

# Raman spectroscopy of GaN nucleation and free-standing layers grown by hydride vapor phase epitaxy on oxidized silicon

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GaN nucleation layers (NL-GaN) and GaN free-standing (FS-GaN) layers are studied using Raman spectroscopy and atomic force microscopy. The layers are deposited onto oxidized silicon substrates by hydride vapor phase epitaxy at 520 °C (NL layers) and 970 °C (FS layers). The effect of high-temperature annealing (1010 °C) on the properties of FS-GaN layers is investigated. The average height of the islands in the NL-GaN layers is found to increase from 15 to 400 nm when the growth time is increased from 10 to 200 min. The average growth rate of NLs is found to be very low, namely,  $\approx 1 \times 10^{-2}$  nm/s.  $E_2$  (566  $\text{cm}^{-1}$ ) and  $A_1$  (longitudinal optical) (730  $\text{cm}^{-1}$ ) peaks are observed on NL-GaN layers when the average size of the islands increases to 400 nm, scattering by  $E_2$  (567.3  $\text{cm}^{-1}$ ) and  $E_1$  [transverse optical (TO)] (558.3  $\text{cm}^{-1}$ ) modes is detected on FS-GaN layers. High-temperature annealing of the FS-GaN layers results in an increase of the intensity of  $E_2$  and  $E_1$ (TO) peaks detected from the front side whereas no effect is observed for detection from the side exposed by removal of the substrate. © 2003 American Institute of Physics.  
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Nitride semiconductors have become important in applications as emitters and detectors of light in the ultraviolet spectral region. They are deposited by hydride vapor phase epitaxy (HVPE), metalorganic vapor phase epitaxy (MOCVD), and by molecular-beam epitaxy (MBE). Because of the high nitrogen overpressure required and low solubility of nitrogen in a Ga melt, production of bulk GaN has not yet been realized. HVPE is used for growing thick GaN layers on sapphire substrates; free-standing GaN substrates of a 2 in. diameter were obtained by the method of laser lift off.<sup>1</sup>

Recently, much attention is being paid to nanometer-scale materials that exhibit vast potential as devices for numerous advanced-technology applications. Raman spectroscopy is recognized as an important probe for studying the structure of both bulk crystals and nanocrystalline GaN.<sup>2</sup> Calculated Raman frequencies of GaN (Ref. 3) and recent experimental results for GaN/sapphire,<sup>4,5</sup> GaN/Si(111),<sup>6</sup> and nanocrystalline GaN synthesized in arc plasma<sup>7</sup> are given in Table I.

In the last few years, Si has come to be regarded as one of the most promising substrates for GaN epitaxy, since it is available in large sizes, of high quality, and at a relatively low cost. Furthermore, GaN epitaxy on Si will facilitate the integration of microelectronics and optoelectronics devices. However, compared with sapphire, the differences in the lattice constants (22%) and the thermal expansion coefficients (56%) between GaN and Si are even larger; therefore, it is actually difficult to grow GaN on a Si substrate.<sup>8</sup> In recent years, great interest has been shown in the growth of GaN

layers on Si(111) substrates by HVPE,<sup>9</sup> MOCVD,<sup>10</sup> and MBE.<sup>11</sup> Also, investigations of MOCVD-grown GaN/Si(111) layers by Raman spectroscopy<sup>6</sup> have been reported.

In this letter, we present the results of an investigation of GaN nucleation and the growth of free-standing layers on oxidized silicon by HVPE. The heteroepitaxial growth of GaN nucleation layers (NL-GaN) was carried out on oxidized Si(111) wafers with a diameter of 50 mm. The epitaxy was carried out at a substrate temperature of  $T=520$  °C. The growth times used were 10, 25, 50, 100, and 200 min. After the heteroepitaxy stage, the morphology and structure of the GaN layers were studied by means of atomic force microscopy (AFM) and Raman spectroscopy. The AFM investigations were performed using an instrument with standard silicon nitride cantilevers by "Molecular Devices and tools for Nano Technology."

The heteroepitaxy of the GaN free-standing layers (FS-GaN) was performed in two stages. First, a NL-GaN layer was grown on an oxidized Si(111) wafer. In the second step, 360  $\mu\text{m}$  thick layers were grown for 3 h at a substrate temperature of 970 °C. After the heteroepitaxy, the Si substrate was etched away to produce a FS-GaN layer. The FS-GaN layers were annealed for 4 h at a temperature of 1010 °C in a  $\text{NH}_3:\text{2H}_2$  flow. The front side of the grown layers and the surface exposed by removal of the substrate ("back" side) were analyzed before and after annealing by Raman spectroscopy.

Raman scattering measurements were carried out at room temperature using a triple monochromator Raman system equipped with a multichannel charge-coupled detector. An  $\text{Ar}^+$  laser ( $\lambda=514.5$  nm) was used as a source of excitation. The typical laser spot size was 1  $\mu\text{m}$  and the spectral

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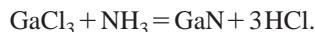
TABLE I. Phonon frequencies in wurtzite GaN obtained by Raman spectroscopy.

Type	Method	$E_2(\text{high})$ ( $\text{cm}^{-1}$ )	$A_1(\text{LO})$ ( $\text{cm}^{-1}$ )	$E_1(\text{TO})$ ( $\text{cm}^{-1}$ )	Reference No.
GaN	Calculation <i>ab initio</i>	579	748	...	2
GaN/sapphire	MBE; HVPE	567.6(300 K) 569(6 K)	734(300 K) 736.6(6 K)	558.8(300K) 560.2(6 K)	3
GaN/sapphire	HVPE	568(300 K)	721(300 K)	558(300K)	4
GaN/Si(111)	MOCVD	566.2(window)–566.8(overgrow)	735.5(window)–738(overgrow)	...	5
GaN nanocrystalline	Plasma synthesized	567(300 K)	...	560(300K)	6
NL-GaN	HVPE	566(300 K)	730(300 K)	...	This work
FS-GaN	HVPE	567.3(300 K)	...	558.3(300K)	This work

resolution estimated from the linewidth of the elastically scattered light was about  $2 \text{ cm}^{-1}$ . The power on the sample was about 20 mW.

A comparative analysis of the AFM images shows that, under the HVPE conditions used, GaN nucleation leads to pronounced island formation. The nuclei have a disklike shape. We believe that the island height  $h$  at the instant of nucleation is comparable with the disk base radius. The number of nuclei per unit surface area decreases with time (Fig. 2). The size distribution of the GaN nuclei over the substrate surface varies as well. As the growth time increased from 10 to 200 min, the average height  $h$  grew from 15 to 400 nm and the nucleus size scatter  $\Delta h$ , (determined as a half-width of the size distribution curve) became 20 times the initial value. The nucleus growth rate  $v$  was about  $3 \times 10^{-2} \text{ nm/s}$ . It should be noted that the average surface roughness of the amorphous silicon oxide after the preliminary heat treatment at  $520^\circ\text{C}$  was about 10 nm.

In the case of HVPE growth, dissociation of ammonia provides N atoms while Ga is made available by dissociation of GaCl. At the surface at a temperature of  $520^\circ\text{C}$ , the two reactants form GaN according to the following reactions:<sup>12</sup>



In order to avoid the undesirable reaction of  $\text{NH}_3$  with Si, the substrate was coated by  $\text{SiO}_2$  layers. However, during the low-temperature nucleation ( $520^\circ\text{C}$ ) GaN must overcome a large barrier in order to form on the amorphous silicon oxide surface. Therefore, the average growth rate of islands in our experiments is very low,  $\approx 10^{-2} \text{ nm/s}$  (Fig. 2), although the HVPE method under normal conditions can provide very high growth rates, up to  $\sim 10^{-2} \mu\text{m/s}$ . When

the growth time is increased from 10 to 200 min, the average height of the nuclei increases, together with the half-width of the nucleus size distribution (by a factor of 20). Apparently, this is the result of two concurrent processes: Emergence of nuclei and the growth of existing islands.

The Raman spectra of the NL-GaN for the growth times of 10, 50, and 100 min were similar and exhibited only one peak at  $\sim 520 \text{ cm}^{-1}$ , corresponding to scattering by the Si substrate [Fig. 1(a)]. This peak is also present in spectra of the NL-GaN layers with a growth time of 200 min and a nanocluster height of about 400 nm along with two additional peaks at 566 and  $730 \text{ cm}^{-1}$  [Fig. 1(b)]. According to published data (Table I) it can be concluded, that these peaks correspond to the  $E_2(\text{high})$  and  $A_1(\text{LO})$  modes, respectively.

The experimental data for the  $E_2(\text{high})$  and  $A_1(\text{LO})$  modes also demonstrate that the strain in GaN nanoclusters deposited onto oxidized Si at a low temperature is relatively low. This could be related to the fact that in the initial growth stage, bonding of the GaN molecules to monocrystalline silicon is impeded by the amorphous  $\text{SiO}_2$  layer.

The Raman spectra of the nonannealed FS-GaN layers from the front side show a weak peak at  $520 \text{ cm}^{-1}$  (Si), indicating stronger absorption in the thicker film, as well as peaks at  $558.3 \text{ cm}^{-1}$  and  $567.3 \text{ cm}^{-1}$ , corresponding the  $E_1(\text{TO})$  and  $E_2(\text{high})$  modes, respectively, and a weak peak at  $659 \text{ cm}^{-1}$ . The peak at  $520 \text{ cm}^{-1}$  can be explained by the fact that the chemical etching of the silicon substrate is not capable of removing the Si atoms, which diffused into the GaN layer. The high-temperature annealing results in an increase by a factor of 1.5 of the intensity ratio of the peaks corresponding to the  $E_2(\text{high})$  and  $E_1(\text{TO})$  modes and a 20% decrease of the linewidths of the spectra full width at half maximum [Fig. 3(a)].

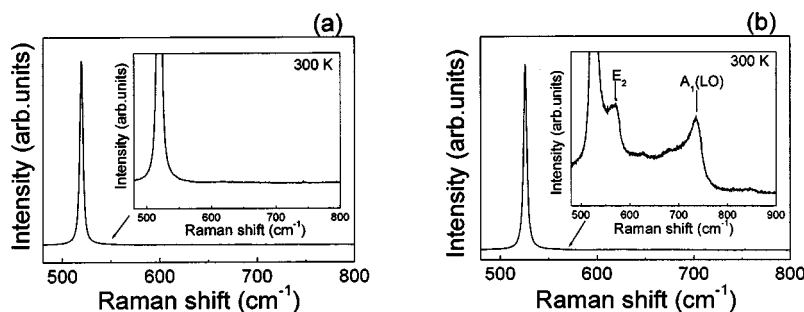


FIG. 1. Raman spectra of NL-GaN for various heteroepitaxial growth times: a—100 min, b—200 min. The inset in Raman spectra shows high-resolution Raman spectra of the  $E_2$  and  $A_1(\text{LO})$  modes.

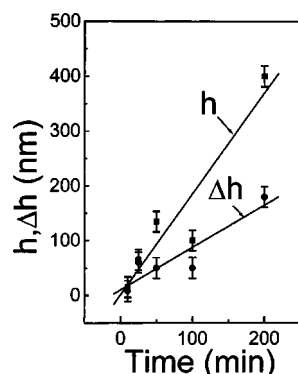


FIG. 2. Plot of the average GaN nucleus height  $h$  and average nucleus size scatter  $\Delta h$  vs growth time  $t$ .

The Raman spectra of the nonannealed FS-GaN layers taken from the back side have peaks at about  $558.3\text{ cm}^{-1}$  and  $567.3\text{ cm}^{-1}$  as well as weak peaks at  $520$  and  $659\text{ cm}^{-1}$ . The annealing affects neither the intensity ratio of the peaks corresponding to  $E_2(\text{high})$  and  $E_1(\text{TO})$  modes nor the line-widths of the spectra [Fig. 3(b)].

The value of  $566\text{ cm}^{-1}$  for the  $E_2(\text{high})$  mode in NL-GaN layers, as in the case of Ref. 5, can be related to the presence of elastic strain in the GaN nanocrystals. During the epitaxial growth of thick GaN layers at high temperatures, threading dislocations and defects form as a result of the escape of the nitrogen atoms. The higher value of  $567.3$

$\text{cm}^{-1}$  for the  $E_2(\text{high})$  mode indicates a partial removal of the strain, in agreement with observations for thick GaN layers grown on sapphire by HVPE.<sup>3</sup>

The difference in the behavior of the peak intensities recorded from the front and back sides after high-temperature annealing can be explained as follows. The amount of defects in the layer during the growth of  $360\text{ }\mu\text{m}$  thick GaN layers decreasing away from the interface with the substrate toward the surface. Annealing of FS-GaN results in a further quality improvement at the front side, while the large amount of defect near the back side cannot be healed by annealing.

In summary, by using Raman spectroscopy and AFM, we have evaluated epitaxial GaN nucleation layers and  $360\text{ }\mu\text{m}$  thick FS-GaN layers grown on oxidized silicon substrates by HVPE. It has been found that the average growth rate of the nucleation layers is very low, being  $\approx 1 \times 10^{-2}\text{ nm/s}$ .

The  $E_2$  ( $566\text{ cm}^{-1}$ ) and  $A_1$  ( $730\text{ cm}^{-1}$ ) peaks were observed in NL-GaN layers when the average size of the islands reached  $400\text{ nm}$  and the  $E_2$  ( $567.3\text{ cm}^{-1}$ ) and  $E_1$  ( $558.3\text{ cm}^{-1}$ ) modes were found in FS-GaN layers. Annealing of the  $360\text{ }\mu\text{m}$  thick FS-GaN layers improves the quality of only the front side of the sample.

These results have shown that low-temperature HVPE is a simple and effective technique to grow nanocrystals of GaN and a promising technology for the growth of FS-GaN layers on oxidized silicon substrates.

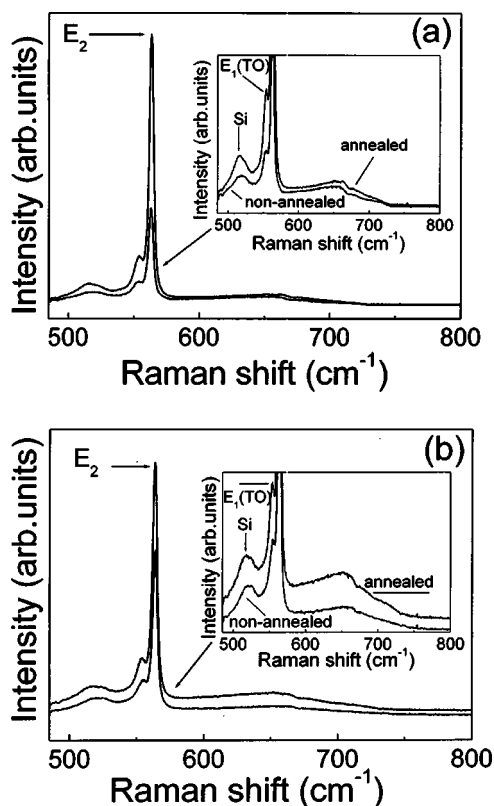


FIG. 3. Raman spectra of FS-GaN obtained from the front side (a) and the back side (b). The inset shows a high-resolution Raman spectrum of the  $E_1(\text{TO})$  mode.

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