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Raman analysis of the *E*1 and *A*1 quasi-longitudinal optical and quasi-transverse optical modes in wurtzite AIN

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This article presents a study of the quasi-longitudinal optical and quasi-transverse optical modes in wurtzite AlN which originate from the interaction of phonons belonging to the A1 and E1 symmetry groups. In order to analyze the allowed quasi as well as pure Raman modes, the modes were observed in a rotating crystallographic coordinate system, and the Raman tensors of the wurtzite crystal structure were calculated as a function of the crystallographic rotation. The frequencies of the quasimodes of wurtzite AlN were also analyzed in terms of the interaction of the polar phonons with the long range electrostatic field model. The experimental values of the Raman frequencies of the quasiphonons concur with these expected from the model, implying that the long range electrostatic field dominates the short range forces for polar phonons in AlN. © 1999 American Institute of Physics. [S0021-8979(99)03407-6]

INTRODUCTION

Raman spectroscopy has proven to be a useful and informative tool in the investigation of semiconductors with the wurtzite (WZ) crystal structure, in particular in the investigation of material quality as well as in the study of phonon dynamics and interactions.¹⁻⁹ Due to the long range electrostatic field associated with the longitudinal optical (LO) phonons, various types of interactions are allowed in the WZ semiconductors, among them the phonon-plasmon coupling.³ Another is the possibility of interaction between polar modes belonging to different symmetry groups which result in the creation of new mixed-symmetry phonons referred to as quasimodes.¹ This article presents a study of the LO and transverse optical (TO) quasimodes in AlN crystallite which originate from the interaction of phonons belonging to the A1 and E1 symmetry groups; the study focuses on the mode-selection rules and mode-frequency calculations as well as on the Raman technique which enables observation of the modes.

The theory developed by Loudon formulates that in uniaxial materials the polar phonon characteristics may be affected via two interaction mechanisms: one due to the long range electrostatic field, and the other due to the short range field which exhibits the anisotropy of the vibrational force constants.¹⁰ The phonon dynamics and thus the Raman spectra depend on which of the two mechanisms is the dominant interaction.

For the case where the long range electrostatic field is the dominant mechanism, the interaction of the polar phonons with the long range electrostatic field may result in a significant frequency separation between the group of the TO phonons relative to that of the LO phonons, as is schematically depicted in Fig. 1(a). Moreover, the TO phonons belonging to a different symmetry are grouped together in a relatively narrow frequency range; the same holds for the LO phonons. One consequence of the dominant electrostatic field interaction is that the phonons exhibit nearly pure longitudinal or transverse character: essentially no mixing occurs between the transverse and the longitudinal atomic vibrations. The other consequence is that under certain propagation and polarization conditions, phonons of mixed A1 and E1 symmetry character exist and can be observed in the Raman spectra. These mixed symmetry modes are termed quasi-LO and -TO modes. The frequencies of such quasimodes are predicted by the theory to be between the values of the pure A1 and the pure E1 for each of the LO and the TO bands.

Alternatively, for the case where the short range interatomic forces are dominant, the LO–TO splitting will be small and in this case the TO and LO mode of each symmetry group will occur in a relatively narrow band as shown in Fig. 1(b). The theory predicts that the phonons will exhibit essentially pure symmetry character (either A1 or E1). A consequence is that under certain propagation conditions the phonons will exhibit mixing of the transverse and longitudinal vibrations for a given symmetry. These mixed LO–TO modes are termed quasi-E1 and -A1 modes. The frequencies of such quasimodes are predicted by the theory to be in bands between the values of the TO–LO modes of the pure A1 or E1 phonons.

In AlN the E1(TO) and A1(TO) Raman frequencies are grouped together in ~60 cm⁻¹ frequency range, the E1(LO)A1(LO) in ~20 cm⁻¹ range, and the LO–TO group splitting is ~220 cm⁻¹. The frequency scheme of AlN thus implies the dominance of the long range electrostatic force interaction. The mode mixing in AlN may occur if the propagation direction (q vector) of the quasipolar phonons, their polarization LO, and one of their two TOs, lie in the plane which

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FIG. 1. Raman frequency scheme and directions of phonon vibration for: (a) the case when the long range electrostatic field is the dominant interaction, and (b) when the anisotropy of the short range dominates the interaction.

spans between the *c* and the a_1 (or a_2) crystallographic axes.¹ This plane is referred as to the mixing plane. For example, the pure *A*1 phonon has a *c*-direction polarization while the pure *E*1 phonon is polarized in the basal plane; thus a quasiphonon with the *q* vector between the *c* and the a_1 axes would exhibit a mixed polarization of A_1-E_1 symmetry. When the *q* vector lies along the crystallographic axes or in the a_1-a_2 plane only pure phonons are observed in the spectra.

Arguello *et al.* investigated the long range electrostatic field interaction and the quasimodes in the WZ materials: ZnO, ZnS, and CdS.¹ In their study a frequency shift was observed for the quasimodes relative to that of the pure modes, in agreement with Loudons' theory. Filippidis *et al.* have carried out plane-wave pseudopotential calculations to investigate the optical modes in GaN and AlN;⁹ their model and experiment concerning the A1(TO) mode agree with that of Loudons'.¹⁰

In our study we investigate the behavior of the quasi-TO and the quasi-LO in AlN crystallite. We present calculations of the WZ Raman tensors as a function of rotation angle from which the allowed modes, pure and quasi, can be deduced and analyzed for different crystal orientations. The experimental values of the quasifrequencies agree well with those predicted by the phonon-electrostatic field interaction model. The motivation behind the present study was to gain information on the Raman frequencies from scattering geometries which are not along the crystallographic directions. As mentioned above, Raman spectroscopy has been successfully utilized in the characterization of the group III-nitrides semiconductors and has proven useful in studies of the stress state of films grown on the c axis. However for films grown on other crystallographic directions, a technique which potentially might minimize film-substrate interfacial stress, the contribution of the long range electrostatic field to the Raman shift has to be taken into consideration. This contribution has to be deconvoluted in order to isolate the Raman shift due to stress.



FIG. 2. A micrograph of the wurtzite AIN crystallite, size $\sim 500 \times 25 \times 25$ μ m. Along the *c* axis is the face of the (1010) plane, the face of the (0001) plane is at the base of the hexagonal crystallite.

EXPERIMENT

The micro-Raman scattering experiments were carried out at room temperature utilizing the 514.5 nm line of the ion argon laser and the J-Y U1000 scanning double monochromator. The spot size of the laser on the sample was $\sim 2 \ \mu m$



FIG. 3. The geometry of the experimental setup. The laboratory coordinate system is: *X*, *Y*, and *Z* (*X* is out of the paper plane). The crystal-rotating system is: *c*, a_1 , and a_2 (a_2 out of the paper plane coinciding with the *X* axis). *N* is the normal to the surface and coincides with the a_1 axis. The angle of rotation about the *X* axis is θ , while the angle of refraction and phonon propagation is β . The dashed line represents the propagation of the phonon with a *q* vector; the arrows represent its LO and TO components. The Raman spectra were acquired in a backscattering geometry from the *Y*. The inset to the figure describes the A1-E1 mixing of the LO and the TO components.

in diameter. The experimental error of the Raman peak position and the angle of rotation θ is ± 0.5 cm⁻¹, and $\pm 5^{\circ}$, respectively. The AlN crystallite, depicted in Fig. 2, was grown via the sublimation process and its size is ~500 $\times 25 \times 25 \ \mu m.^5$ In the Fig. 2, the face of the (1010) plane is along the *c* axis while the face of the (0001) plane is at the base of the hexagonal crystallite.⁵

RESULTS AND DISCUSSION

In this study we observed the AlN quasi-TO and -LO modes by rotating the crystallite relative to the laboratory coordinate system as schematically depicted in Fig. 3. In Fig. 3, the *X*, *Y*, and *Z* are the axes of the fixed coordinate laboratory system (where *X* is out of the paper plane), while the *c*, a_1 , and a_2 are the axes of the rotating coordinate system of the crystal (where a_2 is out of the paper plane and coincides with the *X* axis), and *N* is the normal to the crystallite

surface (and coincides with the a_1 axis). The AlN crystallite was rotated through an angle θ about the *X* axis such that the quasiphonon propagation direction, the *q* vector (**q**), as well as its LO and one of its two TO components lay in the mixing c- a_1 plane (the other TO is along the *X* axis). The micro-Raman spectra was acquired in a back scattering geometry from the *Y* axis for various values of θ .

In order to investigate the polarization conditions upon which the quasimodes appear in the spectra, the Raman tensors, R_{θ} of the rotating crystal (relative to a fixed *X*, *Y*, *Z* laboratory coordinate system) are calculated via the rotational transformation equation:¹¹

$$R_{\theta} = T_X R T_X^{-1}, \tag{1}$$

where T_X is the rotation matrix about the X axis.¹² The Raman tensors of the WZ structure take the form:

$$A1_{c}(\theta) = \begin{pmatrix} h & 0 & 0\\ 0 & h\cos^{2}\theta + b\sin^{2}\theta & b\sin\theta\cos\theta - h\sin\theta\cos\theta\\ 0 & b\sin\theta\cos\theta - h\sin\theta\cos\theta & h\sin^{2}\theta + b\cos^{2}\theta \end{pmatrix}$$

$$E1_{X}(\theta) = \begin{pmatrix} 0 & d\sin\theta & d\cos\theta \\ d\sin\theta & 0 & 0 \\ d\cos\theta & 0 & 0 \end{pmatrix}$$
$$E1_{a_{1}}(\theta) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2d\sin\theta\cos\theta & d(\cos^{2}\theta - \sin^{2}\theta) \\ 0 & d(\cos^{2}\theta - \sin^{2}\theta) & -2d\sin\theta\cos\theta \end{pmatrix}$$
(2)

$$E2(\theta) = \begin{pmatrix} 0 & f\cos\theta & -f\sin\theta\\ f\cos\theta & 0 & 0\\ -f\sin\theta & 0 & 0 \end{pmatrix}$$
$$E2(\theta) = \begin{pmatrix} f & 0 & 0\\ 0 & -f\cos^2\theta & f\cos\theta\sin\theta\\ 0 & f\cos\theta\sin\theta & -f\sin^2\theta \end{pmatrix}.$$

The tensors describe the in-crystal projections, due to the rotation, of the incident and scattered polarizations of the light. The group theory analysis indicates that the A1 is a nondegenerate mode and thus has a one matrix representation, while the E1 and E2 are both doubly degenerate modes and therefore each mode representation requires two matrices. The entries of each matrix, i.e., the constants h, b, d, and f, are related to the Raman cross section which determines the Raman intensity of each of the modes.¹³ Moreover, for each polar mode the direction of the polarization is indicated in the subscripts: A1 is polarized along the c axis while E1 is polarized along a_1 and a_2 , the latter which coincides with the X axis $(E1_X)$. The polarization direction of the polar modes, like the Raman tensors, can be expressed in terms of

the laboratory coordinate system; however, it is not necessary for the present study. For $\theta=0$ the crystal coordinate system coincides with that of the laboratory $(a_1=Y \text{ and } c=Z, \text{ see Fig. 3})$, and Eq. (2) takes the usual form.^{1,13}

For the first set of experiments we chose the Raman setup such that the incident light is polarized along the X axis and the scattered light has both X and Z polarization directions, expressed in Raman notation as:

$$Y(x_Z^X)\overline{Y}.$$

This choice of polarization implies that the XX and the XZcomponents of each of the Raman tensors will contribute a Raman signal provided they are not zero. Figure 4 presents the Raman spectra for this setup for rotations: $\theta = 0^{\circ}$, 35°, and 70°. Inspection of Eq. (2) indicates that the E2 mode should appear in the spectra since the XX and the XZ components of its tensors are not zero; our spectra display the E2 mode at 655 cm^{-1} . This mode is nonpolar and as such no change in frequency is expected as a function of the rotation. The XZ component of the $E1_X$ is nonzero, and although the q vector of the mode lies in the a-c mixing plane its polarization is not: it is in the X direction (TO component) and thus no symmetry mixing is expected. This analysis indicates that the spectra should exhibit the pure E1(TO) with no change of frequency upon rotation. The pure E1(TO) in our spectra is at 669 cm^{-1} and is independent of rotation.

Next we investigated the A1 mode which contributes a signal to the Raman spectra via the nonzero value of its XX tensor component. The pure A1 mode has solely c polarization; however, upon rotating the crystal quasimodes are created for which their TO and LO components have a



FIG. 4. The Raman spectra for rotation angle $\theta = 0^{\circ}$, 35°, and 70°. The pure A1(TO) is at 608 cm⁻¹, and the quasi-TO modes are at 614 and 620 cm⁻¹. All intensities are normalized to that of the E2 mode.

c-polarization component of A1 symmetry as well as an a_1 -polarization component of E1 symmetry. This situation is schematically depicted in the inset to Fig. 3. In Fig. 3, the TO component of the quasimode lies in the mixing plane and is composed of A1 and E1 polarization symmetry components; the quasi-TO mode will have mostly A1 symmetry for q vectors near the a axis and mostly E1 symmetry for q vectors near the c axis. The frequency of the quasi-TO, according to Loudons' theory, should be between the frequency of the pure A1(TO) mode and that of the pure E1(TO) mode. As can be seen in Fig. 4, the frequency of the A1(TO) mode shifts from its pure value at 608 cm⁻¹ toward that of the E1(TO) mode as a function of the rotation angle: for $\theta = 35^{\circ}$ the peak of the quasi-TO is at 614 cm⁻¹ and for θ =70° is at 620 cm⁻¹. The spectrum of θ =70° exhibits a small peak of the pure A1(TO) and is attributed to an internal reflection.

The frequencies of the quasi-TO can be calculated via the relation 1,10

$$\omega_{Q(\text{TO})}^2 = \omega_{E1(\text{TO})}^2 \cos^2(90 - \beta) + \omega_{A1(\text{TO})}^2 \sin^2(90 - \beta), \quad (3)$$

where β (see Fig. 3) is the propagation angle of the *q* vector of the quasiphonon (**q**) in the crystallite, and is related to the angle of rotation θ via Snell's law and the momentumconservation law of the Raman scattering effect as is discussed next. The conservation law states that in the scattering medium $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_S$, where \mathbf{k}_1 and \mathbf{k}_S are wave vectors of the incident and scattered photons, respectively.^{13,14} Thus, for our backscattering geometry the *q* vector lies along the



FIG. 5. The normalized Raman spectra of the quasi-LO modes for rotation angle θ =15°, 35°, and 70°. The pure A1(LO) is also presented for which θ =90°.

same path as that of the incident and scattered photons. To find the angle β of that path the index of refraction has to be taken into account via Snell's law: $n_1 \sin \theta = n_2 \sin \beta$, where for air $n_1 = 1$ and for AIN $n_2 = 2.2$ which is the accepted value in the visible range and of negligible anisotropy.¹⁵ Our calculations yield a value of $\beta = 15^{\circ}$ for the rotation $\theta = 35^{\circ}$, and from Eq. (3), $\omega_{Q(TO)} = 612 \text{ cm}^{-1}$, a value which concurs with our experimental finding of 614 cm⁻¹. For the 70° rotation, $\beta = 25^{\circ}$ and $\omega_{Q(TO)} = 619 \text{ cm}^{-1}$, a value which is similar to the experimental result of 620 cm⁻¹.

Last we investigated the quasi-LO Raman mode. In order to observe this mode the incoming polarization of the light was set at the Z direction such that the Raman geometry was

$$Y(z_Z^X)\overline{Y}$$

This Raman geometry enables the observation of the quasi-LO modes since the ZZ component of the $E1_{a_1}$ Raman tensor is nonzero for $\theta > 0$ as is indicated by Eq. (2). In this configuration the q vector of the phonon as well as its polarization directions lie in the mixing plane. Figure 5 presents the Raman spectra of the quasi-LO mode for $\theta=15^{\circ}$, 35° , and 70° , and the pure A1(LO) mode at $\theta=90^{\circ}$; the Raman peak positions are at 913, 912, 908, and 890 cm⁻¹, respectively. Taking into account the index of refraction and utilizing the equation for the quasi-LO frequencies, ^{1,10}

$$\omega_{Q(\text{LO})}^2 = \omega_{A1(\text{LO})}^2 \cos^2(90 - \beta) + \omega_{E1(\text{LO})}^2 \sin^2(90 - \beta), \quad (4)$$

where $\omega_{A1(\text{LO})}$ is 890 cm⁻¹ and $\omega_{E1(\text{LO})}$ is 916 cm^{-1,4} we



FIG. 6. The behavior of the quasi-LO and -TO modes as a function of phonon propagation angle β (measured from the *a* axis). The lines represent the TO and LO quasifrequencies calculated using Loudons' model equations (3) and (4); the dots represent our experimental values for the LO and TO modes, the value of the pure E1(LO) is from Ref. 4 (presented by a triangle), while the X's represent the data points of the quasi-TO from Ref. 9.

found the calculated quasifrequencies to be 915, 914, and 911 cm^{-1} , which agree well with the above experimental values.

Figure 6 summarizes our findings. In Fig. 6 the lines denote the TO and LO quasifrequencies calculated utilizing Loudons' model [Eqs. (3) and (4)], and the dots represent our experimental values for the modes. The additional data points of the quasi-TO modes, represented by X's, are from Filippidis et al. who were the first to observe the quasi-TO modes in AIN;⁹ our results are in agreement with theirs. Moreover, as depicted in Fig. 6, our study of the quasi-TO as well as the quasi-LO concur with Loudons' model, implying the presence of a long range electrostatic field which is active in the coupling of modes belonging to the different symmetry groups.

One important implication of the above findings involves the accurate determination of the Raman frequency acquired from AIN thin films. In such films, due to their micron-size dimension along one of the crystallographic axes, the determination of the various Raman frequencies requires the data to be acquired at grazing angle geometry. Such an experimental setup, which deviates by an angle from the crystallographic coordinate system, may result in a mode mixing of a characteristic Raman frequency. Due to the strong angular dispersion of the quasi-TO mode frequency, a disparity in the TO Raman frequency values of thin films is expected to be observed; less disparity is expected for the LO mode. A similar effect in which the frequency is shifted from its pure value is also expected to occur in films grown on crystallographic directions which do not coincide with the caxis. As Raman spectroscopy is widely used in the determination of stress in thin films via the Raman frequency shift, the possible additional shift due to the electrostatic field effect has to be considered.

CONCLUSIONS

The Raman tensors of the WZ structure were calculated as a function of the crystallographic rotation and the allowed modes for various rotations were studied. The LO and TO quasimodes of AIN crystallite were observed and analyzed in terms of the phonon-electrostatic field interaction model. The Raman selection rules as well as the experimental values of the Raman frequencies concur with the model, implying the dominance of the long range electrostatic field in AIN. The quasi-TO mode exhibits a shift of 12 cm^{-1} relative to its pure value for the mode-propagation angle $\sim 25^{\circ}$ measured from the *a* axis. For the same propagation direction, the quasi-LO mode exhibits a shift of $\sim 5 \text{ cm}^{-1}$.

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