On the stress relaxation mechanism of GaN thin films grown on Si(111) substrates

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Abstract. Gallium nitride (GaN) thin films grown on Si(111) substrates via plasma-assisted molecular beam epitaxy were investigated. The morphology of GaN films was studied by scanning electron microscopy. It was found that GaN films at nanoscale contain a large amount of cavities. The Raman measurements of GaN/Si(111) system were performed and showed that the position of the GaN E₂(LO) band is close to that of unstrained GaN. We proposed a stress relaxation mechanism to explain the low stress state of GaN films.

1. Introduction
Gallium nitride (GaN) thin films have been the object of intensive study for decades because of their potential applications in electronics and optoelectronics. At present, high electron mobility transistors, light-emitting diodes, detectors of ultraviolet radiation have been fabricated based of GaN thin films. The epitaxial growth of GaN thin films on silicon substrates is particularly of great interest due to the availability of high-quality silicon substrates of large size. Moreover, the use of nonpolar silicon substrates allows the growth of N- and Ga-polar GaN films. The main problem of GaN film growth on silicon is the thermal mismatch. As a result, the maximal thickness of crack-free GaN film on Si(111) is usually less than 1 μm [1].

Raman spectroscopy has been extensively used for studying stress in GaN thin films [2–4]. The mechanical stress in thin films is an important factor because it can influence the energy band structure and vibrational properties. The sensitivity of the E₂ (TO) phonon frequency to strain allows the finding of stress in thin films. The method used in paper [3] for finding the Raman stress factor of GaN thin film on Si(111) is as follows. Firstly, the micro-Raman measurements in the vicinity of a crack in the GaN film were performed. As a result, the dependence of the E₂ (TO) phonon frequency on the distance from the crack was found. The residual stress was evidenced by the red shift of the E₂ (TO) phonon frequency with respect to the value of ω₀. This value was obtained by measuring of the Raman spectra of bulk GaN. Secondly, the shear-lag model was used to calculate theoretically the biaxial stress field in the vicinity of a crack, namely, the dependence of the σxx component of stress tensor on the distance from the crack. Thirdly, the Raman stress factor K was found by comparison of these two dependencies. As a result, the following formula was obtained:

$$\Delta \omega = K \sigma_{xx} \text{cm}^{-1} \text{GPa}^{-1},$$

(1)
where $\Delta \omega = \omega_0 - \omega$ and $\omega$ is the $\text{E}_2$ (TO) phonon frequency of GaN thin film on Si(111). The sign of $\Delta \omega$ indicates whether the stress in a film is tensile (the sign is positive) or compressive (the sign is negative).

In this paper, we continue the series of works [4–6] devoted to investigation of the growth mechanism and physical properties of GaN thin films grown on Si(111) substrates via plasma-assisted molecular beam epitaxy (PA-MBE). We study the morphology of GaN films that at nanoscale contain cavities by scanning electron microscopy (SEM). In order to characterize a stress state of these GaN films Raman microscopy is used.

2. Experiment

The GaN thin films were grown on semi-insulating Si(111) substrates ($R > 10000 \ \Omega \ cm$) by PA-MBE using Veeco Gen 200 setup. The high-frequency plasma source (13.56 MHz) RFN 50/63 (Riber) was used to activate nitrogen. The Si(111) substrates were chemically cleaned by the Shiraki method and annealed in the growth chamber at the temperature of $\sim 850 \ ^\circ C$ for 30 min to remove the oxide layer and form the Si(111)7x7 surface reconstruction. Then, the Si(111) substrates were nitrided for 30 min at the temperature of $\sim 850 \ ^\circ C$ with a fixed Ga flux corresponding to the GaN equivalent growth rate of $0.1 \ \mu m/h$. The GaN thin films were grown at the temperature of $\sim 700 \ ^\circ C$, the material fluxes were equal to $F_{\text{Ga}} = 0.5 \ ML/s$ and $F_{\text{N}} = 0.1 \ ML/s$, respectively, for gallium and nitrogen. The reflection high-energy electron diffraction (RHEED) was used to monitor the growth process.

The morphology of GaN films was investigated by SEM (Figure 1). It is seen that the GaN films at nanoscale contain a large amount of cavities with the surface density of $\sim 20 \ \mu m^{-2}$. These cavities widen at the distance of $\sim 60 \ nm$ from the GaN top surface. The depth of the cavities often equals to the thickness of GaN layer as seen on the cleavage surfaces. Such a structure of the GaN films is likely a result of the coalescence of nanocolumns that were observed at the beginning stages of GaN growth on Si(111) [5].

The vibrational properties of GaN were studied by Raman spectroscopy. Raman spectrum was obtained using Witec alpha 300R microscope with an excitation wavelength of 532 nm and a 100x objective lens. A typical Raman spectrum of the sample GaN/Si(111) is shown in Figure 2. The $\text{E}_2$ (TO) phonon frequency of our samples equals to $568.2 \pm 0.2 \ cm^{-1}$. 

![Figure 1(a,b). SEM images of GaN film on the Si(111) substrate: (a) the tilted view at the angle of 20° and (b) the cross-sectional view.](image)
Figure 2. Raman spectrum of the GaN/Si(111) system. The position of the GaN $E_2$ (TO) band in the sample and its position in unstained GaN (568 $cm^{-1}$) are shown in the insert.

3. Results and discussion
The $E_2$ (TO) phonon frequency obtained by Raman measurements is close to that of unstained GaN (568 $cm^{-1}$) found in [7]. However, the GaN $E_2$ (TO) band of the GaN/Si(111) system is usually shifted to longer wavelength [3,4]. The red shift corresponds to the presence of tensile stress in GaN films. In paper [4], for instance, the tensile stress in GaN film grown on Si(111) equals to ~0.15 GPa. This value was obtained using equation (1) with $K = 4.2 $ cm$^{-1}$GPa$^{-1}$, $\omega_0 = 568 $ cm$^{-1}$ and $\omega \approx 567.37 $ cm$^{-1}$.

We suppose that the presence of the low stress state in our samples can be explained, at least partly, by the specific morphology of GaN film. The large amount of cavities allows the efficient stress relaxation on free surfaces. To validate this assumption, we find the ratio of the elastic energy stored in continuous GaN film and GaN film with cavities provided that the effective lattice mismatch between GaN and Si(111) is the same in both cases. For a simplified modeling, the model geometry of the GaN film shown in the insert in Figure 3 is considered instead of the real geometry with randomly distributed cavities. The size $l$ corresponds to the average cavity size calculated by using SEM images (the area of 13 $\mu m^2$ was analyzed). The size $s$ is calculated to satisfy the condition $1/s^2 \approx 20 $ $\mu m^{-2}$. We use the following values of parameters in our computation: $l = 140 $ nm, $L = 600 $ nm, $s = 224 $ nm, $\delta = 0.5–10 $ nm.

We calculate the dependence of the elastic energy per GaN pair on the effective lattice mismatch between GaN film and Si substrate that includes the thermal mismatch and the difference in crystal lattice constants. The elastic constants of wurtzite GaN were taken from the paper [8]. The result of computation by the finite element method (FEM) is shown in Figure 3. This graph is plotted by using the value $\delta = 1 $ nm. The variation of $\delta$ leads to a negligible variation of the elastic energy. We find that the elastic energy of GaN film is about two times smaller than that of continuous GaN film. Consequently, the $\sigma_{xx}$ component of stress tensor and the shift of the position of GaN $E_2$ (TO) band $\Delta\omega$ (equation(1)) is approximately two times smaller in the first case. If we consider the GaN film grown in [4] as an approximation for the continuous GaN film we find that the GaN $E_2$ (TO) band
Figure 3. The elastic energy dependence on the effective lattice mismatch. The insert shows the model geometry of the GaN film used in the FEM computation.

shifts on ~0.3 \( \text{cm}^{-1} \). Therefore, we can conclude that the low stress state of the GaN layer might be associated with the presence of cavities with a high surface densities. Although, the presence of other defects (misfit dislocations etc.) can also cause a decrease of stress in the film.

To summarize, the morphology and vibrational properties of GaN thin films grown on Si(111) substrates via PA-MBE were investigated. The position of the GaN \( E_2 \) (TO) band was determined (568.2 ± 0.2 \( \text{cm}^{-1} \)). If we take into account the value of 568 \( \text{cm}^{-1} \) for the \( E_2 \) (TO) band in unstrained GaN the obtained value of the \( E_2 \) (TO) phonon frequency indicates that the stress in GaN film is relatively small. Finally, it was shown that the presence of a large amount of cavities in the GaN thin film observed by SEM caused effective stress relaxation. However, further studies are required to fully explain the stress relaxation mechanism in the GaN/Si(111) system.

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References
[1] Dadgar A, Blasing J, Diez A, Alam A, Heuken M, Krost A 2000 *Jpn. J. Appl. Phys.* **39** L1183
[2] Kiselowski C, Kruger J, Ruvmov S, Suski T, Ager III J W, Jones E, Liliental-Weber Z, Rubin M, Weber E R 1996 *Phys. Rev. B* **54** 17745
[3] Tripathy S, Chua S, Shen P, Miao Z 2002 *J. Appl. Phys.* **92** 3503
[4] Kukushkin S A, Mizerov A M, Osipov A V, Redkov A V, Timoshnev S N 2018 *Thin Solid Films* **646** 158
[5] Mizerov A M, Timoshnev S N, Sobolev M S, Nikitina E V, Shubina K Yu, Berezovskaia T N., Shtrom I V, Bouravleuv A D 2018 *Semiconductors* **52** 1529
[6] Timoshnev S N, Mizerov A M, Sobolev M S, Nikitina E V 2018 *Semiconductors* **52** 660
[7] Wang D, Jia S, Chen K J, Lau K M, Dikme Y, van Gemmern P, Lin Y C, Kalisch H, Jansen R H, Heuken M 2005 *J. Appl. Phys.* 97 056103

[8] Polian A, Grimsditch M, Grzegory I 1996 *J. Appl. Phys.* 79 3343