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Raman Scattering from Wurtzite GaN Bulk Crystal

P. Verma and A. Yamada

[1] Department of Electronics and Information Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

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Abstract. In order to understand the fundamental vibronic and electronic properties of hexagonal wurtzite GaN bulk crystals, we present Raman scattering studies on this material. We employed polarization-dependent Raman scattering in various scattering configurations at room temperature. Various first-order and combination modes have been observed, which are identified using their selection rule depending on the geometrical configuration in Raman scattering measurement. Absence of the LO modes suggests that the sample has large amount of charge carriers. The assignment of all observed modes and their frequency positions are in good agreement with those previously observed for epitaxially grown wurtzite GaN crystal.

Introduction

GaN has long been considered as a promising material for semiconductor device applications due to its unique electronic and mechanical properties and has been the focus of intensive studies in the resent years [1-3]. With a direct wide band-gap and high thermal stability, GaN is a suitable material for blue and near-UV light-emitting-devices and high-temperature electronic devices [4]. Highly efficient GaN-based blue and green-light-emitting diodes and violet lasers have been successfully fabricated. However, the major difficulty that has hindered GaN epilayer research and its commercial applications is the lack of a suitable substrate material that is lattice-matched and thermally compatible with GaN. Nevertheless, GaN has been grown commonly on Al_2O_3, SiC, and ZnO. In fact, several other materials have also been used as the substrate, but the optical and electrical properties of the grown epilayers have not been satisfactory. Although GaN bulk crystal itself is the best choice as the substrate material, there has hardly been any success in the bulk growth of crystalline GaN crystals with good quality, mainly due to the high melting temperature of GaN and low reactivity between gallium and nitrogen. Moreover, in spite of the technological perspective of this material, only little work has been performed on the fundamental properties of GaN compared to the other III-V semiconductors, which is partly due to the unavailability of good GaN bulk crystals. Under ambient conditions, GaN crystallizes in the hexagonal wurtzite (2H) structure with the space group C_{6v}^4 [5]. However, some epitaxial growths have also resulted in the cubic zincblend (3C) structure. The two structures basically differ in the stacking of the Ga-N bilayers perpendicular to the hexagonal [0001] and cubic [111] directions, respectively. Recently, there has been some success in the growth of 2H bulk GaN with large size and good crystalline quality.

Micro-Raman scattering is an effective technique to characterize and understand the vibronic and electronic properties of a semiconductor material. This non-destructive technique with high spatial resolution has several advantages over the other characterization techniques commonly used. Particularly for wide band-gap materials, such as GaN, the sample is transparent to the probing laser wavelength (514.5 nm), which brings an advantage of large scattering volume, resulting in strong scattering intensities. First-order Raman scattering provides information about the vibrations at the zone-center, which can be used to interpret many crystalline qualities, such as the crystal structure, bond strength, the lattice strain, structural disorder, as well as charge carrier concentration through phonon-plasmon interaction. On the other hand, second-order Raman scattering provides

information about the vibrational states throughout the entire Brillouin zone, which is important for considering, for example, the electronic conduction or the non-radiative relaxation process of electrons. In this paper, we report some basic characterization results in wurtzite 2H bulk GaN crystal in a view to understand the fundamental vibronic and electric properties of this material, studied by polarization-dependent micro-Raman scattering technique under various scattering configurations.

Sample and Experiment

The sample used in the present study is a wurtzite bulk GaN crystal. The as-grown crystal was cut in to a 0.5 mm thick and 1 cm square-shaped sample and was mirror polished for better scattering. Raman scattering studies were performed under various scattering configurations at room temperature using the 514.5-nm line of an Ar-ion laser as the excitation source. The laser was focussed on the sample to a spot of about 1 μm size and the scattered signal was collected by a Spex double monocromator equipped with a liquid-nitrogen-cooled charge coupled device (CCD) detector. For high accuracy and better signal-to-noice ratio, the near-laser signal was chopped-off using a suitable notch filter and the slit-width was sufficiently reduced. We used all necessary scattering geometries to obtain the desired selection rules. The spectral region investigated contains the first-order optic phonons as well as the second-order acoustic and optical combination and overtone modes.

Results and discussion

Due to the momentum conservation, the first-order Raman spectrum shows phonons corresponding to the Γ-point (k = 0). In the wurtzite structure, the group theory predicts eight types

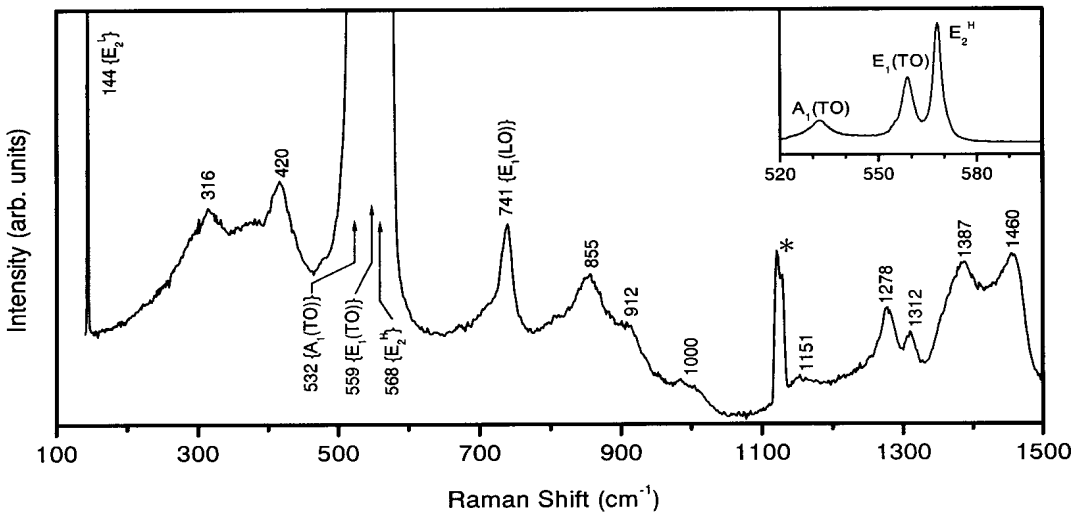

Fig. 1 Raman spectrum from GaN bulk crystal measured at room temperature in combined [z(x,x)-z + z(x,y)-z] backscattering configuration. The numbers indicate phonon frequencies in cm^{-1}. The details of phonon modes between 520 and 580 cm^{-1} are shown in the inset.

of phonons, $2A_1$, $2E_1$, $2B_1$, and $2E_2$, out of which $1A_1$ and $1E_1$ modes are acoustic and the rest are optic. Depending upon the scattering configuration, all or some of these optic phonons along with various combination modes can be observed in a Raman spectrum. Taking the z-direction along the c-axis and the x and y directions in the perpendicular plane, the typical A_1, E_1 and E_2 backscattering geometries can be indicated by z(x,x)-z, z(x,y)-z and x(y,z)-x, respectively, where the symbols, from left to right, outside the bracket indicate the direction of incident and scattered light and inside bracket indicate the polarization direction of incident and scattered light, respectively. An unpolarized scattering in the backscattering geometry can be described by the combined configuration [z(x,x)-z + z(x,y)-z].

Figure 1 shows an overview of a room-temperature Raman spectrum measured from a hexagonal bulk GaN crystal in the [z(x,x)-z + z(x,y)-z] scattering configuration. The details of phonon structures between 520 and 580 cm^{-1} are displayed in the inset. Apart from the strong first-order phonon modes at 532, 559 and 568 cm^{-1} (A_1(TO), E_1(TO) and E_2^H, respectively), a rich spectrum due to the second-order scattering can be seen. The acoustic overtones can be seen in the low frequency region (below 500 cm^{-1}), acoustic and optic combination modes appear between 800 and 1300 cm^{-1}, and the optic overtones can be found in the high frequency range above 1350 cm^{-1}. Table 1 lists the frequency modes observed in Fig. 1, along with their symmetry and the scattering configuration in which they are observed. The LO modes in Raman spectrum from this sample have very weak intensity, which indicates that the sample has large charge carriers, which screen the LO phonons. Although a phonon-plasmon coupled mode could not be observed, it was otherwise confirmed that the sample has a charge carrier density of about 10^{18} cm^{-3}. We could not observe the B_1 modes in our experiments, probably due to their weak intensities. The origin of an unidentified mode assigned by asterisk (*) in Fig. 1 could not be understood at this time.

Further, Raman scattering experiments were performed in various scattering configurations, where the A_1(TO) mode was observed in both x(y,y)-x and x(z,z)-x scattering configurations and the E_1(TO) mode was observed in both x(y,z)-x and x(y,z)y scattering configurations. A weak

Table 1 The frequency positions and the symmetries of the first- and second-order phonon modes observed in Fig. 1. Also listed are the scattering configurations for the first-order modes.

Frequency (cm^{-1})	Symmetry	Scattering Process	Scattering Configuration
144	E_2(low)	Acoustic overtone	
316	A_1	Acoustic overtone	
420	A_1,E_2	Acoustic overtone	
532	A_1(TO)	First-order	x(y,y)-x; x(z,z)-x
559	E_1(TO)	First-order	x(y,z)-x; x(y,z)y
568	E_2(high)	First-order	z(y,y)-z; z(x,y)-z; x(y,y)-x; x(y,y)z
~741	A_1(LO),E_1(LO)	First-order	z(x,x)-z
855	A_1,E_1,E_2	Acoustic-optic combination	
912	A_1	Acoustic-optic combination	
1000	A_1	Acoustic-optic combination	
1151	A_1	Optic overtone	
1278	A_1	Optic combination	
1312	A_1	Optic combination	
1387	A_1	Optic overtone	
1460	A_1	Optic overtone	

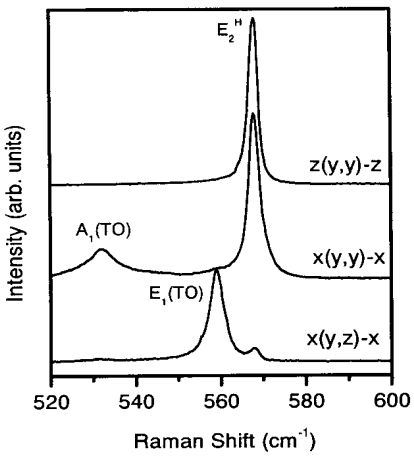

Fig. 2 Raman spectra measured from bulk GaN crystal in the spectral range of 520 to 580 cm^{-1} with the three different scattering configurations.

structure observed around 741 cm^{-1} is a combination of A_1(LO) and E_1(LO) modes, which was seen in the z(x,x)-z scattering configuration. Figure 2 displays Raman spectra between 520 and 580 cm^{-1} in three different scattering configurations. The E_2^H mode was observed in four different scattering configurations, listed in Table 1. In the z(y,y)-z configuration, only E_2^H mode could be observed, whereas both A_1(TO) and E_2^H modes were observed in the x(y,y)-x configuration. The E_1(TO) mode could be observed in the x(y,z)-x configuration. Although the E_2^H mode is forbidden in this configuration, a weak signal from this mode was observed. This could be due to the so called "leakage effect". The low-frequency E_2 mode at 144 cm^{-1} shows fairly small line width, indicating long lifetime. The mode at 316 cm^{-1} shows A_1 symmetry, where as the mode at 420 was observed in both A_1 and E_2 symmetries. The modes around 855, 912 and 1000 cm^{-1} have A_1 symmetry. The mode at 855 cm^{-1} shows additional E_1 and E_2 symmetries. All optic overtones and combinations show A_1 symmetry. The assignment of all observed modes and their frequency positions, listed in Table 1, are in good agreement with those reported earlier [6] for epitaxially grown wurtzite GaN crystal.

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