Epitaxial strain energy measurements of GaN on sapphire by Raman spectroscopy

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This study reports a non-destructive method of measuring the residual strain in the GaN epilayer grown on sapphire substrate by micro-Raman spectroscopy. Operating in confocal mode this method allows a depth-dependent measurement of residual strain in the epitaxial layer without prior treatment of the sample. This approach to measurement of residual strain is demonstrated on GaN epitaxial films grown by both MOCVD and H-MOVPE. In the case of MOCVD grown films, the biaxial strain energy was found to vary from 0 (GaN surface) to 5.0 kJ/mole (GaN/sapphire interface), but in the case of H-MOVPE grown samples the strain energy varied from 6.5 kJ/mole - hydrostatic strain (GaN surface) to 25.0 kJ/mole - biaxial strain (GaN/sapphire interface), indicating that the surface layer of the N-terminated H-MOVPE material is not free from strain. Estimates are given for the curvature of substrate, lattice parameter of epitaxial layer, and the interface shear modulus.

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1 Introduction

There is considerable interest in the growth of high structural quality GaN epitaxial films for optoelectronic and electronic devices. GaN epitaxial layers grown on the commercially available substrates such as sapphire, however, contain residual strains produced by mismatch in the lattice constants and thermal expansion coefficients between the GaN film and substrate [1]. Sufficient residual strain in the film will induce formation of dislocations and stacking faults, which degrade device performance. Residual strain also leads to wafer bowing, making device processing more difficult. Thus a method to non-destructively measure residual strain is important.

Raman spectroscopy is well established as a non-destructive and relatively rapid method to determine the averaged values of residual strain. Strain energy profiles have been measured by using multiple samples of different thicknesses or probing a sample with variable absorption characteristics (e.g., variable excitation wavelength, confocal optics.) Given potential run-to-run variations in the sample strain state, the latter approach is preferred. The Raman shift of the GaN E_2 mode has been reported by several groups, and the reported values vary in the relatively large range 565 to 572 cm^{-1} [2, 3], reflecting differences in the residual strain in the epilayer after growth and thus the sensitivity of the method. The reported shifts of the E_2 mode for freestanding GaN samples, however, show the relatively wide range 566–568 cm^{-1} [2–5], suggesting that freestanding GaN films grown by HVPE techniques usually contain high impurity levels, resulting in hydrostatic stress. The E_2 mode of strain-free GaN is known to be 567.6 cm^{-1} at room temperature [6]. The curvature of the substrate is also related to the strain in the film

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and is usually measured by laser interference or stylus profiling technique. Raman spectroscopy can be used as a versatile technique to measure the curvature of the substrate, and it provides a measurement that is insensitive to the surface roughness, as compared to the other techniques.

In this study, Raman spectroscopy was utilized to measure the residual strain in the epilayer, the curvature of the substrate, and the lattice parameters of the epilayer. Stoney's equation [7] was used to calculate the curvature of the substrates, and Shen's approach [8] was used to estimate lattice parameters and elastic compliances. Frank-van der Merwe's thick overgrowth model [9] was then applied to the MOCVD grown sample to check the validity of the assumption of isotropic strain by comparing the calculated shear modulus at the GaN/sapphire interface with those of the bulk crystals. Finally, the measured strain energy was added to the Gibbs energy of formation of GaN, and the lowering of the GaN decomposition temperature was thereby predicted. The corrected decomposition temperature can guide the practical maximum annealing temperature of GaN thin films.

2 Experimental

GaN epilayers were grown by metalorganic chemical vapor deposition (MOCVD) and a novel growth method that combines hydride vapor phase epitaxy with MOCVD (H-MOVPE). For MOCVD growth TEGa (triethylgallium) and NH_3 were used as source in a N_2 carrier gas, and the films were grown at 850 °C, a reactor pressure of 76 Torr, and an inlet N/Ga molar ratio of ~3000. The thickness of MOCVD grown GaN was measured by cross-sectional SEM to be ~1.0 μm . H-MOVPE is an approach that reacts a organometallic (trimethylgallium in this study) with HCl to supply volatile GaCl, which then reacts with NH_3 downstream to form GaN. The detailed description of H-MOVPE and its operation conditions is given elsewhere [10]. The samples for this study were grown at 900 °C, atmospheric pressure, and an inlet N/Ga ratio of 125. The HCl/Ga ratio was set to 2 to provide optimum film quality and scavenge gas phase metallic residuals. The thickness of H-MOVPE grown GaN was also measured by cross-sectional SEM and it was ~3.2 μm .

The depth-dependent Raman measurements of MOCVD and H-MOVPE deposited GaN films were made using a Renishaw System-2000 in confocal mode. The laser output power was set at 20 mW with an excitation wavelength of 514.5 nm. The focused beam size was approximately 2 μm , accumulation time was 10 sec, and a CCD detector was employed. By controlling the slit width and CCD pixel size, the signals from different depth could be separated.

3 Theoretical

The relation between the film stress and substrate curvature (κ) is well known and given by Stoney's equation, $\kappa = 6\sigma_f h_f / (M_s h_s^2)$ [7]. In this expression, σ_f is the biaxial stress in the film, h_f , h_s are the thicknesses of the film (3.2 μm : H-MOVPE, 1.0 μm : MOCVD) and substrate (300 μm : sapphire), respectively. M_s is the substrate biaxial modulus, which is 602 GPa for sapphire [11].

Shen et al. [9] recently developed equations for hexagonal GaN epitaxial thin films assuming isotropic strain of epitaxial film. These equations predict the changes in strain energy of the film with respect to the growth plane for the case when the planes of film growth and the underlying substrate are both hexagonal. Substituting and rearranging the original equation gives:

$$a(\text{\AA}) = a_0 - a_0 \{ (s_{11} + s_{12}) E_s \}^{0.5}. \quad (1)$$

The range in the reported values for the elastic compliances in Eq. (1) are $s_{11} = 0.00297$ to 0.00502 and $s_{12} = -0.00066$ to -0.00121 GPa^{-1} [6, 12–14]. In this work the range-centered values $s_{11} = 0.003995$ and $s_{12} = -0.000935$ were selected. The values of a_0 are the unstrained GaN lattice parameters (3.189 $\text{\AA}$ for MOCVD and 3.067 $\text{\AA}$ for H-MOVPE films) and a is the lattice parameter of the strained GaN epilayers.

Frank-van der Merwe's thick overgrowth model was used to estimate the MOCVD grown GaN/sapphire interface shear modulus. The total strain energy per atom, E_s , of epilayer containing misfit dislocations and periodic elastic strains, is expressed as [9]:

$$E_s = \frac{G_i c^2}{4\pi^2 d} \left[\underbrace{\frac{1 + \lambda - \sqrt{1 + \lambda^2}}{E_i = \text{Interface Energy}}}_{E_i = \text{Interface Energy}} - \underbrace{\left\{ 1 + \frac{G_b(1 - \nu_a)}{G_a(1 - \nu_b)} \right\}^{-1} \lambda \ln(2\lambda\sqrt{1 + \lambda^2} - 2\lambda^2)}_{E_f^s = \text{Strain Energy in the Film}} - \underbrace{\left\{ 1 + \frac{G_a(1 - \nu_b)}{G_b(1 - \nu_a)} \right\}^{-1} \lambda \ln(2\lambda\sqrt{1 + \lambda^2} - 2\lambda^2)}_{E_s^s = \text{Strain Energy in the Substrate}} \right], \quad (2)$$

where $\lambda = \frac{4\pi}{G_i} \left\{ \frac{G_a G_b}{G_a(1 - \nu_b) + G_b(1 - \nu_a)} \right\} \left(\frac{b - a}{b + a} \right)$ is misfit, G_i is the shear modulus at the interface, $d \approx c$

is the separation of the atoms of the crystal planes, and $c = 2ab/(a + b)$. The lattice parameters of substrate and film are a and b , respectively. G_a and G_b are the shear moduli of substrate and film and ν_a and ν_b are Poisson's ratio for the substrate and film, respectively.

4 Results and discussion

Fig. 1 shows the measured Raman shifts of GaN E_2 mode of MOCVD and H-MOVPE grown epilayers at varying depths from the surface. In the case of MOCVD grown films, the E_2 peak was found to vary from 568 cm^{-1} (GaN surface) to 569 cm^{-1} (GaN/sapphire interface). In the case of H-MOVPE grown samples, however, the E_2 peak varied from 570 cm^{-1} (GaN surface) to 575 cm^{-1} (GaN/sapphire interface). This indicates that the surface of H-MOVPE grown epilayer was not free from hydrostatic strain, whereas MOCVD grown film contained no residual strain at the surface.

Fig. 1 Raman shift (E_2 mode) depth profile of MOCVD and H-MOVPE grown GaN layers.

It is known that a biaxial stress of 1 GPa shifts the E_2 Raman mode by $2.7 \pm 0.3 \text{ cm}^{-1}$ [4], and a hydrostatic stress of 1 GPa shifts it by 4.17 cm^{-1} [15], thus these values were used to calculate strain energy of the epilayer. The hydrostatic component of the strain energy was neglected when calculating the strain energy of the MOCVD sample. The H-MOVPE grown sample, however, contained sufficient impurity so the hydrostatic component was counted. The curvature radius of the sapphire substrate at the thick H-MOVPE film/sapphire interface was estimated to be 1.5 m and thus substrate bowing is expected by the Stoney's equation. The calculated results by Eq.(1) for H-MOVPE sample are tabulated in Table 1.

Table 1 Strain energy and lattice parameter of the H-MOVPE sample with depth

Depth from the surface [μm]	Strain energy [GPa]	Lattice parameter [$\text{\AA}$]
0–0.6	0.48 (hydrostatic)	3.067 ± 0.030
	0 (biaxial)	
1.5	0.37 (biaxial)	2.964 ± 0.025
3.2 (interface)	1.85 (biaxial)	2.836 ± 0.056

For the MOCVD sample, the strain seems to release quickly, so only interface was measured to contain residual stress (0.37 GPa). Frank-van der Merwe's thick overgrowth model was used to calculate the interface shear modulus, since the stress was small near the interface and the surface was strain-free. The value of G_i can be calculated from Eq. (3), as the total strain energy of the interface is measured by Raman peak shift. In this system, the values $G_a = 1.38 \times 10^{11}$ Pa, $G_b = 1.01 \times 10^{11}$ Pa, $\nu_a = 0.2224$, $\nu_b = 0.2578$ [12], $a = 2.747$ Å, $b = 3.189$ Å, and $E_s = 0.37$ GPa were used to calculate the interface shear modulus of MOCVD sample. The estimated G_i is 0.14×10^{11} Pa which implies that the MOCVD interface is much less rigid than the overlying GaN layer and the sapphire substrate.

The measured strain energy of MOCVD grown GaN/sapphire interface (0.37 GPa = 5.0 kJ/mole) was used to correct the formation Gibbs energy of GaN, and the decomposition temperature of GaN was calculated using the ThermoCalc Software. The thermochemical data of unstrained GaN were taken from the work of Davydov et al. [16]. The decomposition temperature of MOCVD GaN with residual strain was found to be 1011 K at the interface, which is lower than the unstrained GaN (1055 K). Kumar et al. [17] observed that the GaN/sapphire interface begins to be heavily damaged on annealing the substrate, which suggests that the decomposition initiates at the interface. The result of this study agrees qualitatively with Kumar's observation.

5 Summary

Strain energy in the GaN epilayer on sapphire was measured by micro-Raman Spectroscopy. Depth profiling in confocal mode was demonstrated to be a versatile and non-destructive approach for depth dependent stress and curvature measurement. The strain energy at MOCVD grown GaN/sapphire interface was estimated to be 5.0 kJ/mole. Significant curvature was calculated by Stoney's equation for H-MOVPE sample. Shen's approach was utilized to calculate lattice constants of strained films, and Frank-van der Merwe's thick overgrowth model was used to calculate the shear modulus of the MOCVD grown GaN/sapphire interface. Finally the decomposition temperature of GaN was estimated and temperature lowering was predicted at the GaN/sapphire interface.

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