InN nanocolumns grown by plasma-assisted molecular beam epitaxy on *A*-plane GaN templates

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This work reports on the growth of wurtzite InN nanocolumns on *A*-plane GaN templates and on their structural and optical characterization by scanning and transmission electron microscopy, photoluminescence, and Raman spectroscopy. InN nanocolumns grown on *A*-plane substrates show sharp and pyramidal-like top surfaces that could be attributed to *A*-plane and *M*-plane facets, instead of the hexagonal top surfaces observed in nanocolumns grown on *C*-plane surfaces. The results of these characterization techniques show that the nanocolumns preserve the nonpolar growth orientation of the GaN templates. Good crystal quality is expected from the low temperature (13 K) photoluminescence dominant peak at 0.69 eV. © *2009 American Institute of Physics*.
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The presence of an electron accumulation layer at the surface of InN layers is a striking feature related to fundamental material properties that needs to be understood. Aside from basic aspects, practical issues such as *p*-type doping are still pending on the control and avoidance of the unintentional strong *n*-type conductivity.[1,2] High crystal quality InN nanocolumns (NCs) have already been reported to be defect-free and strain-free, providing an almost ideal structure for reliable studies of fundamental aspects.[3] Evidence of this electron accumulation at the nonpolar sidewalls (*M*-planes) of InN NCs has been reported by different techniques.[4,5] Recent calculations performed by Segev and Van de Walle[6,7] on InN layers grown on polar (*C*-plane) and nonpolar (*M*-plane, *A*-plane) orientations, predict a pinning of the Fermi level in both cases when the surface reconstruction occurs under metal-rich conditions. However, before being able to measure the electron accumulation at the polar surfaces of the InN NCs, the priority is the achievement of defect and strain free nonpolar InN NCs.

In spite of the interest to obtain nonpolar III-nitrides, avoiding polarization field effects, which are detrimental to the efficiency of optoelectronic devices, there are a scarce number of reports on the growth of nonpolar InN layers. Furthermore, most of them reported on films with high densities of defects.[8] The growth of high quality polar InN films poses difficulties that become even worse in the case of nonpolar orientations.

Wurtzite III-nitride NCs have been grown on very different substrates [Si(111), Si(100), *C*-plane Al_2O_3, and GaN (0001) templates] with a high crystal quality.[1,9–11] In all the above mentioned cases, the NCs were grown along the *c* axis having nonpolar (*M*-plane) sidewalls.

This work focuses on the growth and characterization of InN NCs on *A*-plane GaN templates. Structural characterization was carried out by scanning (SEM) and transmission electron microscopy (TEM). Optical characterization was performed by photoluminescence (PL) and Raman spectroscopy (RS).

Samples were grown on a plasma-assisted molecular beam epitaxy system equipped with a rf-plasma source (Addon) for active nitrogen and a standard Knudsen cell for In. Details on the growth system can be found elsewhere.[12] The *A*-plane GaN templates, grown on *R*-plane sapphire substrates, were thermally cleaned in the growth chamber at 800 °C for 30 min before the growth of the InN NCs. *In situ* growth monitoring was performed by reflection high energy electron diffraction. PL was excited with the 780 nm line of a laser diode and detected with a Hamamatsu P4638 PbS photodetector. RS measurements were carried out at room temperature in backscattering geometry using a Spex 1404 double grating spectrometer with a multichannel detector. TEM images were obtained with a JEOL JEM-3010 microscope operating at 300 kV. Cross-sectional specimens were prepared by standard methods of mechanical grinding, dimpling, and Ar-ion beam milling in a cold stage to minimize sample damage.

Concerning growth, substrate temperature is known to be the most critical parameter for *C*-plane InN layers.[13] In fact, no growth is observed for temperatures above 500 °C (Refs. 13 and 14) for In-polar and 600 °C (Ref. 15) for N-polar InN. In order to determine the optimal nanocolumnar regime for *A*-plane InN, a series of samples was grown under highly N-rich conditions varying the substrate temperature from 475 to 550 °C. Samples grown at 475 °C consisted in compact layers with rough surfaces and a very poor crystal quality, similar to the case when growing on *C*-plane at temperatures below 450 °C due to the reduced surface mobility of In adatoms. Samples grown above 550 °C presented In droplets on top of the GaN template, typical from InN decomposition[13] and no InN was grown. Only samples grown in the range of 500–525 °C showed good crystal quality NCs with no compact InN epilayer between them and

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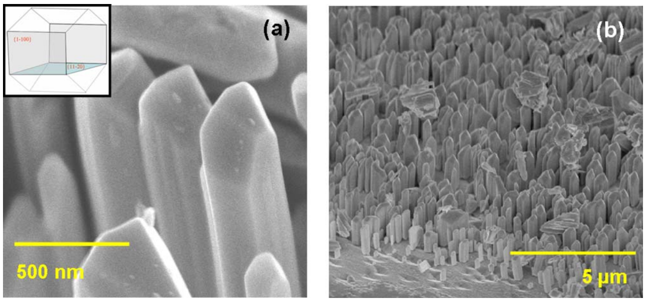

FIG. 1. (Color online) (a) SEM image of InN NCs grown on *A*-plane GaN, showing faceted *A*- and *M*-plane topsides. The inset shows the *A*-plane base rectangular geometry. (b) SEM image of the InN NCs grown directly on *A*-plane GaN templates.

the GaN template so the optimal growth temperature was set to 525 °C.

The SEM images in Fig. 1 display the morphology of the InN NCs grown on *A*-plane templates. The columns with high aspect ratio show clear side facets and even inclined facets on top, in contrast to *C*-plane oriented NCs with flat end. This shape of the NCs arises from the specific growth orientation and the anisotropy in the surface energies. Assuming the *A*-plane base with rectangular geometry (see inset in Fig. 1), the perpendicular side facets are given by *M*- and *C*-planes ({1−100} and {0001} planes, respectively), whereas the top facets point to low-index planes of {10−11} and {1−100} types. This kind of morphology and NC shape has also been observed in AlGaN and InN nanorods grown on *R*-plane sapphire substrates[16,17] by metal-organic vapor phase epitaxy (MOVPE) and hydride-MOVPE, respectively.

The microstructure and hexagonal crystallinity are investigated by TEM, demonstrating that no compact epilayer was formed between the GaN template and the NCs and that most of the columns are defect-free with smooth interfaces between the InN NCs and the GaN template (inset Fig. 2). The high-resolution (HR) TEM images as well as the corresponding selected area electron diffraction (SAED) pattern are taken along the [1−101] zone axis, which is perpendicular to the growth direction, i.e., to the [11−20] direction. The SAED pattern represents the superposition of diffraction spots from the InN (squares) and GaN (circles) lattices. This result confirms that the InN NCs have hexagonal structure with the same orientation as the template, i.e., the epitaxial orientation relationship is $(11-20)_{GaN} \| (11-20)_{InN}$ and $[1-101]_{GaN} \| [1-101]_{InN}$. Furthermore, the distance between the diffraction spots is measured in order to estimate the lattice parameter revealing that the InN NCs are almost fully relaxed. The HRTEM image [Fig. 2(b)] of the interface supports the orientation relationship as well as the smoothness of the interface on an atomic level.

RS measurements confirmed the wurtzite structure of the NCs and their crystallographic orientation. For a 632.8 nm excitation, the nanocolumnar sample shows the allowed E_2 mode at 488.5 ± 0.5 cm^{-1}. Wang *et al.*[18] determined experimentally that the strain-free Raman frequency of the E_2 high mode of hexagonal InN is 490.1 ± 0.2 cm^{-1}. According to their experiments, we can conclude that the InN NCs grown on *A*-plane GaN templates are fully relaxed ($\varepsilon_a < 0.08\%$, with the measurement accuracy being $\pm 0.05\%$). Measurements were performed in backscattering configuration with light propagating along the growth axis and a polarizer placed perpendicular to this direction, modifying the polarization angle of the incident light. Selection rules[19] imply that the intensity of the E_2 mode should be maximum for polarization perpendicular to the *c* axis and zero for polarization parallel to it. For the case of InN NCs grown along the *c* axis, the polarization of the incident light is always perpendicular to the growth direction; therefore, the E_2 mode intensity is independent of the angle of the polarizer (dots in Fig. 3). In the case of InN NCs grown on *A*-plane GaN templates, the intensity of the E_2 mode reaches maxima and minima as the polarization angle varies from perpendicular to parallel to the *c* axis, respectively (squares in Fig. 3). The same behavior is observed for the *A*-plane GaN template (stars in Fig. 3), as expected. The minimum at 135° of the InN NCs does not go to zero due to some elastic light scattering at the NCs which is absent in the flat GaN template.[5] This result unambiguously shows that the NCs grow perpen-

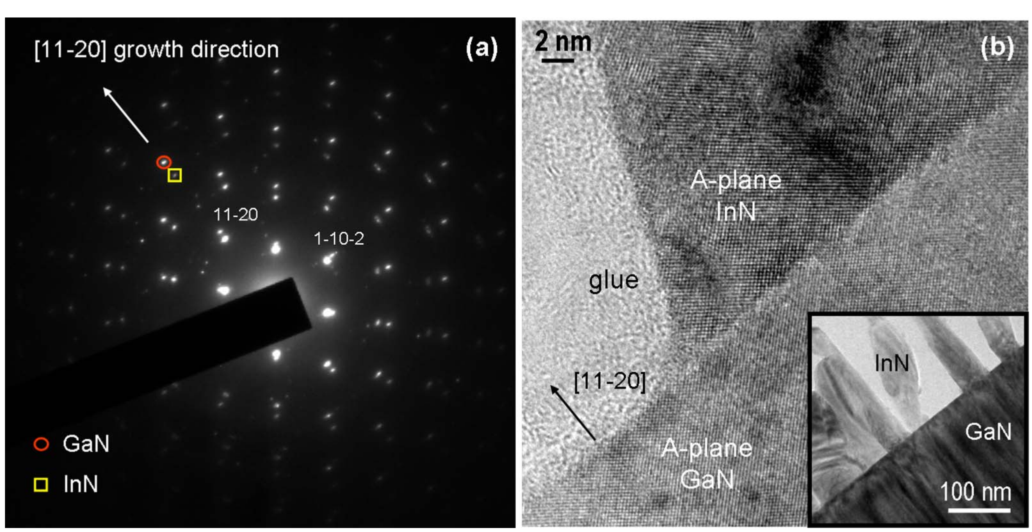

FIG. 2. (Color online) (a) SAED pattern taken along the [1−101] zone axis revealing two different diffraction patterns corresponding to the GaN template (circles) and the InN NCs (squares), respectively. (b) Cross-sectional HRTEM image revealing an atomically flat and abrupt interface between the InN NCs and the *A*-plane GaN template. A lower magnification TEM image of the NCs is shown in the inset. No InN compact epilayer is formed between the GaN template and the NCs.

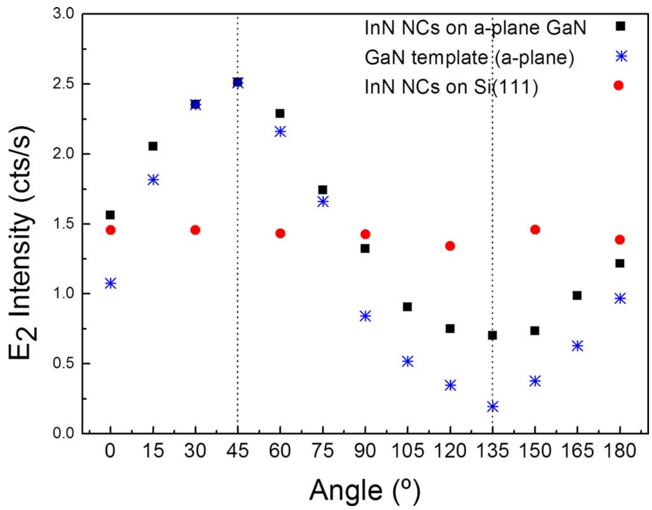

FIG. 3. (Color online) E_2 mode intensity variation as a function of the polarization angle. The dots represent the InN NCs grown along the *c* axis, the squares correspond to the InN NCs grown on *A*-plane GaN templates and the stars to the *A*-plane GaN template.

dicular to the *c* axis, which corresponds to the measurement taken at 135° angle in Fig. 3.

Low temperature (13 K) PL measurements of InN NCs grown on *A*-plane GaN templates reveal a main emission at 0.69 eV, typical of good quality wurtzite InN, with a second one at 0.63 eV (Fig. 4). The emission intensity decreases as temperature increases and the position of both peaks experiment a small redshift before total quenching at 77 K. No variation was observed on the peak position energy when changing the excitation power over two orders of magnitude while a linear increase of the main emission (0.69 eV) integrated intensity was obtained.

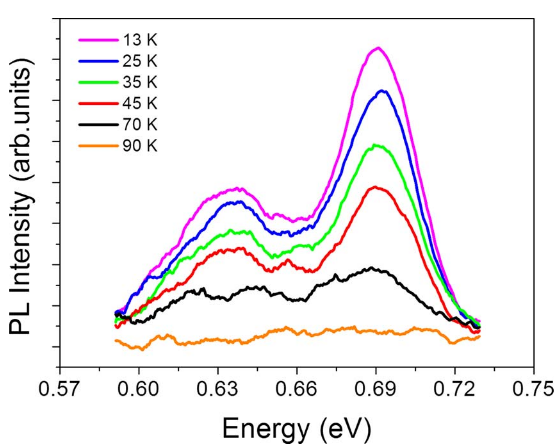

FIG. 4. (Color online) PL spectra of InN nanocolumns grown on *A*-plane GaN templates as a function of temperature.

In summary, good crystal quality wurtzite InN NCs were grown directly on *A*-plane GaN templates. RS measurements indicate that the InN NCs grow fully relaxed and their crystallographic orientation is along the *a* axis. Experimental evidences of the growth along this direction were also obtained by the analysis of the SAED and HRTEM images. Most of the columns are defect-free and are epitaxially aligned with respect to the GaN template with abrupt template-NC interfaces. These results indicate that obtaining high crystal quality InN NCs grown along the *a* axis is promising.

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