWHM less than 3.8 cm\(^{-1}\) located at around 657 cm\(^{-1}\) is allowed and is in agreement with the calculated selection rules as Eqs. (16)–(18). In addition, it is worth noting that the E\(_{1}^{\gamma}\) (LO) phonon mode does not appear in Figs. 3(c) and 3(d), because this phonon mode is forbidden in the back-scattering geometry here. Sander et al. suggested that a weak signal of the E\(_{1}^{\gamma}\) (LO) mode would occur when the measured geometry deviates from an ideal backscattering geometry [26]. The unallowed E\(_{j}^{\gamma}\) (LO) mode reveals that deviations of our measured backscattering geometry are negligible.

B. Raman Tensor of AlN

The Raman intensities of the A\(_{1}^{\gamma}\) (TO), E\(_{1}^{\gamma}\) (TO), E\(_{2}^{\gamma}\), and A\(_{1}^{\gamma}\) (LO) phonon modes for parallel and perpendicular polarization geometries, as shown in Figs. 3(a)–3(d), are extracted from Lorentzian fitting. The fitting results, which are plotted versus the rotation angle for the two polarization geometries, are shown in Figs. 4(a)–4(b) as squares. The error bars of fitting results are too small to be clearly illustrated in the figures. To determine the Raman tensor elements, the angle variations are fitted with the functions calculated in Section 3 using least-squares fit procedures. The best fitting curves shown in Fig. 4 are in agreement with experimental data. The ratios of the fit parameters yield the relative values of the Raman tensor elements for AlN, which are summarized in Table 1. As a comparison, the relative values of the Raman tensor elements for ZnO crystal are also listed in Table 1, and are taken from Ref. [26].

AlN and ZnO, both of which are advanced wide-band-gap semiconductor compounds, can be potentially applied in the optoelectronic field, and they have the same wurtzite symmetry that belongs to the space group C\(_{6h}\) (P\(_{6}_{3}\)mc). During Raman scattering, six modes (2A\(_{g}\) + 2E\(_{g}\) + 2E\(_{u}\)) for wurtzite AlN and ZnO are active. Among these modes, the A\(_{1}\) branch is polar mode polarized in the \(z\) direction. In doped semiconductors, the A\(_{1}\) branch can influence the electronic transport properties due to the resonant coupling of polar phonons and plasmons (free carrier systems) [31]. As shown in Table 1, the ratio of \(|a|/|d|\) for the A\(_{1}\) (LO) phonon of AlN is much smaller than that for A\(_{1}\) (TO), which is mainly attributed to A\(_{1}\) (LO) suppression caused by destructive interference of the deformation potential with the Fröhlich contributions [30]. Such a small ratio of \(|a|/|d|\) for A\(_{1}\) (LO) is also observed in ZnO as shown in Table 1. Therefore, it is believed that the Raman tensor elements of \(|a|\) and \(|b|\) extracted from the A\(_{1}\) (TO) mode are more accurate.

For A\(_{1}\) (TO) of AlN, the amplitude of \(|a|\) is about twice as strong as that of \(|d|\). However, this is different from the situation of ZnO whose amplitude of \(|a|\) is about half that of \(|d|\). Determination of the ratio of \(|a|/|d|\) is necessary since it reflects the Raman tensor anisotropy of the polar A\(_{1}\) mode. The \(|a|/|b|\) ratio of AlN is up to 2.5, while that of ZnO is only 1.0. The large \(|a|/|b|\) ratio of AlN leads to an intensity ratio \(I_{A_{1}^{\gamma}(TO)}/I_{A_{1}^{\gamma}(TO)}^{|a|} \) [e.g., \(I(90\degree)/I(0\degree)\)] of Fig. 4(a) of more than 6.5, as we reported previously [32], while the \(I_{A_{1}^{\gamma}(TO)}/I_{A_{1}^{\gamma}(TO)}^{|b|}\) of ZnO is only 1.1 [26], where the superscripts represent the polarization of incoming and scattering light. Such results reveal that the Raman tensor of the A\(_{1}\) mode in AlN has strong anisotropy, which could be caused by its large difference in bond polarity.

As shown in Table 1, the phase difference \(\varphi_{a-b}\) between elements \(|a|\) and \(|b|\) of AlN is 91.24\(^\circ\) and 91.18\(^\circ\) for parallel and cross-polarized scattering geometries. The phase difference \(\varphi_{a-b}\) of AlN is still close to that of ZnO, despite the fact that the anisotropy ratios of \(|a|/|b|\) for AlN and ZnO differ by a factor of about 1.5. This implies that the origin of the anisotropy ratio should differ from that of the phase difference for the A\(_{1}\) Raman tensor elements in a wurtzite crystal.
While this problem is not addressed here, it would be interesting to repeat the present Raman scattering measurement on other materials with wurtzite structure to determine the relationship between the anisotropy ratio and the phase difference.

Figures 4(a) and 4(b) show the angle-independent intensity of $A_{1}(LO)$ and $E_{2}$ phonon modes, recording from the $c$-plane surface of the AlN sample for parallel and crossed polarization vectors of the incoming laser and the scattered light, respectively. The relative values of the Raman tensor elements for the $c$-plane AlN can be extracted by dividing the square of the mean values of the fitted areas, which are also summarized in Table 1.

The second-rank Raman tensor $R$ describes the characteristics of a phonon with respect to Raman scattering, which is an entity proportional to the Raman susceptibility [28]

$$\frac{\partial \chi}{\partial \varepsilon} = V_{c}^{1/2}\sum_{i \text{unit-cell}} \frac{\partial \chi}{\partial u_{i}} M_{i}^{1/2} \varepsilon_{i},$$  

(19)

where $\chi$ denotes the polarizability tensor (the dipole moment induced by an unit incident electric field), $\xi$ denotes the nominal mode coordinate, $V_{c}$ denotes the volume of the primitive cell, $u_{i}$ and $M_{i}$ represent the static atomic displacement and the mass of atom $i$, and $\varepsilon_{i}$ is the eigenvector of the vibrational mode. In this work, we determined the Raman tensor of AlN using angle-dependent polarized Raman spectra. In addition, the Raman tensor can also be calculated by Eq. (19). However, such a first-principles calculation is too difficult to achieve. A semi-empirical method based on the concept of bond polarizabilities, which only depends on the band length $l$ of two neighboring ions, has been developed to estimate $\partial \chi / \partial u_{i}$ and successfully used to interpret the Raman spectra in semiconductors [33]. It is well known that the wurtzite-type polar crystals, such as AlN, GaN, and ZnO, have two polar bonds (in-plane bond and out-plane band) with different lengths [34]. We believe that the unique Raman scattering behaviors of AlN bulk single crystal are related to its bond polarizabilities.

5. CONCLUSION

The angle-dependent Raman spectra for the $m$-plane and $c$-plane surfaces of an AlN single crystal for parallel and crossed polarized scattering geometries at room temperature were presented and discussed. The variations of intensity for $A_{1}(TO)$, $E_{1}(TO)$, $A_{1}(LO)$, and $E_{2}$ modes versus rotation angle were calculated according to the Raman selection rules. The Raman tensor elements of such modes were determined by a combination of the experiment data and the calculated results. Moreover, the Raman tensor elements for $A_{1}(TO)$, $E_{1}(TO)$, $A_{1}(LO)$, and $E_{2}$ of AlN were compared with that of ZnO, and the differences of the Raman tensor between AlN and ZnO were demonstrated.

ACKNOWLEDGMENTS

This work was financially supported by the Special Program for the State Key Program of National Natural Science of China (No. 61136001) and the Major Research Plan of the National Natural Science Foundation of China (No. 91333207).

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