Surface enhanced Raman scattering by GaN nanocolumns

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Received 25 October 2005, accepted 13 April 2006
Published online 1 June 2006

PACS 63.22.+m, 68.37.Hk, 68.70.+w, 78.30.Fs, 81.15.Hi

The GaN nanocolumns were grown by plasma-assisted molecular beam epitaxy (PAMBE) on Si(111) substrates. Scanning electron microscopy shows that the nanocolumns with diameters of 20–150 nm and lengths of 300-500 nm grow parallel to the [111] direction of the Si substrate. The vibrational spectrum (including optical and interface phonons) of the nanocolumns was studied using conventional and surface enhanced Raman scattering.

1 Introduction

A rapid development in the field of one-dimensional materials can be observed in recent years. The fabrication of a wide variety of nanocolumns or nanowires in several semiconductor material systems has been achieved (Si [1], III-V [2, 3], III-nitride [4, 5]). Intense research concentrating on physical properties [6, 7] and sophisticated applications, such as single electron transistors (SETs) and field-effect transistors (FETs) [8, 9], has been developed. GaN nanowires with improved electronic and optical properties in comparison to bulk single GaN crystals are considered also as promising materials for the production of optoelectronic devices with superior performance.

Raman spectroscopy is successfully employed to obtain comprehensive knowledge of the optical and electronic properties of both crystals and nanostructures [10, 11]. In the present paper, we report on a Raman study of optical and interface phonons in GaN nanocolumnar structures.

2 Experimental

The GaN nanocolumns were grown on Si(111) substrates by PAMBE using a radio frequency plasma source to activate the nitrogen and standard Knudsen effusion cells for Ga and Al. The growth chamber was pumped down to a base pressure of 5 × 10⁻¹¹ mbar by a combination of an ion pump, a cryopump, a turbo pump and a liquid nitrogen cryopanel. During growth only the turbo pump and the cryopanel were used and the nitrogen partial pressure was stabilized at 3 × 10⁻⁵ mbar.

Silicon (111) substrates were cleaned before being loaded into the MBE system using a standard chemical cleaning procedure and outgassed in the growth chamber at 925 °C for 15 minutes. A low-energy electron diffraction pattern shows a clear 7x7 surface reconstruction.
Nanocolumns were grown under N-rich conditions obtained at an N\textsubscript{2} flux of 4.0 sccm and plasma cell power of 500 W, while a Ga beam equivalent pressure was selected in the range of $(2.1\pm5.5) \times 10^{-8}$ mbar. The substrate temperature during growth was chosen between 770 °C and 800 °C measured by an optical pyrometer with emissivity set to 0.58.

A GaN compact film was grown under metal-rich conditions. It was nucleated using 8 sec of Al deposition followed by multiple AlN/GaN buffer layers. The growth temperature was in the range of 770-800 °C and the deposition rate 4.3 nm/min for AlN and 8.2 nm/min for GaN layers resulting in a total sample thickness of about 2270 nm. A detailed experimental description of the growth mechanisms related to growth conditions is described elsewhere [5, 12].

Raman spectra of nanocolumnar structures were taken from planar and cleaved sample surfaces using a Dilor XY800 triple spectrometer supplied with a microscope which allows the light to be focused to a 1 µm spot. In order to avoid heating of the sample the laser power measured in front of the microscope was kept at 5 mW. The scattering geometries applied were $z(x-\overline{z})$, $y(x-\overline{y})$ and $y(z-\overline{y})$, where $z$ is parallel and $x$ and $y$ are perpendicular to the growth direction. After growth a part of the samples were transferred ex-situ to an ultra-high vacuum chamber for the deposition of Ag clusters and Raman spectra were taken during the process in macro-Raman geometry. The 488 and 514.5 nm lines of an Ar\textsuperscript{+} laser with a power of 300 mW were used for excitation. Raman spectra from planar GaN films were measured for comparison. The spectral resolution was 2 cm\textsuperscript{-1} over the entire spectral range.

### 3 Results and discussion

The morphology and the layer thickness of the GaN nanocolumnar samples were studied by cross-sectional scanning electron microscopy (SEM) using a Leo 1550 microscope. A typical morphology of the GaN nanocolumns grown by MBE is shown in an oblique cross-sectional SEM image (Fig. 1). Highly dense isolated hexagonal nanocolumns vertically aligned with respect to the sample surface are homogeneously grown on the whole substrate. The majority of the nanocolumns have a length of about 300-500 nm with diameters ranging from 20 nm to 150 nm.

Typical Raman spectra measured in a backscattering geometry from planar and cleaved sample surfaces are shown in Fig. 2. Raman spectra of nanocolumnar GaN measured in the $z(x-\overline{z})$ scattering geometry exhibit peaks at 568 and 733 cm\textsuperscript{-1} assigned to the E\textsubscript{2} and A\textsubscript{1}(LO) GaN phonons, respectively [13]. The strong Raman line at 520 cm\textsuperscript{-1} and a feature located near 650 cm\textsuperscript{-1} are due to Si phonons and phonon contribution from the AlN buffer layer, respectively. Raman scattering from cleaved surfaces allows additional lines at 531 and 558 cm\textsuperscript{-1} due to A\textsubscript{1}(TO) and E\textsubscript{1}(TO) phonons, respectively, to be

**Fig. 1** Cross-sectional SEM micrograph of GaN nanocolumns grown on a Si(111) substrate.
observed. The $E_1(LO)$ mode at 736 cm$^{-1}$ which is not allowed in the Raman spectra measured from planar surfaces becomes active in Raman spectra taken from cleaved surfaces. These results are consistent with the data obtained for hexagonal GaN epilayers grown on (111)-oriented MgAl$_2$O$_4$ substrates [14].

A well-developed surface of the samples allows an investigation of the surface-related vibrational modes using surface enhanced Raman scattering. This technique which is traditionally used for the investigation of organic substances has been already successfully used for studying the vibrational modes in various inorganic materials ([15–18] and refs. therein). Therefore, Raman monitoring of the GaN nanocolumnar structures during deposition of Ag was performed. Raman spectra of GaN nanocolumns measured in the $z(x-z)$ scattering geometry with the 514 nm laser excitation line for various thickness of deposited Ag are shown in Fig. 3. As the deposition of Ag clusters proceeded the intensity of the Si phonon decreases due to absorption by Ag clusters while the intensity of the $E_2$ phonon line increases. In addition, a new strong band occurs in the spectra between the frequency positions of the $A_1(LO)$ and $A_1(TO)$ phonons at about 680-730 cm$^{-1}$. The increasing intensity of the mode by three orders of magni-

![Fig. 2](image1.png)  
**Fig. 2** Raman spectra of GaN nanocolumns grown on a Si(111) substrate measured in different scattering geometries with the 488nm laser excitation line.

![Fig. 3](image2.png)  
**Fig. 3** Raman spectra of GaN nanocolumns grown on a Si(111) substrate measured in the $z(x-z)$ scattering geometry with 514nm laser excitation line for various thickness of deposited Ag. The vertical lines indicate the frequency positions of $A_1(TO)$ and $A_1(LO)$ modes. The spectra of the samples with deposited Ag are shifted in the vertical direction equidistantly.
titude with increasing Ag nominal thickness (from 0.1 to 10 nm) manifests surface enhanced Raman scattering. Note, that neither enhancement of Raman scattering nor appearance of additional Raman lines was observed by Ag deposition on GaN planar structures.

Recently, a similar feature was observed in the Raman spectra for a nanocolumnar structure at 716 cm\(^{-1}\) and interpreted as caused by the Fröhlich vibrational mode [19]. The frequency position of the band observed in our experiments is independent on the volume concentration of GaN nanocolumns and therefore can not be explained in terms of the Maxwell-Garnett approximation. Moreover, the asymmetric line shape of the band indicates that more than one vibrational mode contributes to the Raman scattering in this region. It is most probable that this band is due to interface modes localized in the vicinity of the GaN nanocolumn surface or/and tips [20]. According to calculations performed within the dielectric continuum model [20] the frequency positions of these modes are either near 690-715 cm\(^{-1}\) or have an almost continuous spectrum in the range of 670-725 cm\(^{-1}\), respectively. Thus the calculated values account well for the experimental observation.

4 Conclusions

The vibrational spectrum of GaN nanocolumns grown by PAMBE was investigated by Raman spectroscopy. Raman spectra taken in different scattering configurations exhibit optical vibrational modes similar to those of GaN planar films. Deposition of Ag clusters on GaN nanocolumnar structures allows surface enhanced Raman scattering by interface vibrational modes in GaN nanocolumns to be observed. Calculated frequency positions of interface modes in GaN columns performed within the dielectric continuum model are in good agreement with the experimental data.

References