Temperature dependences of Raman scattering in different types of GaN epilayers*

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First-order Raman scatterings of hexagonal GaN layers deposited by the hydride vapour phase epitaxy and by metal-organic chemical vapour deposition on SiC and sapphire substrates are studied in a temperature range between 303 K and 503 K. The temperature dependences of two GaN Raman modes (A_1 (LO) and E_2 (high)) are obtained. We focus our attention on the temperature dependence of E_2 (high) mode and find that for different types of GaN epilayers their temperature dependences are somewhat different. We compare their differences and give them an explanation. The simplified formulas we obtained are in good accordance with experiment data. The results can be used to determine the temperature of a GaN sample.

Keywords: GaN, Raman scattering, temperature dependence

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1. Introduction

Due to its wide bandgap, large breakdown field and high mobility, gallium nitride is extremely attractive for an array of both high power and high frequency applications.[1−3] Of particular interest is the continued development of the AlGaN/GaN high electron mobility transistor (HEMT) that is capable of both large power density and fast switching speed.[4,5] Since the electronic performance of a device is limited only by the number of carriers and their ability to be transported, obviously the temperature will then be a major determinant in the performance of the HEMT device,[6] it is imperative that the temperature should be accurately measured and quantified during the operation of the device. The size of device is becoming smaller and smaller, so it is important to frame an approach capable of identifying even the smallest temperature gradients and has little or no effect on the device. The Raman spectroscopy can be used to nondestructively and accurately measure temperature with a high spatial resolution of nearly 1 μm, so for the temperature measurement of GaN devices, the Raman thermography is an ideal method. As a result, it is important to pay more attention to the relationship between Raman spectrum and temperature.

Although several papers dealing with this aspect have been published, the theoretical equations used in these papers are so complicated and strongly dependent on fitting parameters that they are not applicable to all samples generally.[7−11] Furthermore, up to now, there have been carried out few general studies of the Raman scattering spectroscopy of GaN grown by the hydride vapour phase epitaxy (HVPE). In this paper, we investigate the temperature dependences of the shift and the linewidth of GaN by using micro-Raman spectroscopy analysis, especially detailedly study the differences in shift and linewidth between different GaN epilayers with temperature increasing. Simplified formulas are obtained and are in good accordance with experimental results.

2. Experimental procedure

Three characteristic samples of hexagonal GaN films were used for the present study. Samples A and B were grown by metal–organic chemical vapour deposition (MOCVD) on sapphire and SiC substrates, respectively and sample C was grown by HVPE. The

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growth process of the MOCVD GaN initiated by a low temperature AlN (20 nm) nucleation layer. In the epitaxial growth stage, the pressure was kept at 5.3×10^3 Pa and the flow rates were kept constant at 1020 °C for the two samples. For the growth of HVPE GaN, GaCl formed by *in situ* reaction of HCl with Ga, was combined with NH_3, with V/III ratio 10. The HVPE film up to 300 μm in thickness was grown on a substrate at a temperature of 1040 °C. All GaN layers have a wurtzite structure with the c axis normal to the surface.

The micro-Raman measurements were carried out in backscattering geometry with the Raman spectrometer Jobin Yvon LavRam HR800. An argon laser of 514-nm wavelength was used as an excitation light source and a 50× objective was used to focus the incident laser light of a power of 14.2 mW on the sample. The spectrometer was calibrated using single-crystal silicon as a reference. Samples were measured at temperatures ranging from 303 K to 503 K in steps of 10 K by using a Linkam-Examina-THMS 600 heating stage. A curve-fitting program was used to fit the Raman spectra to determine the Raman frequencies and linewidths. The program allows peak to be fitted by using a combination of Lorentz and Gauss peak profiles and subtracting a background.

3. Results and discussion

In the hexagonal structure, group theory predicts eight sets of phonon normal modes at the Γ point, $2A_1+2E_1+2B_1+2E_2$. Among them, one set of A_1 modes and one set of E_1 modes are both acoustic, two B modes are silent, while the remaining four modes, $A_1+E_1+2E_2$, are Raman-active.[12] Furthermore, the polar modes, A_1 and E_1, their vibrations polarize the unit cell and create a long-range electrostatic field. This makes the A_1 and E_1 modes split into longitudinal optical (LO) and transverse optical (TO) modes.[13]

By back scattering from the c plane with no polarization detection, two E_2 phonon peaks (E_2 (low), E_2 (high)) and one LO phonon peak A_1 (LO) can be observed, as the Raman selection rules for the $z(-,-)\bar{z}$ geometry. The E_2 (high) and the A_1 (LO) modes are much stronger than E_2 (low), so we investigate the relations between these two phonon modes and temperature.

After all measurements are completed, we can readily observe in Fig. 1 that for any kind of sample the two Raman peaks both shift toward lower frequencies and broaden with temperature increasing.

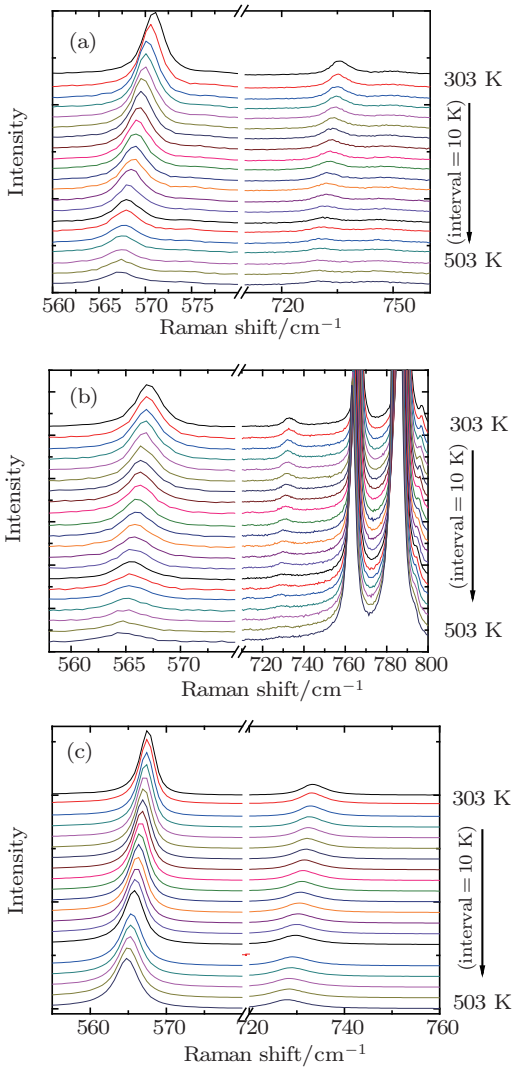


Fig. 1. (colour online) First-order Raman spectra recorded at temperatures varying from 303 K to 503 K in steps of 10 K: (a) GaN on sapphire substrate, (b) GaN on SiC substrate, (c) GaN grown by HVPE.

3.1. Raman frequency shift

The Raman shifts of the two Raman peaks are shown in Fig. 2 and the temperature dependency of

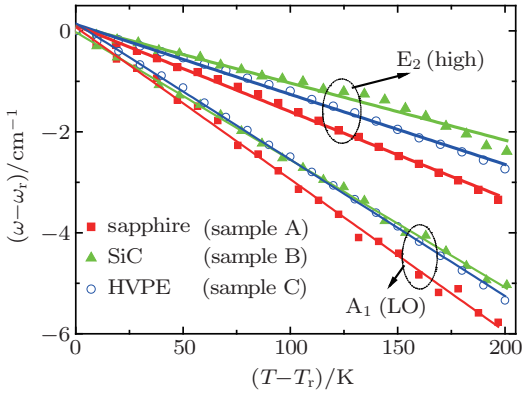


Fig. 2. (colour online) Raman shifts of GaN each as a function of temperature.

peaks are found to follow the expected linear trends. So, any change in the spectrum can be correlated to an equivalent change in temperature through fitting of these trends. The Raman shifts of the two modes at temperature T both can be well represented by

$$\omega = A(T - T_{\rm r}) + \omega_{\rm r}, \quad (1)$$

where $\omega_{\rm r}$ is the reference peak position measured at the reference temperature of $T_{\rm r}$. A is the calibration constant. This fitting parameters of the two Raman modes for different kinds of samples are listed in Table 1.

Table 1. Fitting parameters used in the least square fit of the Raman shift versus temperature for GaN.

	A/(cm^{-1}/K)	
	E_2 (high)	A_1 (LO)
Sample A	–0.01707±0.00020	–0.03014±0.00036
Sample B	–0.01131±0.00036	–0.02528±0.00021
Sample C	–0.01387±0.00020	–0.02701±0.00021

The temperature dependences of the phonon frequency and damping follow from anharmonic terms in the vibrational Hamiltonian of the crystal lattice.[14,15] Heating of the lattice results in a volumetric expansion of the lattice, then the restoring force of lattice vibration decreases. The change in interatomic force modifies the phonon vibrational frequency that, in turn, is reflected in the result of the phonon peak shifting toward lower frequency. If the lattice is cooled, the reverse case will occur. Besides the effect of thermal expansion, as the crystal is heated, the anharmonic interactions between phonons will increase, or, in other words, the phonon decay channel increases.[12] So, the Raman shift dependence on temperature can be written as a result of two factors, one is the change in vibrational frequency due to the thermal expansion of the lattice and the other is the decay of the optical phonon into phonons with lower energy. The temperature-dependent shift $\Delta\omega(T)$ of the phonon frequency $\omega(T)$ at temperature T relative to the frequency ω_0 in the perfect harmonic lattice can be written as

$$\Delta\omega(T) = \omega(T) - \omega_0 = \Delta\omega_{\rm e}(T) + \Delta\omega_{\rm d}(T), \quad (2)$$

where $\Delta\omega_{\rm e}(T)$ denotes the frequency shift due to the thermal expansion of the lattice and $\Delta\omega_{\rm d}(T)$ denotes the frequency shift due to the decay of the optical phonon into phonons with lower energy. In an isotropic approximation, the term $\Delta\omega_{\rm e}(T)$ is given by[7,14,15]

$$\Delta\omega_{\rm e}(T) = -\omega_0\gamma \int_0^T [\alpha_{\rm c}(\tilde{T}) + 2\alpha_{\rm a}(\tilde{T})]{\rm d}\tilde{T}, \quad (3)$$

where $\alpha_{\rm c}$ and $\alpha_{\rm a}$ are the temperature-dependent coefficients of linear thermal expansion parallel and perpendicular to the hexagonal c axis, respectively, and γ is the Gruneisen parameter. The term $\Delta\omega_{\rm d}(T)$ reads[16]

$$\Delta\omega_{\rm d}(T) = A[1 + 2n(T, \omega_0/2)] + B[1 + 3n(T, \omega_0/3) + 3n^2(T, \omega_0/3)], \quad (4)$$

where $n(T, \omega) = [\exp(\hbar\omega/k_{\rm B}T) - 1]^{-1}$ is the Bose–Einstein distribution function and A and B are constants.

Giehler *et al.*[8] reported that the phonon frequency shift is only weakly influenced by phonon scattering with temperature changing, so the effect of the decay of the optical phonon into phonons with lower energy can be omitted. For the values of the temperature-dependent expansion coefficients, we use $\alpha_{\rm c} = 3.17 \times 10^{-6}$ K^{-1} and $\alpha_{\rm a} = 5.59 \times 10^{-6}$ K^{-1}.[12] For Gruneisen parameters, we use $\gamma[{\rm E}_2\ ({\rm high})] = 1.8$ and $\gamma[{\rm A}_1\ ({\rm LO}) = 1.2$.[17,18] Then for E_2 (high) mode, equation (2) can be written as $\Delta\omega(T) = \Delta\omega_{\rm e}(T) = -0.0145T$, where we have used $\omega_0 = 560$ cm^{-1} that is calculated by Miwa and Fukumoto.[19]

From Table 1, we can see that the slopes of different kinds of samples are different. It is noted that the slope of sample C is close to the calculated value -0.0145, while sample A is much higher and sample B is much lower. The difference implies that the influence on temperature dependence of a third factor, the strain-induced contribution $\Delta\omega_{\rm s}(T)$ is not negligible due to the thermal mismatch between the substrate and the GaN layer. For sample A, GaN grown on sapphire substrate, there is tensile stress which will shift the E_2 (high) peak towards a lower wave number with temperature increasing due to the fact that the thermal expansion coefficient of sapphire is higher than that of GaN. So the influence of the strain-induced contribution is consistent with that of the thermal expansion of the lattice. And for the sample B, GaN grown on SiC substrate, the SiC substrate has lower thermal expansion coefficient than GaN, so the trend of the Raman shift dependence on temperature, induced by strain due to the thermal mismatch between the substrate and layer, is opposite. As a result, the shift of the Raman peak while increasing each 1 K of temperature of GaN grown on sapphire substrate is higher than that of GaN without substrate and the shift of GaN grown on SiC substrate is lower. This can be explained well with our experimental results.

For a simple estimate of $\Delta\omega_{\rm s}(T)$, we assume that the strain induced by the lattice mismatch between GaN layer and substrate is relaxed by the formation of dislocations at high growth temperature, which means that the residual strain $\varepsilon_{\rm g}$ at the growth temperature $T_{\rm g}$ is equal to zero. The temperature-dependent in-plane strain caused by the difference in thermal expansion coefficient between GaN and substrate can be written as[7]

$$\varepsilon_{\rm a}(T) = \frac{L_{\rm S}(T) - L_{\rm L}(T)}{L_{\rm L}(T)} = \frac{L_{\rm S}(T_{\rm g})[1 + \int_{T_{\rm g}}^{T} \alpha_{a,S}(\tilde{T})\mathrm{d}\tilde{T}] - L_{\rm L}(T_{\rm g})[1 + \int_{T_{\rm g}}^{T} \alpha_{a,L}(\tilde{T})\mathrm{d}\tilde{T}]}{L_{\rm L}(T_{\rm g})[1 + \int_{T_{\rm g}}^{T} \alpha_{a,L}(\tilde{T})\mathrm{d}\tilde{T}]}$$
$$= (1 + \varepsilon_{\rm g})\frac{1 + \int_{T_{\rm g}}^{T} \alpha_{a,S}(\tilde{T})\mathrm{d}\tilde{T}}{1 + \int_{T_{\rm g}}^{T} \alpha_{a,L}(\tilde{T})\mathrm{d}\tilde{T}} - 1, \quad (5)$$

where $\alpha_{\rm a,S}$ and $\alpha_{\rm a,L}$ are the temperature-dependent in-plain expansion coefficients of the substrate and the GaN layer, respectively. So we can obtain the relationship between $\Delta\omega_{\rm s}(T)$ and temperature due to the Poisson effect $\varepsilon_{\rm c} = \beta\varepsilon_{\rm a}$ ($\varepsilon_{\rm c}$ is out-of-plane strain) which reads

$$\Delta\omega_{\rm s}(T) = -\omega_0\gamma(2 + \beta)\varepsilon_{\rm a}. \quad (6)$$

We use for the Poisson effect of the GaN lattice $\beta = -2c_{13}/c_{33} = -0.5$, where c_{13} and c_{33} are the elastic stiffness constants.[17,20] The values of temperature-dependent expansion coefficient $\alpha_{\rm a}$ of sapphire and SiC are 7.5×10^{-6} K^{-1} and 4.2×10^{-6} K^{-1}, respectively.[21] Then the expressions $\Delta\omega_{\rm s} = -0.0029(T - T_{\rm g})$ for GaN grown on sapphire substrate and $\Delta\omega_{\rm s} = 0.0021(T - T_{\rm g})$ for GaN grown on SiC substrate are obtained.

The total temperature dependence of the phonon frequency can now be modified into $\Delta\omega(T) = -0.0174T + 0.0029T_{\rm g}$ for GaN of sapphire substrate and $\Delta\omega(T) = -0.0124T - 0.0021T_{\rm g}$ for GaN of SiC substrate. Comparing these values of slope of lines with the data listed in Table 1, we can find that the theoretical result is in good agreement with the experimental values, apart from the slope value of line for GaN grown on SiC substrate which is slightly larger than experimental result. The temperature-dependent frequency of the E_2 (high) mode can be used to derive the temperature of measured sample.

Moreover, the Raman shift of the A_1 (LO) phonon is not suited for the determination of the temperature of sample, which is generally acknowledged, because this polar longitudinal-optical mode, A_1 (LO) phonon, interacts with free carriers (plasmons). It may be affected by other factors, such as temperature-dependent carrier density and the plasmon damping.[7,22] So, this can also explain why there is a non-ignorable difference between the theoretical result of A_1 (LO) phonon obtained by using the method the same as that in calculating the E_2 (high) phonon and the experimental value. But it should be noted that the slope values of $\Delta\omega_{\rm s}(T)$ of GaN grown on sapphire substrate and GaN grown on SiC substrate obtained by Eq. (6) are -0.0025 and 0.0018, respectively, which are very close to the difference value (-0.0031) between sample A and sample C and the difference value (0.0017) between sample B and sample C, respectively. So, we can reach a conclusion that either for E_2 (high) mode or A_1 (LO) mode, the difference in slope value between lines of GaN on different substrates is induced primarily by stress in the GaN layer due to the difference in thermal expansion coefficient between GaN and substrate.

3.2. Linewidth of Raman peak

Besides the frequency shift of Raman spectrum, heating induces peak broadening. It is because anharmonic interactions between phonons will increase, which means that the decay of phonon increases and the scattering time of phonon decreases. It is well known that the measured linewidth of a Raman peak is inversely proportional to scattering time of the phonon mode.[6] So, as temperature increases, the likelihood of a scattering event increases, that is to say, phonon damping increases and the phonon lifetime is reduced which brings about the increase of the linewidth.

Figure 3 shows the temperature dependences of the linewidth of the E_2 (high) phonon for samples grown on different substrates. The temperature dependences of all samples are found to follow the parabolic trend. By other studies of temperature dependence of Raman scattering in GaN, peak broadening arises mainly from the phonon–phonon scattering, so the increase of the linewidth due to sample heating should be nearly the same.[7–9] But in our experiment, it is apparent that the increase of the linewidth of sample B is different from those of sample A and sample C. This is possibly because except the anharmonic interaction between phonons the scattering time of phonon can be influenced by a variety of factors including microstructural defects and material boundaries.[6] The difference in crystal quality results in the decrease of scattering time and the increase of linewidth. From Fig. 3, we can find that the fluctuation of the experimental data of heteroepitaxially grown GaN layers (sample A and sample B) is nonnegligible which is probably because of the inaccuracy of linewidth value introduced by the weak intensity and asymmetry

of peak with the rise of temperature. So, if we use the variation of linewidth to obtain the temperature, a large error may be produced.

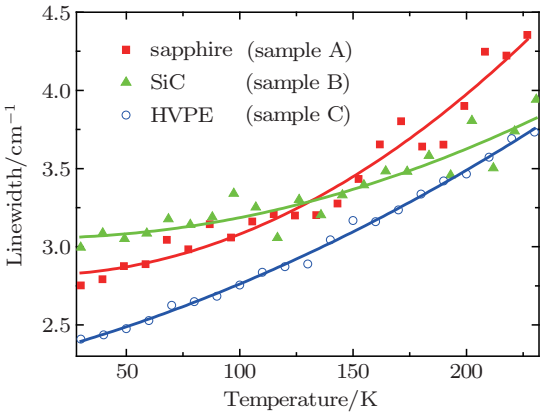


Fig. 3. (colour online) Linewidths of E_2 (high) phonon versus temperature for three samples.

4. Conclusions

We presented experimental results of the E_2 (high) and A_1 (LO) Raman peaks of hexagonal GaN films. The redshift of the Raman peak with sample heating is strongly influenced by the thermal expansion of the lattice and the stain due to the thermal mismatch between the substrate and the GaN layer. From this we simplify the theoretical equations and the agreement with the experimental data for E_2 (high) mode is satisfactory and for A_1 (LO) mode it is less satisfactory. The temperature dependence of linewidth has a parabolic trend, but the fluctuation of data is nonnegligible. As a result, the peak position of E_2 (high) is most suited to measure the temperatures of samples.

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