Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2006) 961 – 966
www.elsevier.com/locate/tsf

Near-infrared photoluminescence of vertically aligned InN nanorods grown on Si(111) by plasma-assisted molecular-beam epitaxy

H.-Y. Chen [a], C.-H. Shen [a], H.-W. Lin [a], C.-H. Chen [a], C.-Y. Wu [a], S. Gwo [a,*], V. Yu. Davydov [b], A.A. Klochikhin [b]

[a] Department of Physics, National Tsing-Hua University, Hsinchu 300, Taiwan, Republic of China
[b] Ioffe Physico-Technical Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia

Available online 11 September 2006

Abstract

We demonstrate that vertically aligned InN nanorods have been grown on Si(111) substrates by plasma-assisted molecular-beam epitaxy (PA-MBE) at low and high growth temperatures (LT- and HT-InN nanorods). High-resolution scanning electron microscopy images clearly show that InN nanorods grown on Si(111) are hexagonal in shape, vertically aligned, well separated and densely distributed on the substrate. The size distribution of LT-InN nanorods is quite uniform, while the HT-InN nanorods exhibit a broad, bimodal distribution. The structural analysis performed by Raman scattering indicates that PA-MBE grown InN nanorods have the wurtzite-type InN single-crystal structure with the rod axis (growth direction) along the *c*-axis. In addition, both types of nanorods contain high concentrations of electrons (unintentionally doped). Compared to the HT-InN nanorods and the PA-MBE-grown InN epitaxial film, the LT-grown InN nanorods have a considerable number of structural defects. Near-infrared photoluminescence (PL) from LT- (~0.77 eV) and HT-InN (~0.70 eV) nanorods is clearly observed at room temperature. In comparison with the LT-InN nanorods, the PL efficiency of HT-InN nanorods is better and the PL peak energy is closer to that of InN-on-Si epitaxial films (~0.66 eV). We also find that the PL band at low temperatures from nanorods is significantly weaker (compared to the InN film case) and exhibits anomalous temperature effects. We propose that these PL properties are results of considerable structural disorder (especially for the LT-InN nanorods) and strong surface electron accumulation effect (for both types of nanorods).

Keywords: Indium nitride (InN); Silicon; Nanorods; Molecular-beam epitaxy; Photoluminescence; Raman scattering

1. Introduction

Indium nitride (InN) has received considerable attention because of its newly discovered narrow direct band gap [1–6] and superior electron transport properties (small effective mass, high mobility and high drift velocity). The recently reported one-dimensional (1-D) growth modes of InN in the forms of nanowires, nanorods, nanotubes and nanotips [7–13] have also inspired novel bottom-up applications of 1-D InN nanomaterials for near-infrared (NIR) optoelectronics, photovoltaics and chemical/biological sensing. Due to the intrinsic property of electron accumulation at the InN surface [14–16], InN is considered a very promising material for high-sensitivity detection of gases, vapors and liquids [17,18]. Especially, the high surface-to-volume ratios of InN nanowires and nanorods render them excellent candidates for the sensor applications. Despite all the prospects, at present, fundamental studies about the material properties of 1-D InN are scarce. In particular, in contrast to the converging view about the optical properties of high-quality InN epilayers [1–6], the reports on the optical properties of 1-D InN are still controversial. Both red [7,10,11] and NIR [8,9,12,13] photoluminescence (PL) bands have been observed from 1-D InN samples. Furthermore, the observed PL signal is typically weak (compare to the thin film cases) and exhibits a reduced temperature effect [19].

Since both impurities and native point defects can affect the PL properties, to better understand the PL properties of 1-D InN, high-purity 1-D InN samples grown by plasma-assisted molecule beam epitaxy (PA-MBE) are desirable. In this work, we report on the structural and PL properties of vertically self-aligned InN nanorods grown along the wurtzite *c*-axis on Si (111) substrates by PA-MBE. In order to study the fundamental

* Corresponding author.
E-mail address: gwo@phys.nthu.edu.tw (S. Gwo).

0040-6090/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.tsf.2006.07.086

properties of InN nanorods and to compare the differences between InN epitaxial films and nanorods, we carried out growth experiments of InN nanorods under different conditions (different sample growth temperatures and flux ratios, samples are denoted here as low-temperature (LT) and high-temperature (HT) InN nanorods). *In situ* reflection high-energy electron diffraction (RHEED), high-resolution scanning electron microscopy (SEM) and Raman scattering measurements were undertaken to analyze the structural properties of InN nanorods grown under different conditions. From room-temperature (300 K) and low-temperature (12 K) PL measurements, we found that the PL band of the InN nanorod samples lies in the NIR region (consistent with the PL band of InN epitaxial films) and is significantly weaker in intensity as compared to that of InN epitaxial films. We attribute the low efficiency of radiative recombination by photogenerated carriers in InN nanorods as a consequence of considerable structural disorder (especially for the LT-InN nanorods) and strong surface electron accumulation effect (for both types of nanorods).

2. Experimental

The samples used in this study were grown on 3-in. Si(111) substrates by PA-MBE with a base pressure in the 10^{-11} torr range. Silicon wafers were first chemically etched to remove the native oxide layer before loading into the MBE chamber and thermally degassed in the MBE chamber prior to the growth. The InN epitaxial film was grown on Si(111) using the epitaxial AlN/β-Si_3N_4 double buffer layer technique. Details of the growth procedure can be found elsewhere [5,20]. Using this growth technique, relaxed wurtzite InN and AlN epilayers can be grown and the *c*-axis is oriented vertically to the Si(111) substrate plane. We have recently demonstrated that high-quality InN/AlN heterostructures can be formed on Si(111) due to the existence of “magic” ratios between the lattice constants of comprising material pairs: 2:1 (Si:Si_3N_4), 5:4 (AlN/Si) and 8:9 (InN:AlN) [21]. This new route of lattice matching allows the formation of commensurate InN/AlN interface with a common two-dimensional superlattice. For InN growth on AlN with nitrogen polarity, we found that the pseudomorphic to commensurate lattice transition occurs within the first monolayer of growth, resulting in an abrupt heterojunction at the atomic scale. The in-plane axes of the wurtzite epilayers were found to follow the epitaxial relations: $\langle\bar{1}\,\bar{1}\,20\rangle_{InN/AlN/Si_3N_4}||[\bar{1}\,10]_{Si}$ and $\langle\bar{1}\,100\rangle_{InN/AlN/Si_3N_4}||[11\,\bar{2}]_{Si}$. The free electron concentration in the as-grown films is about $\sim 3–4\times10^{18}$ cm^{-3} and the mobility is a function of buffer and InN film thicknesses with typical values ranging from 500 cm^2/V s (~0.6-μm-thick InN) to 1200 cm^2/V s (~2.5-μm-thick InN). A large valence band offset (3.10 eV) of type-I band alignment was also determined by photoelectron spectroscopy for the InN/AlN 8:9 commensurate heterojunction [22].

For the InN film growth, the N/In flux ratio was adjusted to be close to the stoichiometric condition. On the other hand, the InN nanorod growth always proceeds under the nitrogen rich conditions, similar to the reported columnar growth mode of vertically aligned GaN nanorods by PA-MBE [23–26]. In our study, the LT-InN nanorods were grown at sample temperatures of ~330 °C and the HT-InN nanorods were grown at ~520 °C on β-Si_3N_4/Si(111) (without the AlN buffer layer). The N/In flux ratios are normalized to the thin film growth case under identical nitrogen plasma conditions. For thin film growth, the In flux was $\sim 1\times10^{-7}$ torr and nitrogen flow rate was ~3 sccm with RF power of 500 W. The N/In flux ratios were ~2.6 and ~6.0 for LT- and HT-InN nanorods, respectively. The N/In flux ratio was adjusted at different growth temperatures to ensure the growth proceeded in the columnar mode. The morphologies and size distributions of InN nanorods were obtained using a field-emission scanning electron microscope. Polarized Raman spectra were measured at room temperature in a backscattering configuration with the excitation energy of 2.54 eV (488 nm). The spectral resolution is typically about 2 cm^{-1}. The PL signal was measured at room temperature (300 K) and low temperature (12 K) by using the 514.5 nm line of an Ar^+ laser as the excitation source. The luminescence signal was analyzed by a 0.19 m monochromator with a 600 g/mm grating and detected by a liquid-nitrogen-cooled extended InGaAs detector (cutoff wavelength ≈ 2.4 μm). All the PL spectra have been corrected by the system response curve.

3. Results and discussion

Fig. 1(a) and (b) are RHEED pattern images taken during MBE growth of LT- and HT-InN nanorods. The observed RHEED patterns indicate that both LT- and HT-InN nanorod

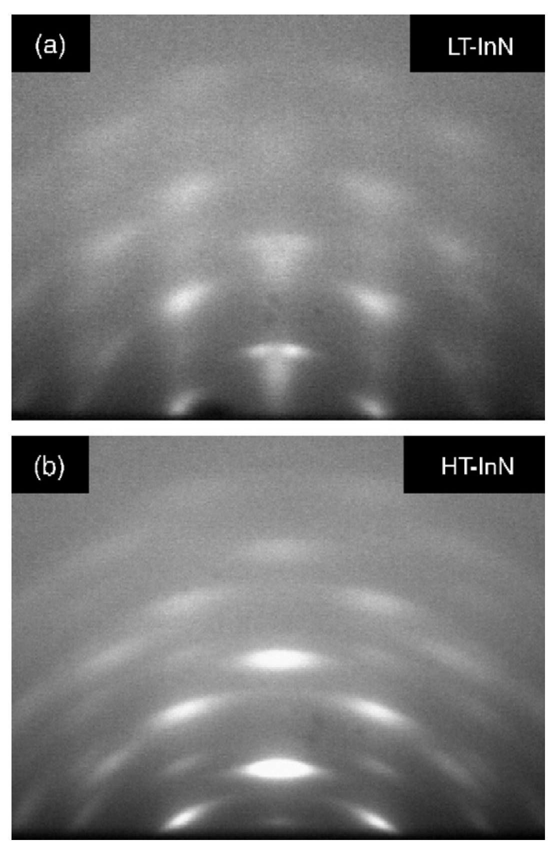

Fig. 1. RHEED patterns of LT- (growth temperature ≈ 330 °C) and HT- (growth temperature ≈ 520 °C) InN nanorods grown on Si(111) substrates by PA-MBE.