Raman scattering by longitudinal optical phonons in InN nanocolumns grown on Si(1 1 1) and Si(0 0 1) substrates

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Abstract

Raman measurements in high-quality InN nanocolumns and thin films grown on both Si(1 1 1) and Si(1 0 0) substrates display a low-energy coupled LO phonon–plasmon mode together with uncoupled longitudinal optical (LO) phonons. The coupled mode is attributed to the spontaneous accumulation of electrons on the lateral surfaces of the nanocolumns, while the uncoupled ones originates from the inner part of the nanocolumns. The LO mode in the columnar samples appears close to the E_1(LO) frequency. This indicates that most of the incident light is entering through the lateral surfaces of the nanocolumns, resulting in pure longitudinal–optical mode with quasi-E_1 symmetry. For increasing growth temperature, the electron density decreases as the growth rate increases. The present results indicate that electron accumulation layers do not only form on polar surfaces of InN, but also occur on non-polar ones. According to recent calculations, we attribute the electron surface accumulation to the temperature dependent In-rich surface reconstruction on the nanocolumns sidewalls.

Keywords: InN nanocolumns; Phonon–plasmon coupled modes; Raman scattering

1. Introduction

Among group III-nitrides, InN is receiving increased attention because it enlarges the range of applications of nitrides to the visible and infrared (IR) spectral region. Also, the small electron effective mass of InN is promising for high-speed device applications. InN-based nanostructures are not abundant because of their specific growth difficulties (mainly due to the InN low dissociation temperature) and the poorer knowledge of InN fundamental parameters, as compared to other nitrides. Indeed, InN systematically shows high electron concentrations, whose origin (unintentional doping during growth, interface effects or surface accumulation) is still under discussion. Free electrons couple to the longitudinal optical (LO) phonons producing mixed phonon–plasmon excitations (L_+, L_-) Coupled modes in InN films have been studied by several groups using Raman scattering, IR reflectance and IR ellipsometry IR and Raman scattering measurements in InN nanocolumns (NC) have also been reported recently An electron density dependent L_- mode in the range 400–450 cm^{-1} has been reported in InN films, coexisting with the uncoupled A_1(LO) phonon. Alternatively, the mode observed at the A_1(LO) frequency has been attributed to a L_- mode shifted to high energies by wavevector non-conservation during the scattering process The massive failure of wavevector conservation required for this explanation implies significant crystalline disorder, which is difficult to understand in samples with high crystalline quality, as the present NC samples. Recent experimental and theoretical works indicate the presence of an intrinsic electron accumulation layer on the polar surfaces of InN

films, due to the low energy of the conduction band minimum of InN and the pinning of the Fermi level at ionized surface donor states.

In this paper, we present Raman scattering and IR reflectance measurements on both thin film and nanocolumnar InN high-quality samples. While the thin films display the allowed E_2 and $A_1(LO)$ modes, the NC samples show the LO mode at the E_1 frequency, together with an L_- coupled mode in the 425–450 cm^{-1} range. The L_- mode is not observed in thin InN layers, probably due to their comparatively low specific surface. The electron concentrations obtained from the L_- frequencies vary from 2.5×10^{18} to $6.0 \times 10^{18}\,cm^{-3}$ depending on the growth temperature. Our results suggest that electron concentration occurs also at the non-polar NC sidewalls, giving rise to coupled modes, while the uncoupled LO phonon originates from the regions inside the NC.

2. Experiment

InN films were grown on Si(1 1 1) and Si(0 0 1) substrates by plasma-assisted molecular beam epitaxy (PAMBE). A 50-nm-thick AlN buffer layer was used to optimize growth conditions.

The III/V ratio was varied from N-rich conditions (NC samples) to quasi-stoichiometry (thin InN layers). The growth temperature was varied between 450 and 480 °C. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) reveal the practical absence of defects and strain in the NC samples Raman scattering and IR reflectance measurements were carried out at room temperature, both in macro- and micro-configurations, using a He–Ne laser for excitation and a charge coupled device detector. The spectra were taken in nominal backscattering configurations, both along the growth direction (c-axis) and perpendicular to it, from the lateral sample surface.

3. Results and discussion

The macro-Raman spectra in backscattering configuration along the c-axis (z-direction) of InN NC sample grown at 475 °C on Si(1 1 1) and thin film are shown in Fig. 1. The scattering directions z and x are indicated in the inset. Mode frequencies have been carefully determined using Ne spectral lines for calibration. Thin InN layer shows the allowed E_2 (491 cm^{-1}) and $A_1(LO)$ (588 cm^{-1}) modes The frequency of the non-polar E_2 mode indicates strain relaxation [15] and its small width (4.0 cm^{-1}) confirms the high crystalline quality observed by HRTEM. The NC sample also shows a narrow E_2 peak at the same frequency. However, the LO mode appears at the $E_1(LO)$ frequency (600 cm^{-1}), which is forbidden in this scattering geometry. We attribute its appearance to the light refraction and/or scattering at the NC sidewalls, resulting in the light (and the phonon) propagating nearly perpendicular to

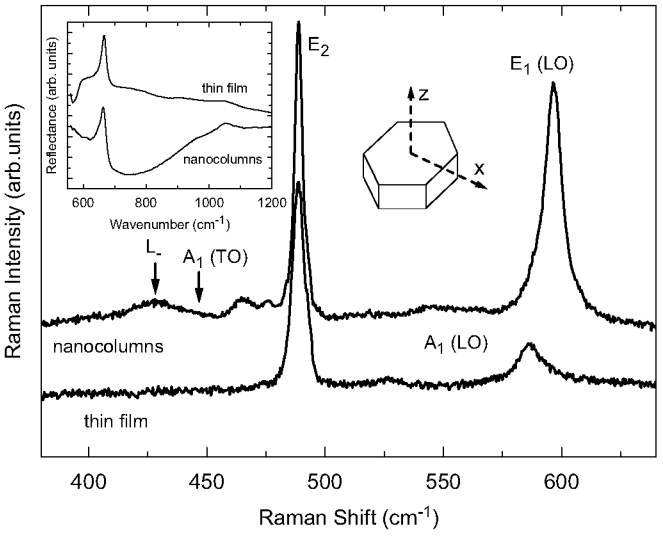

Fig. 1. Macro-Raman spectra of InN thin film (lower trace) and a NC sample grown at 475 °C on Si(1 1 1) (upper trace) in backscattering along the c-axis. The right inset shows the scattering directions relative to the crystal structure. The left inset shows the infrared reflectance spectra of the same samples.

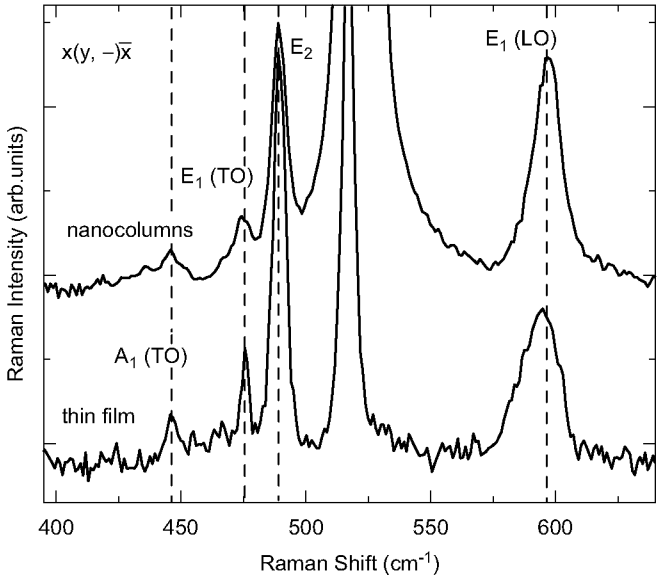

Fig. 2. Micro-Raman spectra of the same samples taken in backscattering at the lateral surface.

the c-axis. To confirm this assignment, we performed micro-Raman measurements in backscattering configuration from the lateral surface (x-direction) of both samples (Fig. 2). Besides the strong peak of the Si substrate, one observes the $E_1(LO)$ phonon in the two samples at 600 cm^{-1}. This clearly demonstrates that the light propagates essentially perpendicular to the NC sidewalls, irrespective of the nominal scattering geometry. The deviation of the light propagation in NC depends on the inhomogeneity of column height or column density in different samples. The "anomalous" light propagation in NC might be a general fact. Thus, the $E_1(LO)$ mode at

740 cm^{-1} systematically appears in nominal backscattering along the *c*-axis in the spectra of GaN NC Also the Raman spectra reported in Fig. 3 of show the NC-LO phonon shifted to higher frequency (3–4 cm^{-1}) than in the reference thick film. This shift amounts one half of the $E_1(LO)$–$A_1(LO)$ splitting, suggesting a significant deviation of the phonon propagation direction away from the *c*-axis. The TO modes are observed in the low frequency region if Fig. 2 in both samples.

Considering that the lateral surfaces of the NC provide the main contribution to the light scattering, we attribute the broad peak observed in the 425–450 cm^{-1} range in NC samples (Fig. 1) to the low-energy branch L_- of the coupled LO phonon–plasmon mode arising from an electron accumulation layer at the lateral surfaces of the NC. The uncoupled $E_1(LO)$ phonon would then arise from the inner part of the NC, where the electron density is expected to be much smaller The presence of free electrons in the NC is confirmed by the infrared reflectance measurements shown in Fig. 1. The strong reflectance minimum in the NC sample in the 700–800 cm^{-1} region is indicative of absorption by free electrons.

The plasma frequency ω_p corresponding to the observed L_- frequency can be estimated from the simplest model for the dielectric function Assuming an effective mass $m^* = 0.05m_0$ the estimated electron concentration for all samples studied are presented in Fig. 3 as a function of the growth temperature. The values roughly coincide with the one expected from the minimum of the NC reflectance spectrum in Fig. 1. The electron concentration (circles) decreases for increasing growth temperature, while the growth rate increases in the same temperature range (triangles). These trends suggest a possible origin of the electron accumulation layer on the NC sidewalls. The higher growth rate observed at higher growth temperature indicates a faster In diffusion along the NC sidewalls. For a fixed In flux, the instantaneous number of In atoms present in the NC sidewalls is smaller as their speed increases.

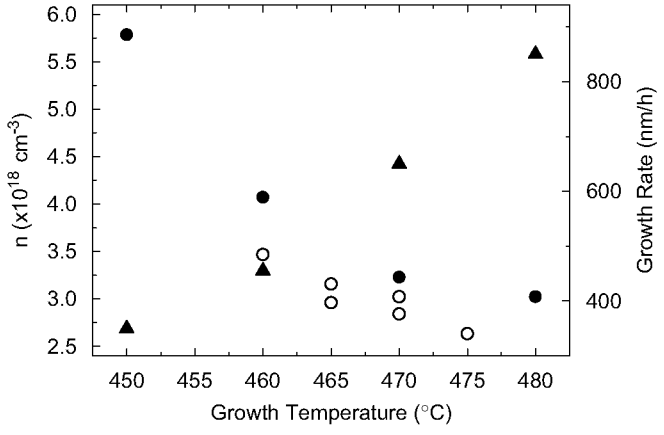

Fig. 3. Electron concentration versus growth temperature obtained from the L-frequency. Full symbols stand for NC samples grown on Si(0 0 1) substrates; open circles for Si(1 1 1) ones. Triangles show the growth rate of NC samples grown on Si(0 0 1) versus growth temperature.

Thus, at higher growth temperature, the instantaneous In coverage of the lateral NC surfaces decreases. This coverage is frozen upon sample cooling at the end of the growth process. The excess In atoms are incorporated into the NC to form an In-rich surface layer responsible for the electron accumulation This accumulation should be proportional to the excess In atoms and consequently, it should be higher for lower growth temperatures, as observed.

4. Conclusion

In summary, the Raman spectra of high-quality InN nanocolumnar and thin layers of InN indicate that electron accumulation occurs also at the non-polar lateral surfaces of the NC. This electron layer couples with the $E_1(LO)$ phonon, giving rise to the observed coupled L_- mode. The electron accumulation is probably due to the formation of an In-rich surface layer at the NC sidewalls, as suggested by recent theoretical work.

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