Temperature-Dependent Raman Scattering of Phonon Modes and Defect Modes in GaN and p-Type GaN Films *

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Abstract: Raman spectra of undoped GaN and Mg-doped GaN films grown by metal-organic chemical-vapor deposition on sapphire are investigated between 78 and 573 K. A peak at 247cm^{-1} is observed in both Raman spectra of GaN and Mg-doped GaN. It is suggested that the defect-induced scattering is origin of the mode. The electronic Raman scattering mechanism and Mg-related local vibrational mode are excluded. Furthermore, the differences of E_2 and A_1(LO) modes in two samples are also discussed. The stress relaxation is observed in Mg-doped GaN.

Key words: GaN; p-type GaN;, Raman scattering; defect modes

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1 Introduction

GaN is a new wide band gap semiconductor material. In recent years it has attracted considerable attention because of the potential to fabricate bright UV- and visible-light-emitting diodes, power devices, and lasers[1]. However, many aspects of the light emission process and physical properties of GaN remain to be understood and improved[2,3]. The defects and impurities in GaN have very important affections on the electric transport and light emission properties of the material. Raman scattering is a powerful technique for studying the defects and impurities in material. The Raman peaks which are located in the low-energy range between 95 and 250cm^{-1} in GaN on GaAs grown by molecular beam epitaxy (MBE) were first reported by Ramsteiner *et al.*[4]. Siegle *et al.*[5] claimed that these peaks are only observable for GaN on GaAs. Subsequently, Jiang *et al.*[6] reported these peaks in MBE GaN layers grown on both sapphire and GaAs substrates. Except the peak of 125cm^{-1} (which has also been observed in p-type GaN and shows a weak temperature dependence, therefore it is even not clear whether this peak is due to electronic Raman scattering (ERS)[7]), they attributed the other peaks to electronic excitation of donors.

Semiconductors contain a variety of electronic excitations due to free and bound charges, and the electronic excitations can couple to the lattice vibration. The LO phonon-plasmon coupled mode at room temperature (RT) has already been reported in GaN[8~10], but there are few reports about the behavior of coupled mode at low temperature.

In this paper the Raman scattering spectra of undoped GaN and Mg-doped GaN films on sapphire grown by metal-organic chemical-vapor deposition (MOCVD) are investigated between 78 and 573 K.

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A peak at 247cm^{-1}, which is very consistent with 30.7meV reported in Ref. [6], appears both in the spectra of undoped GaN and Mg-doped GaN. The origin of this peak is discussed. The differences of E_2 and A_1(LO) modes in two samples are also discussed and explained by the interplay of electronic excitations and lattice vibration.

2 Experiment

The two samples studied in this work were grown by MOCVD on sapphire substrates. They have hexagonal structure and the thickness of the films was about 1μm. The magnesium concentration of p-type sample was 5×10^{19}cm^{-3}. The Raman spectra were measured with a Jobin-Yvon T64000 Raman system in backscattering $Z(X, -)\bar{Z}$ geometry. The accuracy of measured phonon frequencies was less than 0.5cm^{-1}. The line at 532nm of an Ar^+ laser was used for excitation. The output power of laser is 500mW and the power on sample is about 3.2mW. The measure temperature was varied between 78 and 573K.

3 Results and discussion

Figure 1 shows the Raman spectra of undoped GaN and Mg-doped GaN at 78K. A peak at 247cm^{-1} is observed in both spectra, and two additional peaks at 321cm^{-1} and 651cm^{-1} are also observed for Mg-doped GaN sample. In order to study the origins of these peaks, temperature-dependent Raman scattering experiments were performed. Figure 2 displays Raman spectra of Mg-doped GaN from 78 to 573K. 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 321cm^{-1} is softened with the rise of temperature and disappears above 150K. Siegle *et al.*[11] has reported a peak at 317cm^{-1} in GaN and assigned it to an overtone process of acoustic phonons. The peak also be reported in many ion-implanted GaN samples and be attributed to disorder-activated Raman scattering (DARS)[12,13]. We suggested that it results from the DARS instead of second-order scattering because it becomes weaker with increasing temperature and shifts 33cm^{-1} to low frequency between 78 and 100K. The 651cm^{-1} peak is only observed at 78K, it is assigned to the local vibrational mode (LVM) for the Mg—N bond[14].

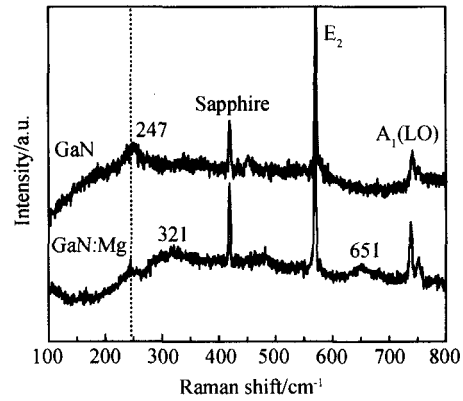

Fig. 1 Raman spectra of undoped GaN and Mg-doped GaN at 78K

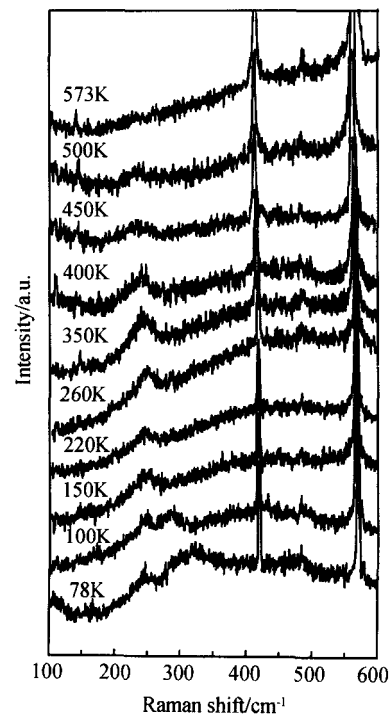

Fig. 2 Raman spectra of Mg-doped GaN at temperature between 78 and 573K

When the temperature is raised, the 247cm^{-1} peak becomes strong at first, but then become

weak again above room temperature and disappears at about 500 K. References[4,6] reported an ERS mode at 247cm^{-1} in GaN, the frequency is consistent with what we observed, they attributed it to 1s →3s transition of shallow donors. For residual donors the concentration is low, it will be ionized completely above room temperature, and there is no chance to see the electronic transition mode of residual donors at high temperature. In our results, the mode does not disappear up to temperature as high as 500 K, so we consider that this mode has different origin from which they reported.

Figure 3 shows the frequencies of 247cm^{-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 frequency of local vibrational modes has remarkable temperature-induced change, so we think this peak results from defect-induced vibrational mode. References[13,14] reported another LVM mode of Mg—N bond at 260cm^{-1} in Mg-doped sample, closes to 247cm^{-1}. However, we exclude this peak related to Mg because we observe this peak in undoped GaN sample simultaneously. Furthermore, Reference[15] reported that the mode at 260cm^{-1} exhibits a temperature behavior similar to that of the host phonon, which has a softening of about 6cm^{-1} from 4 to 590 K. In our work (see Fig. 3), the temperature-induced frequency shift of the 247cm^{-1} peak between 78 and 500 K is 12cm^{-1}. It is larger than the shifts of host phonons, which are 4 and 7cm^{-1} for E_2 and A_1(LO) modes respectively. We attribute it to other defects. The absence of this mode above 500 K can be explained as the decomposition of the defect. In order to prove this opinion, we decrease temperature again. Figure 4 shows the Raman spectra of Mg-doped GaN when is decreased to room temperature and 78 K again. The arrow expresses the frequency of 247cm^{-1}, it can be seen that there is no peak at this frequency both at room temperature and 78 K. This means recovery in crystallinity at high temperature.

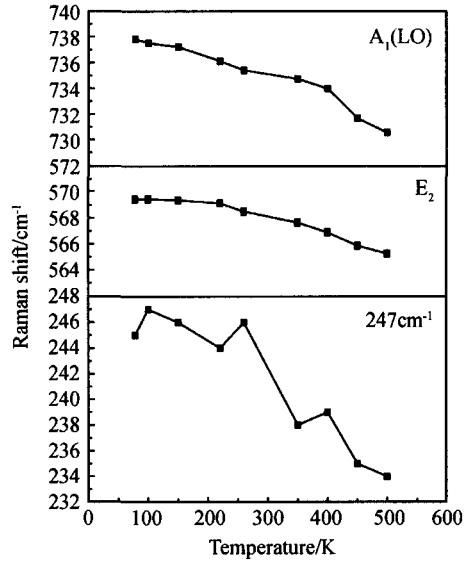

Fig. 3　Frequencies of the defect-induced vibrational modes and host lattice modes as a function of temperature in Mg-doped GaN

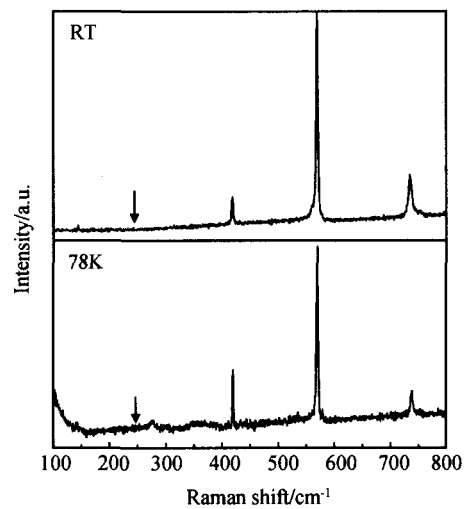

Fig. 4　Raman spectra of Mg-doped GaN when is decreased to room temperature and 78 K again

Table 1 lists the phonon frequency and the full width at half maximum (FWHM) of E_2 and A_1(LO) modes at 78 K and room temperature. For E_2 mode, the FWHM of Mg-doped GaN is larger than that of undoped GaN for about 0.5cm^{-1}, which can be attributed to the lower crystalline quality due to heavy dopping. An interesting phenomenon we observed is that the frequency of E_2 mode in Mg-doped GaN shifts 1cm^{-1} to low energy

side compared with GaN sample, and locates at 568cm^{-1} at room temperature. This indicates the relaxation of residual stress existed in Mg-doped sample[16]. The tetrahedral radius of Mg is larger than Ga and N. It is well known that dopant atoms which are large compared to the host lattice atoms, can introduce compressive stress and make the E_2 mode shift to high energy. Popovici *et al*.[17] 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. The two samples studied in our work were grown on sapphire substrates by MOCVD. We think an alternative explanation is the electron-phonon interaction in Mg-doped sample, because the E_2 mode displays asymmetric structure and its intensity decreases with temperature.

Table 1 Frequency and FWHM of host lattice phonons

		78 K		300 K	
		ω/cm^{-1}	Γ/cm^{-1}	ω/cm^{-1}	Γ/cm^{-1}
E_2	GaN	570	2.5	569	2.5
	GaN:Mg	569	3.0	568	3.2
A_1(LO)	GaN	740	5.3	736	9.0
	GaN:Mg	737	4.4	734	7.0

Another difference between the two spectra is that the A_1(LO) mode of undoped GaN has asymmetric lineshape and shifts to high energy. For undoped GaN, the A_1(LO) phonon is known to be at 733cm^{-1}[18]. The upshift can be explained by the interplay of plasmon and longitudinal phonon in GaN[8,10]. Figure 5 shows the A_1(LO) mode of two samples at 78 K and room temperature. The E_g line of sapphire at 750cm^{-1} has been excluded from the Raman spectra of studied samples. In order to exclude this signal, the Raman spectrum of sapphire was normalized by A_{1g} line at 417cm^{-1} and then subtracted from the spectra of samples. The A_1(LO) mode has a clear tail to the higher frequency side in the spectrum of GaN and becomes prominently at low temperature, we attributed it to the LO phonon-plasmon coupled mode (LPP$^+$) although the forbidden E_1(LO) mode at 741cm^{-1} is very close to the phonon-plasmon mode[19]. If it is the leaky-mode of E_1(LO), it may be observed in Mg-doped GaN, but this feature only appears in GaN sample. Furthermore, E_1(LO) mode can not shift A_1(LO) mode to high frequency side. From the frequency of A_1(LO) mode and the high frequency tail becomes noticeable at low temperature, we believe that the LPP$^+$ is more likely to be its origin. At low temperature the collective excitation of electron will become stronger so this mode becomes prominently. This implies that there are residual donors in unintentionally doped GaN and shows n-type conductivity. For Mg-doped GaN the A_1(LO) mode shows Lorentzian lineshape. Such inactive coupling between the LO phonon and the plasmon in p-type GaN will be mainly attributed to heavy damping of the hole plasmon[20].

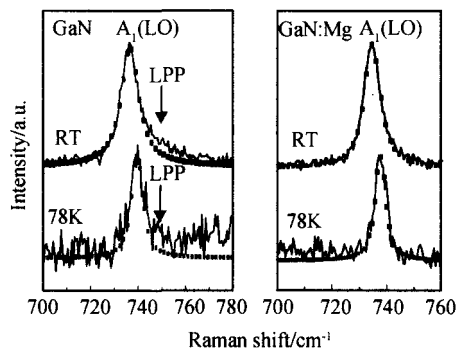

Fig. 5 Spectra of A_1(LO) mode at 78 K and room temperature The solid squares are the Lorentz fit data.

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(LO) mode always be found in some n-doped semiconductors, including GaN[8,21,22]. Furthermore, the intensity ratio of the unscreened LO phonon and the LPP mode depends on the carrier concentration and the exciting laser energy[23]. Two mechanisms are proposed in order 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[24]. For unintentionally doped GaN the carrier concentration is low, so the A_1 (LO) signal probably originates in the surface space-charge region where there are no free carriers.

4 Conclusion

In conclusion, undoped and Mg-doped GaN films on sapphire grown by MOCVD were investigated at low temperature. A peak at 247cm^{-1} was observed in both Raman spectra. Temperature-dependent Raman scattering experiment of Mg-doped GaN shows the frequency and intensity changes of this peak with temperature. We attribute it to the defect-induced vibrational mode. Furthermore, the differences of the host phonon peaks between the two spectra of undoped and Mg-doped GaN were analyzed. The frequency shift and asymmetric lineshape of E_2 and A_1 (LO) mode are explained by the electron-phonon interaction and phonon-plasmon-coupling, respectively.

References

[1] Kisielowski C, Krüger J, Ruvimov S, et al. Strain-related phenomena in GaN thin films. Phys Rev B, 1996, 54(24): 17745

[2] Smith M, Chen G D, Lin J Y, et al. Mechanisms of band-edge emission in Mg-doped p-type GaN. Appl Phys Lett, 1996, 68(14): 1883

[3] Wang T, Bai J, Sakai S, et al. Investigation of the emission mechanism in InGaN/GaN-based light-emitting diodes. Appl Phys Lett, 2001, 78(18): 2617

[4] 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(9): 1276

[5] 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(7): 909

[6] 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(3): 365

[7] Ramsteiner M, Menniger J, Brandt O, et al. Response to "Comment on 'Shallow donors in GaN studied by electronic Raman scattering in resonance with yellow luminescence transitions'". Appl Phys Lett, 1997, 70(7): 910

[8] Kozawa T, Kachi T, Kano H, et al. Raman scattering from LO phonon-plasmon coupled modes in gallium nitride. J Appl Phys, 1994, 75(2): 1098

[9] Zhang Rong, Yang Kai, Qin Linhong, et al. Optical property studies of GaN films grown by MOCVD. Chinese Journal of Semiconductors, 1997, 18(2): 91 (in Chinese) [张荣, 杨凯, 秦林洪, 等. MOCVD 生长的 GaN 膜的光学性质研究. 半导体学报, 1997, 18(2): 91]

[10] Tong Yuzhen, Zhang Guoyi. Micro-Raman-scattering spectra of GaN films. Chinese Journal of Semiconductors, 2000, 21(6): 554(in Chinese) [童玉珍, 张国义. GaN 薄膜的微区 Raman 散射光谱. 半导体学报, 2000, 21(6): 554]

[11] Siegle H, Kaczmarczyk G, Filippidis L, et al. Zone-boundary phonons in hexagonal and cubic GaN. Phys Rev B, 1997, 55(11): 7000

[12] Limmer W, Ritter W, Sauer R, et al. Raman scattering in ion-implanted GaN. Appl Phys Lett, 1998, 72(20): 2589

[13] Kaschner A, Siegle H, Kaczmarozyk G, et al. Local vibrational modes in Mg-doped GaN grown by molecular beam epitary. Appl Phys Lett, 1999, 74(22): 3281

[14] 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(10): 1383

[15] Kaschner A, Kaczmarczyk G, Hoffmann A, et al. Defect complexes in highly Mg-doped GaN studied by Raman spectroscopy. Phys Status Solidi B, 1999, 216: 551

[16] 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(1): 83

[17] 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(8): 4020

[18] Pophristic M, Long F H, Schurman M, et al. Raman microscopy of lateral epitaxial overgrowth of GaN on sapphire. Appl Phys Lett, 1999, 74(23): 3519

[19] Yu D V, Kitaev Yu E, Goncharuk I N, et al. Phonon dispersion and Raman scattering in hexagonal GaN and AlN. Phys Rev B, 1998, 58(19): 12899

[20] Harima H, Inoue T, Nakashima S, et al. Electronic properties in p-type GaN studied by Raman scattering. Appl Phys Lett, 1998, 73(14): 2000

[21] 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, 88(6): 3295

[22] 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(6): 631

[23] Cardona M, Güntherodt G. Light scattering in solids Ⅳ. Berlin: Springer, 1984: 114

[24] Kasic A, Schubert M, Saito Y, et al. Effective electron mass and phonon modes in n-type hexagonal InN. Phys Rev B, 2002, 65(11): 115206

GaN 和 p 型 GaN 薄膜中声子模和缺陷模的变温喇曼散射 *

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摘要: 研究了 MOCVD 生长的 GaN 及掺 Mg GaN 薄膜从 78 到 578 K 下的喇曼散射谱. 在 GaN 和掺 Mg GaN 的谱中都观察到一个位于 247cm^{-1}的峰, 此峰被认为是缺陷诱导的散射峰, 而非电子散射和 Mg 的局域模. 同时讨论了两个谱中 E_2 和 A_1(LO)声子峰的频率和线形. 在掺 Mg GaN 样品中观察到应力松弛现象.

关键词: GaN; p 型 GaN; 喇曼散射; 缺陷模

PACC: 7280E; 7830; 6320P

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