

WANG Rui-min, CHEN Guang-de,  
LIN J. -Y., JIANG H. -X.

## Comparative Analysis of Temperature-dependent Raman Spectra of GaN and GaN/Mg Films

© Higher Education Press and Springer-Verlag 2006

**Abstract** The Raman spectra of unintentionally doped gallium nitride (GaN) and Mg-doped GaN films were investigated and compared at room temperature and low temperature. The differences of  $E_2$  and  $A_1(\text{LO})$  mode in two samples are discussed. Stress relaxation is observed in Mg-doped GaN, and it is suggested that Mg-induced misfit dislocation and electron–phonon interaction are the possible origins. A peak at  $247\text{ cm}^{-1}$  is observed in both the Raman spectra of GaN and Mg-doped GaN. Temperature-dependent Raman scattering experiment of Mg-doped GaN shows the frequency and intensity changes of this peak with temperature. This peak is attributed to the defect-induced vibrational mode.

**Keywords** GaN, P-type GaN, Raman scattering, defect modes

**PACS numbers** 63.20.Pw, 78.30.Fs

### 1 Introduction

The direct wide band gap gallium nitride (GaN) has recently been recognized as a potential material for optoelectronic applications in the short wavelength range, such as light emitting diodes, power devices, and lasers. The defects and impurities in GaN have very important effects on the electric transport and light emission properties of the material. Raman scattering is a powerful and widely used method for studying the defects of and impurities in a material. Raman peaks that are located in the

low-energy range, between  $95$  and  $250\text{ cm}^{-1}$ , were first reported by Ramsteiner et al. [1] in GaN on GaAs grown by molecular beam epitaxy (MBE). Siegle et al. [2] claimed that these peaks are only observable for GaN on GaAs. Subsequently, Jiang et al. [3] reported these peaks in MBE GaN layers grown on both sapphire and GaAs substrates. Because the intensity of these lines decreases with increasing temperature and the lines disappear at room temperature, Ramsteiner et al. attributed these lines to the electronic excitation of donors. However, Siegle et al. [4] reported magnetic-field- and high-pressure-dependent Raman measurements and show, in contrast, that all lines are caused by vibrational Raman scattering in which the temperature dependence is due to the resonance process. Furthermore, the theoretical calculation [5] shows the local modes of As impurities in GaN located at this range; thus, these lines are related to As impurities.

Semiconductors contain a variety of electronic excitations due to free and bound charges, the electronic excitations can couple to the lattice vibration. The influence of free carriers on Raman spectra and their coupling with LO phonons has already been reported in unintentionally doped GaN and N-type GaN films [6], but there are few reports about the behavior of coupled mode at low temperatures.

In this paper, we investigated the Raman scattering spectra of undoped GaN and Mg-doped GaN films at room temperature and low temperature. The differences between the  $E_2$  and  $A_1(\text{LO})$  modes in two samples are discussed and explained by the interplay of electronic excitations and lattice vibration. Apart from the host phonon modes, a peak at  $247\text{ cm}^{-1}$ , which is very consistent with the  $30.7\text{ meV}$  reported in [3], appears both in the spectra of undoped GaN and Mg-doped GaN at low temperature. The origin of this peak is discussed.

### 2 Experiment

The two samples studied in this work were all grown by metal-organic chemical-vapor deposition (MOCVD) on

Translated from *Chinese Journal of Semiconductors*, 2005, 26(4) (in Chinese)

WANG Rui-min (✉), CHEN Guang-de  
School of Science, Xi'an Jiaotong University,  
Xi'an 710049, China  
E-mail: wangrm@mail.xjtu.edu.cn

LIN J. -Y., JIANG H. -X.  
Department of Physics, Kansas State University,  
KS 60502, USA

[0001] sapphire substrates with 20-nm-thick GaN buffer layer. They have a hexagonal structure, and the thickness of the epitaxial layer was about 1  $\mu\text{m}$ . The magnesium concentration of the P-type sample was  $5 \times 10^{19} \text{ cm}^{-3}$ . The Raman spectra were measured with a Jobin-Yvon T64000 Raman system in backscattering  $Z(X, -)\bar{Z}$  geometry. The accuracy of the measured phonon frequencies was  $0.5 \text{ cm}^{-1}$ . The line at 532 nm of an  $\text{Ar}^+$  laser was used for excitation. The power on sample is about 3.2 mW, and the temperature was varied between 78 and 573 K.

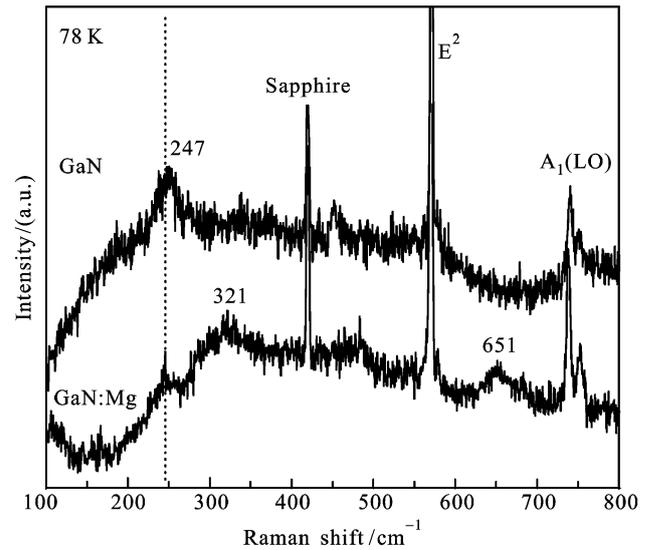
### 3 Results and discussion

#### 3.1 The host phonon modes

For the  $Z(X, -)\bar{Z}$  geometry, the  $E_2$  and  $A_1(\text{LO})$  modes can be observed according to the selection rule. Table 1 lists the phonon frequency and the full width at half maximum (FWHM) of the  $E_2$  and  $A_1(\text{LO})$  modes at 78 K and room temperature. The frequencies and linewidths of the phonon modes were determined by fitting Lorentzian line shapes to the measured Raman lines. Figure 1 shows the Raman spectra at 78 K. For the  $E_2$  mode, the FWHM of Mg-doped GaN is larger than that of undoped GaN by about  $0.5 \text{ cm}^{-1}$ , which can be attributed to the lower crystalline quality due to heavy doping. An interesting phenomenon that we observed is that the frequency of the  $E_2$  mode in Mg-doped GaN shifted  $1 \text{ cm}^{-1}$  to the low-energy side compared with GaN sample and was at  $568 \text{ cm}^{-1}$  at room temperature. This indicated that the relaxation of residual stress existed in the Mg-doped sample [7]. The tetrahedral radius of Mg is larger than that of Ga and N. It is well known that dopant atoms, which are large, compared with the host lattice atoms, can introduce compressive hydrostatic stress and make the  $E_2$  mode shift to high energy. According to the magnesium concentration of our sample and the linear stress-shift coefficient  $k = 3.6 \text{ cm}^{-1} \cdot \text{GPa}^{-1}$  [8], we can deduce that the hydrostatic-pressure-induced frequency blue-shift will be about  $1 \text{ cm}^{-1}$ . Popovici et al. [9] reported that some Mg-doped GaN samples have tensile stress and suggested that the growth conditions, not the Mg impurity, are the major cause of stress in Mg-doped sample. Recently, Xu et al. [10] reported the stress relaxation in Mg-doped GaN and attributed it to the role of buffer layer. In [11,12], the stress relaxation in Si-doped GaN has been explained as Si-induced misfit dislocation. In our work, the two samples have the same growth conditions and buffer

**Table 1** The frequency and FWHM of host lattice phonons

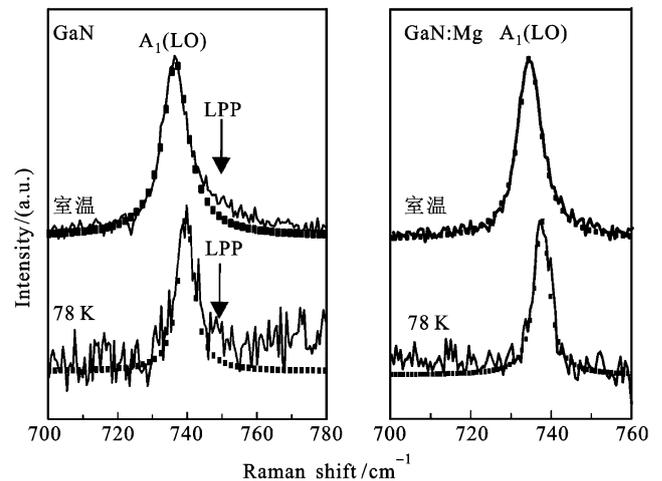
Mode		78 K		300 K	
		$\omega / \text{cm}^{-1}$	$\Gamma / \text{cm}^{-1}$	$\omega / \text{cm}^{-1}$	$\Gamma / \text{cm}^{-1}$
$E_2$	GaN	570	2.5	569	2.5
	GaN/Mg	569	3.0	568	3.2
$A_1(\text{LO})$	GaN	740	5.3	736	9.0
	GaN/Mg	737	4.4	734	7.0



**Fig. 1** Raman spectra of GaN and GaN/Mg at 78 K

layers. We think that Mg-induced generation of misfit dislocation is the possible interpretation. In addition, an alternative explanation is the electron–phonon interaction in Mg-doped sample. The frequency shift induced by electron–phonon interaction has been observed in N-type Si, P-type Si, P-type Ge, and P-type GaAs [13]. In P-type GaN, many holes are located in the heavy-hole band; the transitions between light, heavy hole band, and spin-orbit-split valence band result in the appearance of a broad electronic continuum.  $E_2$  phonon coupled with electronic excitations via the deformation potential mechanism, and the effect of the electron–phonon interaction on the phonon spectra will lead to a softening of the phonon frequency.

Another difference between the two spectra is that the  $A_1(\text{LO})$  mode of undoped GaN has an asymmetric lineshape and shifts to high energy. For undoped GaN, the  $A_1(\text{LO})$  phonon is known to be at  $733 \text{ cm}^{-1}$  [14]. The

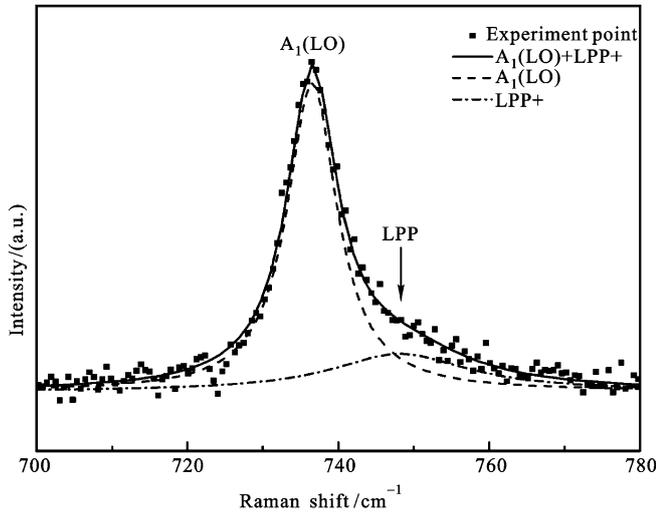


**Fig. 2** The spectra of  $A_1(\text{LO})$  mode at 78 K and at room temperature. The solid squares are the Lorentz fit data

blue shift can be explained by the interplay of plasmon and longitudinal phonon in GaN [6]. Figure 2 shows the  $A_1(\text{LO})$  mode of the two samples at 78 K and room temperature. The  $E_g$  line of sapphire at  $750 \text{ cm}^{-1}$  has been excluded from the Raman spectra of the studied samples. To exclude this signal, the Raman spectrum of sapphire was normalized by the  $A_{1g}$  line at  $417 \text{ cm}^{-1}$  and then subtracted from the spectra of the samples. The  $A_1(\text{LO})$  mode has a clear tail to the higher frequency side in the spectrum of GaN and becomes prominent at a low temperature, and we attribute it to the LO phonon–plasmon coupled mode ( $\text{LPP}^+$ ), although the forbidden  $E_1(\text{LO})$  mode at  $741 \text{ cm}^{-1}$  is very close to the phonon–plasmon mode [15]. If it is the leaky mode of  $E_1(\text{LO})$ , it may be observed in Mg-doped GaN, but this feature only appears in GaN samples. Furthermore, the  $E_1(\text{LO})$  mode cannot shift the  $A_1(\text{LO})$  mode to the high-frequency side. From the frequency of the  $A_1(\text{LO})$  mode and with the high-frequency tail becoming noticeable in low temperatures, we believe that the  $\text{LPP}^+$  is more likely to be its origin. At low temperatures, the collective excitation of an electron will become stronger; thus, this mode becomes prominent. For Mg-doped GaN, the  $A_1(\text{LO})$  mode shows Lorentzian lineshape. Such inactive coupling between the LO phonon and the plasmon in P-type GaN is attributed mainly to the heavy damping of the hole plasmon [16].

In Fig. 3, the experimental data of the  $A_1(\text{LO})$  mode of GaN at room temperature have been fit as a sum of the  $A_1(\text{LO})$  mode and  $\text{LPP}^+$  mode [17]:

$$\begin{aligned} I(\omega) &= I^{A_1(\text{LO})}(\omega) + I^{\text{LPP}^+}(\omega) \\ &= B_1 \left[ \frac{\Gamma_1}{(\omega - \omega_{\text{LO}})^2 + \Gamma_1^2} \right] + B_2 \text{Im}[-1/\varepsilon(\omega)] \end{aligned} \quad (1)$$



**Fig. 3** The *solid squares* are the experimental data of the  $A_1(\text{LO})$  mode of GaN at room temperature. The *solid*, *dashed*, and *dash dotted lines* are  $A_1(\text{LO})+\text{LPP}^+$ ,  $A_1(\text{LO})$ , and  $\text{LPP}^+$ , respectively

$$\varepsilon(\omega) = \varepsilon_\infty \left[ 1 + \frac{\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 - i\omega\Gamma_2} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \right] \quad (2)$$

The plasma frequency,  $\omega_p$ , is given by

$$\omega_p^2 = \frac{ne^2}{\varepsilon_\infty m^*} \quad (3)$$

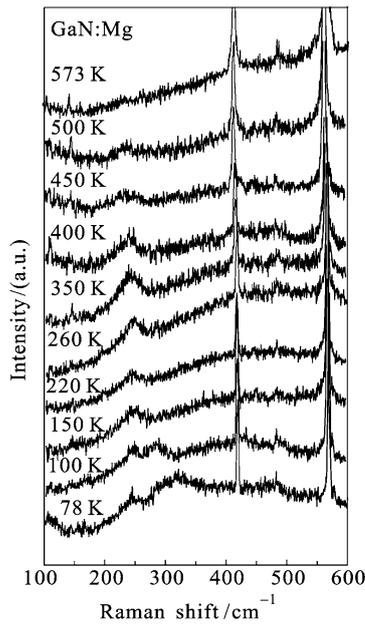
From the fitting value  $\omega_p = 186.63 \text{ cm}^{-1}$  and  $m^* = 0.22m_0$ , we obtain the electron concentration  $n = 4.37 \times 10^{17} \text{ cm}^{-3}$ . This implies that there are residual donors in unintentionally doped GaN and in those that show N-type conductivity.

Generally, in the phonon–plasmon-coupling regime, the unscreened LO phonon mode and the pure plasma oscillation mode should be replaced by two LPP-coupled modes. However, the uncoupled  $A_1(\text{LO})$  mode is always found in some N-doped semiconductors, including GaN [6,17,18]. Furthermore, the intensity ratio of the unscreened LO phonon and the LPP mode depends on the carrier concentration and on the exciting laser energy [13]. Two mechanisms are proposed to explain the unusual behavior: (1) the presence of a thin surface-carrier-depletion layer associated with a near-surface band bending and (2) large wave vector induced decoupling of LO phonon and plasmon modes [19]. For unintentionally doped GaN, in which the carrier concentration is low, it is known that the thickness of the surface depletion layer increases with decreasing electron concentration; thus, we think that the  $A_1(\text{LO})$  signal originated in the surface space-charge region, where there are no free carriers.

### 3.2 The defect and impurity modes

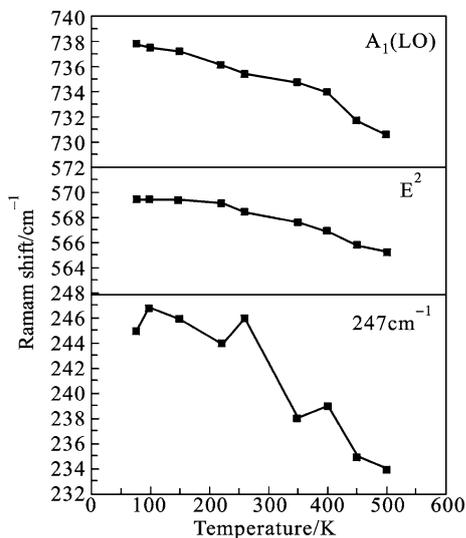
In Fig. 1, a peak at  $247 \text{ cm}^{-1}$  is observed in both spectra, and two additional peaks at  $321$  and  $651 \text{ cm}^{-1}$  are also observed in the spectrum of Mg-doped GaN sample. To study the origins of these peaks, temperature-dependent Raman scattering experiments were performed. Figure 4 displays the Raman spectra of Mg-doped GaN with temperature varying from 78 to 573 K. The spectra were normalized in intensity by the peak height of the high-frequency  $E_2$  mode and shifted to vertical direction for comparison. The peak at  $321 \text{ cm}^{-1}$  is softened with the rise of temperature and disappears above 150 K. This peak has been reported in many ion-implanted GaN samples and is located at the range where states have high phonon density; thus, it is attributed to disorder-activated Raman scattering (DARS; [20,21]). The  $651 \text{ cm}^{-1}$  peak is only observed at 78 K and is assigned to the local vibrational mode (LVM) for the Mg–N bond [22].

When the temperature is raised, the  $247 \text{ cm}^{-1}$  peak becomes strong at first but then becomes weak again at above room temperature and disappears at about 500 K.

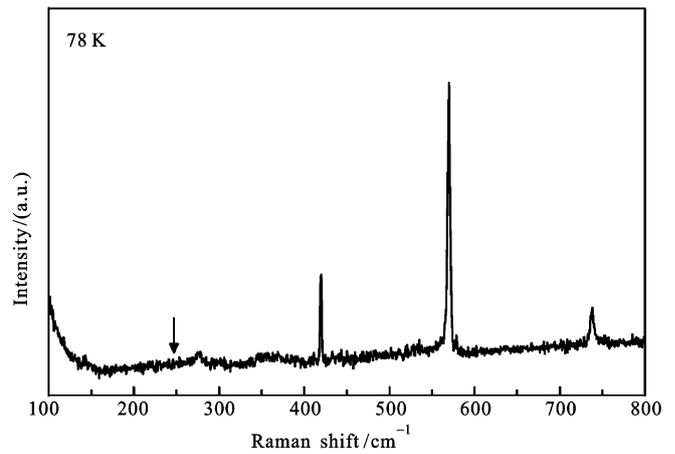


**Fig. 4** Raman spectra of Mg-doped GaN are measured at different temperatures between 78 and 573 K

References [1,3] reported an electronic Raman scattering (ERS) mode at  $247\text{ cm}^{-1}$  in GaN, with frequency consistent with what we observed. They attributed it to the  $1S \rightarrow 3S$  transition of shallow donors. For residual donors, the concentration is low, and it will be ionized completely above room temperature. There is no opportunity that the electronic transition mode of residual donors will be seen at high temperature. In our results, notice that the mode does not disappear up to temperatures as high as 500 K; it is impossible for it to have originated from the electronic transition. On the other hand, Siegle et al. [4] reported this peak in GaN on GaAs, which they attributed to As impurities. But the two samples studied in our work were grown on sapphire, which is related to As; thus, we



**Fig. 5** Frequencies of the defect-induced vibrational mode and host lattice modes as a function of temperature in Mg-doped GaN



**Fig. 6** The Raman spectrum of GaN/Mg when the temperature is decreased from 573 to 78 K again

consider that this mode has a different origin from what they reported.

Figure 5 shows the frequencies of the  $247\text{ cm}^{-1}$  peak as a function of temperature. Below room temperature, there are small changes in Raman shift, but above room temperature, this mode shifts to the low frequency quickly and becomes broader with increasing temperature. It is known that the frequencies of LVMs have remarkable temperature-induced change, and we think that this peak results from defect-induced vibrational mode. References [21,22] reported another LVM mode of Mg–N bond at  $260\text{ cm}^{-1}$  in an Mg-doped sample, close to  $247\text{ cm}^{-1}$ . However, we excluded this peak as related to Mg because we observed this peak in undoped GaN sample simultaneously. Furthermore, [23] reported that the mode at  $260\text{ cm}^{-1}$  exhibits a temperature behavior similar to that of the host phonon, which has a softening of about  $6\text{ cm}^{-1}$  from 4 to 590 K. In our work (see Fig. 5), the temperature-induced frequency shift of the  $247\text{ cm}^{-1}$  peak between 78 and 500 K is  $12\text{ cm}^{-1}$ . It is larger than the shifts of the host phonons, which are 4 and  $7\text{ cm}^{-1}$  for the  $E_2$  and  $A_1(\text{LO})$  modes, respectively. We attributed it to other defect. The absence of this mode above 500 K can be explained as the decomposition of the defect.

To prove this opinion, we decrease the temperature again. Figure 6 shows the Raman spectra of Mg-doped GaN when the temperature is decreased to 78 K again. The arrow expresses the frequency of  $247\text{ cm}^{-1}$ . It can be seen that there is no peak at this frequency and that the broad feature around  $300\text{ cm}^{-1}$  is absent. This means recovery in crystallinity at high temperature.

## 4 Conclusions

The frequency of the  $E_2$  mode in Mg-doped GaN shifts to the low-energy side compared with the GaN sample and is located at  $568\text{ cm}^{-1}$  at room temperature. This indicates that the relaxation of residual stress exists in Mg-doped sample. The Mg-induced misfit dislocation and electron–phonon interaction are the possible origins of stress

relaxation. The  $A_1(\text{LO})$  mode of undoped GaN has an asymmetric lineshape, and the high-frequency tail becomes noticeable in low temperature, which has been explained by phonon–plasmon coupling.

A peak at  $247\text{ cm}^{-1}$  was observed in both Raman spectra. A temperature-dependent Raman scattering experiment of Mg-doped GaN shows that the intensity of this peak became strong at first, but then became weak and disappeared at about 500 K. When the temperature was decreased to 78 K, this peak was absent. We attribute it to the defect-induced vibrational mode.

## References

- Ramsteiner M., Menniger J., Brandt O. et al., Shallow donors in GaN studied by electronic Raman scattering in resonance with yellow luminescence transitions, *Appl. Phys. Lett.*, 1996, 69: 1276–1278
- Siegle H., Loa I., Thurian P. et al., Comment on “Shallow donors in GaN studied by electronic Raman scattering in resonance with yellow luminescence transitions”, *Appl. Phys. Lett.*, 1997, 70: 909
- Jiang D.-S., Ramsteiner M., Ploog K.-H. et al., Defect-induced Raman scattering in resonance with yellow luminescence transitions in hexagonal GaN on a sapphire substrate, *Appl. Phys. Lett.*, 1998, 72: 365–367
- Siegle H., Kaschner A., Hoffmann A. et al., Raman scattering from defects in GaN: the question of vibrational or electronic scattering mechanism, *Phys. Rev., B*, 1998, 58: 13619–13626
- Kaczmarczyk G., Kaschner A., Hoffmann A. et al., Impurity-induced modes of Mg, As, and C in hexagonal and cubic GaN, *Phys. Rev., B*, 2000, 61: 5353–5357
- Kozawa T., Kachi T., Kano H. et al., Raman scattering from LO phonon–plasmon coupled modes in gallium nitride, *J. Appl. Phys.*, 1994, 75: 1098–1101
- Perlin P., Jauberthie-Carillon C., Itie J.-P. et al., Raman scattering and x-ray-absorption spectroscopy in gallium nitride under high pressure, *Phys. Rev., B*, 1992, 45: 83–89
- Harima H., Properties of GaN and related compounds studied by means of Raman scattering, *J. Phys.: Condens. Matter.*, 2002, 14: R967–R993
- Popovici G., Xu G.-Y., Botchkarev A. et al., Raman scattering and photoluminescence of Mg-doped GaN films grown by molecular beam epitaxy, *J. Appl. Phys.*, 1997, 82: 4020–4023
- Xu B., Yu Q.-X., Wu Q.-H. et al., Effects of strain and Mg-dopant on the photoluminescence spectra in P-type GaN, *Acta Phys. Sin.*, 2004, 53: 204–209 (in Chinese)
- Lee I.-H., Choi I.-H., Lee C.-R. et al., Stress relaxation in Si-doped GaN studied by Raman spectroscopy, *J. Appl. Phys.*, 1998, 83: 5787–5791
- Ruvimov S., Liliental-Weber Z., Suski T. et al., Effect of Si doping on the dislocation structure of GaN grown on the A-face of sapphire, *Appl. Phys. Lett.*, 1996, 69: 990–992
- Cardona M. and Güntherodt G., *Light Scattering in Solids IV*, Berlin Heidelberg New York: Springer, 1984, 127–145
- Pophristic M., Long F.-H., Schurman M. et al., Raman microscopy of lateral epitaxial overgrowth of GaN on sapphire, *Appl. Phys. Lett.*, 1999, 74: 3519–3521
- Yu. Davydov V., Kitaev Yu E., Goncharuk I.-N. et al., Phonon dispersion and Raman scattering in hexagonal GaN and AlN, *Phys. Rev., B*, 1998, 58: 12899–12907
- Harima H., Inoue T., Nakashima S. et al., Electronic properties in P-type GaN studied by Raman scattering, *Appl. Phys. Lett.*, 1998, 73: 2000–2002
- Chaldyshev V.-V., Pollak F.-H., Pophristic M. et al., Micro-Raman investigation of the N-dopant distribution in lateral epitaxial overgrown GaN/sapphire (0001), *J. Electron. Mater.*, 2002, 31: 631–634
- Florescu D.-I., Asnin V.-M., Pollak F.-H. et al., High spatial resolution thermal conductivity and Raman spectroscopy investigation of hydride vapor phase epitaxy grown N-GaN/sapphire (0001): doping dependence, *J. Appl. Phys.*, 2000, 73: 3295–3299
- Kasic A., Schubert M., Saito Y. et al., Effective electron mass and phonon modes in N-type hexagonal InN, *Phys. Rev., B*, 2002, 65: 115206
- Limmer W., Ritter W., Sauer R. et al., Raman scattering in ion-implanted GaN, *Appl. Phys. Lett.*, 1998, 72: 2589–2591
- Kaschner A., Siegle H., Kaczmarczyk G. et al., Local vibrational modes in Mg-doped GaN grown by molecular beam epitaxy, *Appl. Phys. Lett.*, 1999, 74: 3281–3283
- Harima H., Inoue T., Nakashima S. et al., Local vibrational modes as a probe of activation process in P-type GaN, *Appl. Phys. Lett.*, 1999, 75: 1383–1385
- Kaschner A., Kaczmarczyk G., Hoffmann A. et al., Defect complexes in highly Mg-doped GaN studied by Raman spectroscopy, *Phys. Stat. Sol., B*, 1999, 216: 551–555