Raman analysis of epitaxial GaN layers grown on Si (111) by PA MBE

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Abstract. Epitaxial GaN layers were synthesised by PA MBE on Si (111) with and without using the high-temperature nitridation. We performed a complete investigation of their structural and optical properties. It was proven that the presence of GaN epitaxial layer less than a micrometer leads to the appearance of tensile stress in the structure. The stress was calculated and compared for the structure with nitridation and without it. The effect of nitridation on holes density was also observed by Raman spectroscopy and Hall measurements.

1. Introduction.
Gallium nitride is considered to be an excellent material for the development of power electronics. This semiconductor with the wide bandgap can possibly lessen the size of electronic devices and their consumption of energy compared to existing ones. Due to their mechanical properties, chemical stability, good thermal conductivity, structures based on GaN more and more penetrate the market. The GaN based electronic components have already been used for the development of VR/AR technologies, microLED displays and charging devices.

Owing to the high cost of GaN substrates, gallium nitride layers are commonly synthesised on silicon (Si), sapphire (Al₂O₃) or silicon carbide (SiC). The lattice mismatches of these materials and GaN are huge as well as the differences in thermal expansion coefficients, leading to the appearance of large number of defects and even micro-cracking. Silicon is considered to be the most promising material due to the ability to produce large size single crystalline substrates with excellent heat dissipation and mechanical strength.

Although over the past decades many studies have been concerned with the improvement of the quality of epitaxial GaN layers grown on Si substrates, the appearance of stress after cooling from growth temperature and interdiffusion of silicon and gallium are still an issue [1].

One of the ways to deal with some of these issues is a surface nitridation before the growth process and synthesis of high-temperature (HT) GaN on low-temperature (LT) GaN. The effect of nitridation for GaN layers grown on p-Si(100) by molecular beam epitaxy was studied in [2]. The results of Raman spectroscopy allowed to make a conclusion about the strain free nature and reasonably good crystallinity of the films [3]. For the GaN synthesis on Si(111) the optimal condition is nitridation of the substrate at the temperature T = 850 °C in the growth chamber [4].

Here we present the complete investigation of the GaN layers structural and optical properties by Raman spectroscopy and Hall measurements.
2. Experimental details.
The studied GaN layers were grown on Si (111) substrates by PA-MBE on a Veeco Gen 200. We used a high - frequency (13.56 MHz) plasma source Riber RFN 50/63 for nitrogen activation. For the synthesis of sample B the substrate nitrided in the growth chamber of Veeco Gen 200 set-up for 60 min at the temperature of ~850 °C was used, while sample A was grown in the absence of substrate nitridation. The growth process consisted of two steps presented in table 1. The stages for both samples were identical. The schematic view of the structure of sample B is presented in figure 1, assuming that nitridation leads to the formation of Si$_x$N$_y$ layer.

Table 1. The stages of growth process.

|                | LT - GaN | HT – GaN |
|----------------|----------|----------|
| Substrate      | 650 °C   | 730 °C   |
| temperature    |          |          |
| Gallium flux   | 0.1 ML/s | 0.6 ML/s |
| Nitride flux   | 0.1 ML/s | 0.1 ML/s |

Figure 1. The schematic view of the sample B.

Optical and mechanical properties of these samples were investigated by means of Raman spectrometer Horiba Jobin-Yvon LabRam HR800 and Hall measurement on an Ecopia HMS-3000 set-up.

3. Results.
The Raman spectra of both samples are shown in figure 2. The experimental data revealed that the spectra of both GaN/Si (111) layers contain the same phonon modes. Frequencies of these modes are presented in table 2.

In both samples the optical Si phonon experienced the negative shift 0.4 cm$^{-1}$ with respect to the value obtained in Si (111) substrate (520.6 cm$^{-1}$). The same frequency of Si optical phonon in both samples indicates that Si$_x$N$_y$ layer is too small (~5 nm) to affect substrate.
Figure 2. The Raman spectra of sample A and B.

Table 2. Frequencies of phonon modes in both samples

| Sample          | Sample A (cm⁻¹) | Sample B (cm⁻¹) |
|-----------------|-----------------|-----------------|
| Si              | 520.2           | 520.2           |
| E₂⁺ GaN         | 142.5           | 142.3           |
| E₂⁻ GaN         | 563.9           | 564.1           |
| A₁ (LO) GaN     | 731.6           | 732.9           |

The frequencies of GaN phonon modes can be used to obtain information about optical and mechanical properties of the GaN epitaxial layers.

The position of E₂⁺ GaN phonon is extremely sensitive to biaxial deformation in GaN epitaxial layers. Thus, the frequency of this phonon mode in Raman spectra can be used to contactless determine the stress distribution in the epitaxial layers. The stress is caused by the differences in the lattice parameters and thermal expansion coefficients and can lead to the appearance of defects and even micro-crack network. The frequency shift (Δω) of E₂⁺ GaN phonon with respect to its position in an unstrained GaN is associated with the biaxial stress σ through the equation:

\[ Δω = Kσ \]  \hspace{1cm} (1)

The parameter K depends on substrate and is equal to 4.2 cm⁻¹/GPa for Si(111). Although this equation was firstly presented in [5], the phonon frequency in the unstrained GaN on sample was corrected only recently [6] and is equal to \( ω₀ = 566.65 \text{ cm}^{-1} \).
Thus, the value of tensile stress in GaN layers is 0.65 GPa and 0.6 GPa for sample A and B respectively. These results indicated that the substrate nitridation before the synthesis of GaN layers leads to small stress relaxation.

Raman spectra were obtained from different spots on the surface proved high quality of the layers surfaces.

Although GaN layers were undoped, the results of Hall measurements demonstrate p-type conductivity of both samples. We attribute it to Ga unintentional doping of Si (111) substrate due to Si-Ga interdiffusion. It was also found that hole density decreases if the high-temperature nitridation is applied.

The continuum band in low-frequency range of Raman spectra indicates p-type conductivity as well. This effect is associated with holes transitions in valence band. The low-energy $E_{2}^h$ optical phonon mode can be used to compare hole density in two samples [2]. Intensities of $E_{2}^h$ mode normalized on $E_{2}^h$ integrated intensity in these GaN layers was compared. This value was higher in sample A, thus, the carrier concentration was higher too.

4. Conclusions
GaN epitaxial layers less than a micrometer were synthesized by PA MBE on Si (111) substrates with and without high-temperature nitridation. The Hall measurements and Raman spectroscopy indicated p-type conductivity, which could be caused by Ga diffusion in Si substrate. The analysis of both methods results demonstrate lower hole density in sample with nitridation. The stress in each sample was calculated by the shift of the frequency of $E_{2}^h$ phonon mode. Thus, nitridation was proven to lessen tensile stress in GaN epitaxial layers synthesized on Si(111) substrate. The results of this research prove that high-temperature nitridation can be used to obtain high in quality GaN epitaxial layers on Si(111) substrate.

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