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Temperature dependence of biaxial strain and its influence on phonon and band gap of GaN thin film*

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Hexagonal GaN epilayer grown on sapphire substrate by metal organic chemical vapour deposition (MOCVD) is studied using Raman scattering and photoluminescence in a temperature range from 100 K to 873 K. The model of strain (stress) induced by the different lattice parameters and thermal coefficients of epilayer and substrate as a function of temperature is set up. The frequency and the linewidth of $E_2^{\rm high}$ mode in a GaN layer are modelled by a theory with considering the thermal expansion of the lattice, a symmetric decay of the optical phonons, and the strain (stress) in the layer. The temperature-dependent energy shift of free exciton A is determined by using Varshni empirical relation, and the effect of strain (stress) is also investigated. We find that the strain in the film leads to a decreasing shift of the phonon frequency and an about 10meV-increasing shift of the energy in a temperature range from 100 K to 823 K.

Keywords: biaxial strain, phonon, band gap, GaN
PACC: 7155G, 7210F

1. Introduction

GaN-based III-V nitride semiconductors have recently attracted extensive attention because of their wide direct band gap of ∼3.9 eV, high external photoluminescence quantum efficiency, and excellent chemical stability.[1−3] Although sapphire, SiC and even Si are the preferred substrate materials for GaN, heteroepitaxy leads to problems related to strain (stress). Wurtzite GaN grown on hetero-substrates with GaN or AlN buffer layers always suffers a certain quantity of in-plane biaxial strains because of the mismatch of the lattice constants and the thermal expansions coefficients between GaN(and /or AlN) and sapphire. The strain modulates the energy gap and the phonons of GaN films, which is supported by many researches.[4−10] A GaN–AlN superlattice grown by molecular beam epitaxy (MBE) has been studied by means of micro-Raman spectroscopy in Ref.[5]. The Raman spectra show that the modes of strained GaN layer all with a blue shift cannot correspond to the unstrained GaN. The presence of a build-in strain is proved to be the most plausible explanation to these shifts by examining the bevelled sample. The influence of stress in thin GaN films on the band gap has also been studied. In Ref.[6], the influence of strain caused by the thickness of AlN buffer layers on optical properties of GaN thin films was studied. Starting from 3.42 eV there is a linear correlation between luminescence shift and stress, which is independently determined by the x-ray and Raman measurements. And GaN films grown on different substrates and in different stress states were analysed in Ref.[7]. Showing that the coefficient of $\mathrm{d}E_{\rm PL}/\mathrm{d}\sigma$ was (21.1±3.2) meV/GPa. In this paper, the structural and optical properties of GaN thin film grown by metal organic chemical vapour deposition (MOCVD) is investigated in a temperature range from 100K to 873 K by Raman scattering and photoluminescence (PL). And temperature-dependent strain (stress) effects on the properties of the thin film is also analysed in the whole temperature range.

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2. Experiment

The sample used for the present study was an undoped GaN film grown by metal organic chemical vapour deposition (MOCVD) on the surface of a 20–25 nm thick AlN buffer layer on a sapphire (α-Al_2O_3) substrate. The thickness of the GaN film was about 2 μm, and the orientation of the c axis was normal to the surface of the film. No crack was found on the surface of the whole sample.

For micro-Raman measurements, Raman spectra were recorded in backscattering geometry using a Renishaw inVia Raman Spectrometer equipped with a 3000 l/mm gating. The 514 nm line of an Ar^+ laser was used as an excitation source, and the power of the laser on the sample was set to be 5 mW. The laser beam was focused by a microscope lens system, yielding a spot size of 1 μm and an excitation density of 50W/cm^2. Because both the GaN film and sapphire substrate are transparent, the temperature deviation due to laser heating is negligible. For PL measurement, the PL spectra were also acquired, using the same instrument as Raman spectrometer. PL spectra were excited with a 3.4 mW He–Cd laser working at 325 nm (3.82 eV), and the 1800l/mm UV gating was used in the experiment.

The sample was mounted on the THMS600 stage. The temperature varied between 77 K and 873 K by using liquid nitrogen as a coolant or by electrically heating the block. The temperature was measured by TS1500 controller within an accuracy of better than$\pm$1 K.

The frequencies and linewidths (full widths at half maximum) of the phonon modes were determined by fitting Lorentzian line shapes to the measured Raman lines. And the PL spectra were fitted by Gauss peak profiles to obtain the energy positions.

3. Theory

3.1. The calculation of temperature-dependent strain in the GaN epilayer

There exist a considerable lattice mismatch and a thermal mismatch between the sapphire substrate and the GaN and AlN layers, respectively. There are two sources resulting in the stress (or strain) between the epilayer and substrate: lattice parameters (intrinsic stress) and thermal coefficients (thermal stress) of epilayer and substrate. The intrinsic stress is built in film during sample cooling from a deposition temperature to room temperature after growth, which can overcompensate for the lattice constant mismatch in this case. Although the GaN or the AlN buffer reduces the strain to some extent, wurtzite GaN grown on sapphire substrates with GaN or AlN buffer layers always suffers a certain quantity of in-plane biaxial strains because the buffer layer is too thin (20–25 nm) to reduce all the stresses after growth. And the different thermal expansion coefficients of layer and substrate result in a temperature-dependent in-plane thermal stress. The analysis shows that the thermal stress between the epilayer and the substrate plays a major role in determining the strain in film.[7] The assumption is made that during the growth at high temperatures, the strain in the layer, induced by the large lattice mismatch between layer and substrate, is greatly relaxed with the formation of dislocation near the interface between layer and substrate. The temperature-dependent strain can be described as

$$\begin{aligned}\varepsilon(T) =& \frac{L_{\rm S}(T) - L_{\rm L}(T)}{L_{\rm L}(T)} \\ =& (1+\varepsilon_{\rm g}) \frac{1 + \int_{T_{\rm g}}^{T} \alpha_{\rm a,S}(T'){\rm d}T'}{1 + \int_{T_{\rm g}}^{T} \alpha_{\rm a,L}(T'){\rm d}T'} - 1, \end{aligned} \quad (1)$$

where $\alpha_{\rm a,S}$ and $\alpha_{\rm a,L}$ are the temperature-dependent in-plane linear expansion coefficients of the substrate (S) and the layer (L) respectively;[11] $L_{\rm S,L}(T) = L_{\rm S,L}(T_{\rm r})[1 + \int_{T_{\rm g}}^{T} \alpha_{\rm a,S,L}(T'){\rm d}T'$ denote the temperature-dependent lengths of the substrate and layer respectively; $\varepsilon_{\rm g}$ is the residual strain in the layer, calculated from the Raman spectra at the growth temperature $T_{\rm g}$, which is neglected according to the assumption above.

Raman spectrum is widely used to determine a strain state. In the linear approximation, the frequency deviation of a given phonon mode γ under a symmetry-conserving stress can be expressed in terms of the biaxial strain ε_{xx} as follows:

$$\Delta\omega_\gamma(T) = K_\gamma \varepsilon_{xx}(T). \quad (2)$$

The $E_2^{\rm high}$ mode in the Raman spectra is used for examining the stress states in GaN layers because it has been proven to be particularly sensitive to biaxial stress in GaN epifilm.[12] Owing to the difference in pressure coefficient, the frequency shift for the A_1

(LO) phonon with a greater uncertainty is found to be lower than for the $E_2^{\rm high}$ phonon. So in this paper, $E_2^{\rm high}$ mode is used to describe the change of strain. For the linear stress coefficient K_γ, its value varies with the differences in substrate and process.[7,13]

The theoretical linear stress coefficient K_γ is obtained as

$$K_\gamma = 2\left(a - b\frac{C_{13}}{C_{33}}\right), \tag{3}$$

where the phonon deformation potentials a and b are defined in Ref.[14], and the C_{ij} are the elastic constants for GaN given in Ref.[15]. Compressive stress will result in an increase of the Raman frequency, while tensile stress results in a decrease.

The in-plane stress σ_{xx} of the GaN layer can be obtained from the following equation:

$$\sigma_{xx} = \left[C_{11} + C_{12} - 2\frac{C_{13}^2}{C_{33}}\right]\varepsilon_{xx}, \tag{4}$$

where the C_{ij} are the elastic constants for GaN given in Ref.[15].

3.2. Temperature dependence of the phonon frequency of GaN epilayer

The temperature dependence of the phonon frequency and damping arise from anharmonic terms in the vibrational Hamiltonian of the crystal lattice.[16,17] The anharmonicity gives rise to the thermal expansion of the lattice and to the phonon-phonon interaction. The Raman shift dependence on temperature can be written as a result of two additive effects: one is the change in the vibrational frequency due to thermal expansion or volume change, and the other is the effect due to anharmonic coupling to phonons of other branches. The temperature-dependent Raman shift of phonon can be written as[16,17]

$$\omega(T) = \omega_0 + \Delta\omega_{\rm e}(T) + \Delta\omega_{\rm d}(T), \tag{5}$$

where ω_0 is the harmonic frequency of the optical mode, $\Delta\omega_{\rm e}(T)$ is the thermal-expansion contribution to the shift, and $\Delta\omega_{\rm d}(T)$ is the effect due to anharmonic coupling. In an isotropic approximation, the term $\Delta\omega_{\rm e}(T)$ is given by

$$\Delta\omega_{\rm e}(T) = -\omega_0\gamma\int_0^T [\alpha_{\rm c}(T') + 2\alpha_{\rm a}(T')]{\rm d}T', \tag{6}$$

where $\alpha_{\rm c}(T)$ and $\alpha_{\rm a}(T)$ are the temperature-dependent coefficients of linear thermal expansion parallel and perpendicular to the hexagonal c axis respectively,[18] and γ is the Grüneisen parameter for the optical Raman mode.

Taking into account cubic and quartic terms in the anharmonic Hamiltonian and considering only symmetric decays of the zone-centre phonons into two phonons (a third-order process) and three phonons (a fourth-order process) with frequencies of $\omega_0/2$ and $\omega_0/3$ respectively, the anharmonic coupling term $\Delta\omega_{\rm d}(T)$ can be modelled as[16,17]

$$\begin{aligned}\Delta\omega_{\rm d}(T) =& A[1 + 2n(T, \omega_0/2)] + B[1 + 3n(T, \omega_0/3) \\ &+ 3n^2(T, \omega_0/3)],\end{aligned} \tag{7}$$

where A and B are constants selected as fitting parameters, and $n(T, \omega) = [\exp(\hbar\omega/k_{\rm B}T) - 1]^{-1}$ is the Bose-Einstein distribution function. The first term on the right-hand side of Eq.(7) couples the optical phonon to two phonons (a third-order process), while the second term represents the higher order process that couples it to three phonons (a fourth-order process).

There are a considerable lattice mismatch and a thermal mismatch between the sapphire substrate and the GaN and AlN layers respectively. This leads to a further strain-induced contribution $\Delta\omega_{\rm S}(T)$ to the phonon shift. As mentioned above, the frequency shift is obtained as

$$\Delta\omega_{\rm S}(T) = 2\left(a - b\frac{C_{13}}{C_{33}}\right)\varepsilon(T), \tag{8}$$

The total temperature dependence of the phonon frequency can now be written as

$$\omega(T) = \omega_0 + \Delta\omega_{\rm e}(T) + \Delta\omega_{\rm d}(T) + \Delta\omega_{\rm S}(T), \tag{9}$$

Similarly, the Raman linewidth can be modelled as[16]

$$\begin{aligned}\Gamma(T) =& \Gamma_0 + C[1 + 2n(T, \omega_0/2)] \\ &+ D[1 + 3n(T, \omega_0/3) + 3n^2(T, \omega_0/3)],\end{aligned} \tag{10}$$

where $n(T, \omega)$ is determined in Eq.(7). C and D are treated as fitting parameters. Equation (10) is similar to Eq.(7), with the first term corresponding to a third-order process (decay into two phonons), and the second term to a fourth-order process (decay into three phonons).

3.3. Temperature dependence of the energy gap of GaN epilayer

The energy gap temperature dependence is usually described by the Varshni equation[19]

$$E_{\rm g} = E_0 - \frac{\alpha T^2}{T + \beta}, \tag{11}$$

where E_0 is the energy gap at 0 K; β is sometimes associated with the Debye temperature; α is an empirical constant.

It is known that the energy band gap of a semiconductor is affected by the residual strain in film. A tensile stress will result in a decrease of energy band gap while a compressive strain causes an increase of the band gap. And the energy gap is linear with the strain (stress) in epifilm.[6] Concerning the strain in film, the temperature-dependent energy gap can be written as

$$E_{\rm g} = E_0 - \frac{\alpha T^2}{T+\beta} + k\sigma_{xx}(T), \qquad (12)$$

where k is defined as the linear strain coefficient. We adopt k=21 meV/GPa from Ref.[7], which is in agreement with (21±5) meV/GPa from Ref.[6].

4. Results and discussion

Figure 1 shows the typical observed temperature-dependent Raman spectrum of GaN epilayer grown by MOCVD. Consistent with the results in Ref.[20]. both $E_2^{\rm high}$ and A_1 (LO) modes of GaN are observed. The bulge of trailing edge of A_1 (LO) peak and the 418 $\rm cm^{-1}$ peak correspond to the $E_{\rm g}$ mode (750 $\rm cm^{-1}$) and $A_{1\rm g}$ mode (417 $\rm cm^{-1}$) of sapphire respectively.[21] With temperature increasing, Raman peaks shift toward lower frequencies and broaden.

The measured temperature-dependent Raman shifts of $E_2^{\rm high}$ phonon are presented in Fig.2. Excellent fitting is obtained by expression (9) for Raman frequency as a function of temperature. The fitting parameters used here are listed in Table 1. The frequency ω_0 of the perfect harmonic lattice is not directly available in experiment, for the phonon decay results in a reduction of the frequency even at T=0 K. The observed phonon shift is a superposition of the intrinsic (bulk) temperature dependence and a contribution arising from a thermal expansion mismatch with the substrate. The contribution of the strain that is shown in dot line is separated from that of intrinsic (bulk) temperature dependence. It can be seen that with the temperature increasing, the strain leads to a decreasing shift of the phonon frequency. So there is no ground to neglect the strain-induced contribution in our fitting. And the contribution of strain is reduced with the temperature increasing for GaN, showing the same behaviour as that for E_2 mode of AlN in Ref.[22]. This is because whether compressive stress exists in SA substrate or tensile stress in SiC substrate or not, the biaxial stress magnitude is reduced with temperature increasing, which has also been verified by the PSI measurement.[13] Since $\Delta\omega_{\rm s}(T)$ is only an estimate of the strain-induced frequency shift, only biaxial strain effects are taken into account, but other possible contributions, such as hydrostatic strain arising from point defects are not considered.

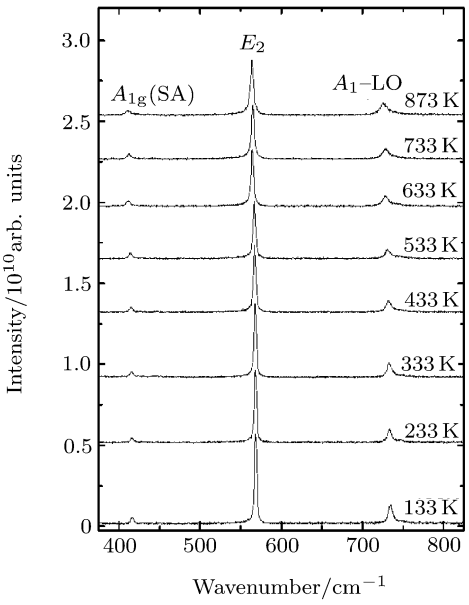


Fig.1. Temperature-dependent Raman spectrum of GaN epilayer.

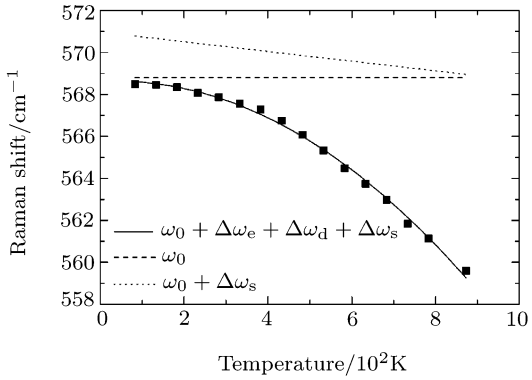


Fig.2. Raman shift of $E_2^{\rm high}$ mode of GaN as a function of temperature (solid line), together with ω_0 (dash line) and strain contribution to the shift $\omega_0+\Delta\omega_{\rm e}(T)+\Delta\omega_{\rm d}(T)$ (dot line).

The temperature-dependent linewidth of the $E_2^{\rm high}$ mode of GaN is shown in Fig.3, which is fitted by Eq.(10). The values of the fitting parameters Γ_0, C and D are given in Table 1. The linewidth increases as the temperature increases, and the linewidth of the A_1 (LO) phonon is always larger than of the $E_2^{\rm high}$ phonon. This is possible because there are more channels for the decay of the A_1 (LO) phonon than of the $E_2^{\rm high}$ phonon. And even the data of the temperature-dependent frequency of the $E_2^{\rm high}$ phonon have been used to derive a calibration curve which returns the temperature of a GaN layer as a function of the relative shift of the $E_2^{\rm high}$ frequency with respect to the frequency at the room temperature.[22]

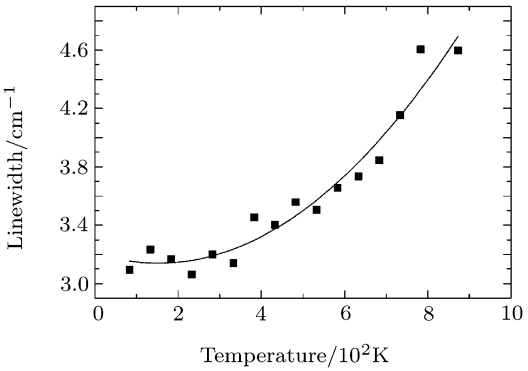


Fig.3. Temperature dependence of the linewidth of the $E_2^{\rm high}$ mode of GaN. The solid line represents the best fits obtained by Eq.(10).

Table 1. Parameters for fitting the Raman shift and the linewidth of GaN by Eqs.(9) and (10).

Mode	γ	ω_0/cm^{-1}	A/cm^{-1}	B/cm^{-1}	Γ_0/cm^{-1}	C/cm^{-1}	D/cm^{-1}
E_2	1.47[a]	568.7	0.51	–0.09	3.2	–0.03	0.002

[a] from Ref.[23].

The typical PL spectra recorded at a low temperature (100K) are shown in Fig.4, together with the result of a fit to the spectra. According to Ref.[24], six transitions are obtained, that is, the LO replica of the A (A-2LO) 3.33 eV and (A-LO) 3.39 eV, the phonon replica of donor bound exciton (I_2-LO) 3.36 eV, neutral donor bound recombination (I_2) 3.41 eV, free A exciton (A) 3.43 eV and free B exciton (B) 3.44 eV. The yellow luminescence band at 2.3 eV is beyond our measurement.

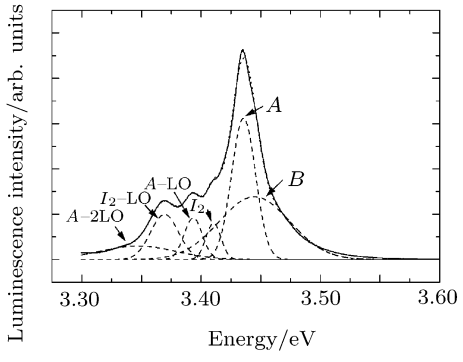


Fig.4. The typical PL spectra recorded at a low temperature (100 K), together with the result of a fit to the spectra. The dash lines represent the contributions of different transitions in the process of luminescence, and the dot line denotes the fitting result.

Figure 5 shows the typical PL spectra of an undoped GaN layer grown by MOCVD, as a function of temperature. We focus attention on the temperature dependence of free exciton A ($\Gamma_9^{\rm V} - \Gamma_7^{\rm C}$), which is shown in Fig.6, and the changes of other transitions are beyond our discussion. As the temperature increases, the PL spectra are red-shifted, less intense and broadened. The experimental data are fitted by Eq.(12), and the fitting parameters are $E_0^{\rm A}$=3.440 eV, α=6.5×10^{-4} eV/K, and β=3500 K, which are not far from the parameters of $E_0^{\rm A}$=3.486 eV, α=8.32×10^{-4} eV/K, and β=835.6 K obtained by PR spectra from Ref.[25]. The $E_0^{\rm A}$ and the strain (stress) contribution are also shown in Fig.6. With the temperature increasing, the stress leads to the increasing shift of the energy, resulting in the compressive stress mentioned above, which is about 10 meV in a temperature range from 100 K to 823 K.

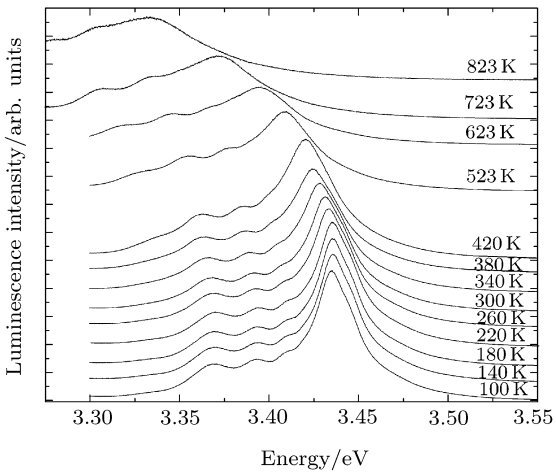


Fig.5. Typical temperature dependence of the luminescence spectra of undoped GaN layer grown by MOCVD.

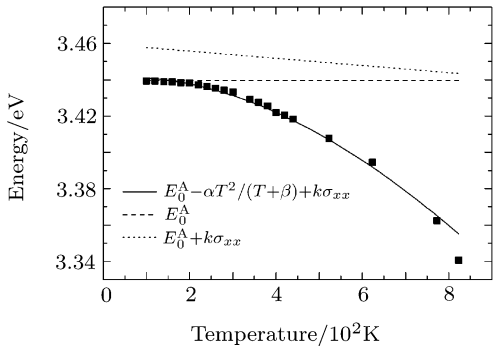


Fig.6. Temperature dependence of free A transition, where the solid line represents the fitting by Eq.(12), the dash line denotes $E_0^{\rm A}$, and the dot line refers to the strain (stress) contribution to the energy shift.

5. Summary

In this paper, the experimental results on the temperature variation of the Raman and PL spectra of GaN epilayer on the sapphire substrate have been presented. And the mode describing the temperature-dependent biaxial strain (stress) between the GaN layer and sapphire substrate has been set up. The Raman shift of $E_2^{\rm high}$ mode and energy shift of free exciton A as a function of temperature is analysed. And the contribution of strain (stress) is discussed in the whole temperature range.

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