High-phase-purity zinc-blende InN on *r*-plane sapphire substrate with controlled nitridation pretreatment

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High-phase-purity zinc-blende (zb) InN thin film has been grown by plasma-assisted molecular-beam epitaxy on *r*-plane sapphire substrate pretreated with nitridation. X-ray diffraction analysis shows that the phase of the InN films changes from wurtzite (w) InN to a mixture of w-InN and zb-InN, to zb-InN with increasing nitridation time. High-resolution transmission electron microscopy reveals an ultrathin crystallized interlayer produced by substrate nitridation, which plays an important role in controlling the InN phase. Photoluminescence emission of zb-InN measured at 20 K shows a peak at a very low energy, 0.636 eV, and an absorption edge at ~ 0.62 eV is observed at 2 K, which is the lowest bandgap reported to date among the III-nitride semiconductors. © 2008 American Institute of Physics. [DOI: 10.1063/1.2898214]

III-nitride semiconductors with zinc-blende (zb) structure have attracted much attention in recent years.^{1–7} Since the cubic system has a higher crystallographic symmetry than the hexagonal one, it is expected to have lower phonon scattering, better electron transport properties, absent or reduced built-in spontaneous polarization, etc.^{8–10} Moreover, theoretical calculations have predicted that the zb-InN will exhibit an even narrower bandgap (0.5–0.6 eV) than wurtzite (w) InN.^{11–13} Recently, a revised bandgap of w-InN at 0.65–0.70 eV has been suggested by a number of experimental data and theoretical calculations,^{12–18} but the bandgap of zb-InN is still not well established. In the past, zb-InN films have been grown on different substrates, including GaAs(001), InAs(001), 3C-SiC(001), *r*-plane sapphire, etc., with proper buffer layers.^{1–7} However, in most of these studies, photoluminescence (PL) emission peak energies above 0.68 eV were reported, similar to that of w-InN. Direct evidence from absorption spectra to support that zb-InN has a lower bandgap than w-InN is still lacking. In this paper, we controlled the phase of InN grown on *r*-plane sapphire by tuning the substrate nitridation conditions. The phase of the InN films was analyzed by x-ray diffraction (XRD) and transmission electron microscopy (TEM). PL measured at 20 K shows that the zb-InN has an emission peak at 0.636 eV, which is about 45 meV lower than that of high quality w-InN.¹⁴ Furthermore, the absorption edge measured at 2 K was found to be ~ 0.62 eV, which further supports that the zb-InN should have the lowest bandgap among all III-nitride semiconductors.^{12,13}

The method used to grow InN thin films is a plasma-assisted molecular-beam epitaxy (SVTA Model SVT-V-2). 8N elemental indium was evaporated by a conventional Knudsen cell. The atomic nitrogen source was supplied by a radio-frequency (rf) plasma generator, fed with ultrahigh

pure (6N) nitrogen gas. Before the sample growth, the substrate was degreased using acetone, methanol, de-ionized water with ultrasonic bath, and chemically dipped into H₂SO₄/H₃PO₄ solution. Then, the Al₂O₃(1102) (*r*-plane sapphire) substrate was outgassed at 800 °C in the growth chamber. Afterward, the InN films were grown on these substrates with or without substrate nitridation. Table I shows the growth conditions of the InN thin films. Substrate nitridation was performed before InN growth at 200 °C. Subsequently following the nitridation, the growth of InN films was carried out at 400–420 °C for 3 h. The growth rate of the InN films is in the range of 110–120 nm/h. Figure 1 shows the $\theta/2\theta$ -scan XRD (Bruker D8 Advance) patterns of the InN films. By increasing the initial nitridation time, the phase of the InN films changes from (a) w-InN(1011) at 33.1° (sample A) to (b) a mixture of w-InN and zb-InN (sample B), to (c) zb-InN(200) at 35.8° (sample C). The lattice constant of the zb-InN calculated from XRD is 0.501 nm, which is consistent with previously reported values.^{1–5}

To further understand the role of the interface after nitridation, high-resolution TEM was employed to study the interface between the film and the substrate. Figure 2(a) shows a TEM image of a 350-nm-thick zb-InN film (sample C). Some inclined stacking faults with $\sim 57^\circ$ to the sapphire substrate, as shown by the indicator in Fig. 2(a), appeared in the film. These stacking faults are related to the wurtzite phase with the w-InN(0001) plane stacked along the zb-InN(111)

TABLE I. Growth conditions of the InN films.

Sample	Nitridation time (min)	Growth temperature(°C)	Growth time (h)	rf power (W)
A	0	420 ± 20	3	450
B	15	400 ± 20	3	450
C	30	400 ± 20	3	450

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FIG. 1. (Color online) $\theta/2\theta$ -scan XRD analyses. These InN thin films were grown on *r*-plane sapphire substrates with different substrate nitridation times (t_N) of (a) 0 (sample A), (b) 15 (sample B), and (c) 30 min (sample C). The phase of InN changes from wurtzite to zinc blende with increasing nitridation time.

plane.³ Although the TEM image shows inclusion of some fraction of wurtzite phase, the film structure is still dominated by the zinc-blende phase. The corresponding selected area diffraction (SAED) pattern taken at the interface [Fig. 2(b)] reveals that the relationships along surface normal and in-plane orientation are $zb\text{-InN}(200) \parallel r\text{-Al}_2\text{O}_3(1\bar{1}02)$ and $zb\text{-InN}[011] \parallel r\text{-Al}_2\text{O}_3[02\bar{2}1]$, respectively. Figure 2(c) shows a high-resolution atomic image taken at the interface of sample C. An ultrathin layer (~ 1 nm) appears at the interface and the $zb\text{-InN}$ film is stacked on top of this interlayer. Using the interplanar spacing of $d_{(1\bar{1}02)} = 0.348$ nm of the sapphire substrate as the reference scale, the lattice constant of $zb\text{-InN}$ is obtained as $a = 0.499$ nm. This result is consistent with the lattice constant obtained from XRD analysis. Inter-

FIG. 2. (Color online) TEM images. (a) A 350-nm-thick $zb\text{-InN}$ film grown on *r*-plane sapphire substrate (sample C). (b) Corresponding SAED pattern taken at interface shows a growth relationship of $zb\text{-InN}(200) \parallel r\text{-Al}_2\text{O}_3(1\bar{1}02)$. (c) High-resolution atomic image reveals an ultrathin interlayer, generated through nitridation process, between the InN film and the sapphire substrate. (d) Directly deposited InN on sapphire substrate exhibits sharp interface without any interlayer (sample A).

FIG. 3. (Color online) Low-temperature PL measured at 20 K and absorption spectra measured at 20 K of $zb\text{-InN}$ film, $w\text{-InN}$ film, and NDF MCs, respectively. (a) The $zb\text{-InN}$ film shows a very low PL emission peak at 0.636 eV, which is 68 and 45 meV lower than $w\text{-InN}$ film and NDF MCs, respectively. The absorption spectrum of the $zb\text{-InN}$ film also shows a rather low edge at ~ 0.62 eV. (b) The PL peak energy vs temperature reveals that all the peak energies of $zb\text{-InN}$ film locate below those of $w\text{-InN}$ and NDF MCs.

estingly, the interlayer exhibits a similar crystalline structure to that of the $zb\text{-InN}$ and its thickness is twice the interplanar spacing of $d_{\text{interlayer}} = 0.435$ nm, which is very close to the lattice constant of $zb\text{-AlN}$.¹⁹ In contrast, InN film directly deposited on *r*-plane sapphire without nitridation pretreatment displays a completely different appearance, as shown in Fig. 2(d) (sample A). No interlayer was formed at the interface and the crystalline structure of the InN film shows wurtzite phase with a surface normal orientation of $w\text{-InN}(10\bar{1}1)$, consistent with the XRD analysis. Formation of an AlO_xN_y ($y > 0.9$) layer has been reported for sapphire substrates after sufficient nitridation, which is believed to improve the subsequent GaN film quality.²⁰ Meanwhile, Lozano *et al.* have suggested that a thin indium oxide buffer layer on a *c*-plane sapphire substrate would help in mediating the growth of the high-purity $zb\text{-InN}$ film.⁷ In our case, an interlayer, presumably of AlO_xN_y , is proposed to play an important role to promote the $zb\text{-InN}$ film growth on a non-cubic phase substrate with rectangular surface symmetry.

Figure 3(a) shows low-temperature PL and absorption spectra of a $zb\text{-InN}$ film, a $w\text{-InN}$ film, and nearly defect-free microcrystals (NDF MCs)¹⁶ performed at 20 and 2 K, respectively. A frequency-doubled $\text{Nd}^{3+}\text{-YAG}$ (yttrium aluminum garnet) laser at 532 nm was used as the PL excitation source. The collected PL light was dispersed through a 0.5 m monochromator equipped with a 300 g/mm grating and detected by an extended-InGaAs detector (detecting range: 0.5–1.1 eV). The absorption spectroscopy was performed in a BOMEM DA8 Fourier transform interferometer with a CaF_2 beam splitter, a light source of quartz halogen lamp, and an InSb detector. The PL peaks of the $w\text{-InN}$ film, NDF MCs, and the $zb\text{-InN}$ film are located at 0.704, 0.681, and 0.636 eV with full widths at half maximum of 80, 21, and 71 meV (fitted by Gaussian), respectively. The absorption edge (E_{abs}) of the $zb\text{-InN}$ film is determined at ~ 0.62 eV by extrapolating the nearly linear region down to its baseline and the curve shows a prominent redshift as compared with the $w\text{-InN}$ film. Although the E_{abs} of the $w\text{-InN}$ film cannot be determined precisely due to the Fabry–Pérot oscillation, the E_{abs} at ~ 0.76 eV, which is extracted by a fitting curve with a sigmoidal equation (Boltzmann function),¹⁴ is estimated. The above results are remarkable because the band-gap difference between wurtzite and zinc-blende InN would be larger than 45 meV based on the results of PL peak energy and absorption edge. Besides, both $w\text{-InN}$ and $zb\text{-InN}$

films have the same level of carrier densities in the range of $(1-2) \times 10^{19} \text{ cm}^{-3}$ as determined in Hall measurements. If we further consider the band filling (Burstein–Moss shift) and the band tailing effects, which resulted in a large blueshift and a weak redshift of the observed PL peak and absorption edge, respectively, in degenerate semiconductors, such as high-carrier-density w-InN,^{14,21,22} the bandgap of the zb-InN with zero carrier concentration would be even lower than 0.62 eV.

Figure 3(b) shows the plot of PL peak energy versus the temperature. Only the NDF MCs follow the Varshni equation well because of its high crystalline quality and low carrier concentration. An anomalous (S-shaped) temperature-dependent PL peak of the zb-InN film could be observed. This behavior have been discovered from ternary or quaternary alloy and multiple quantum wells.^{23,24} In order to elucidate the somewhat strange temperature dependence in our case, one has to consider the high carrier density. The high carrier density will likely give rise to the localization phenomena but cannot fully explain the temperature dependence. Also, for material with a high carrier density, a redshift is primarily expected, at least from somewhat elevated temperatures.²⁵ Another factor taken into account is the content of a small amount of w-InN embedded in the zb-InN film. Mixture phases of wurtzite and zinc blende have been similarly observed in GaN film with a resulting type II semiconductor system.²⁶ Unfortunately, for the case of InN, the band offset for the zb-InN/w-InN system has not been reported to the best of our knowledge, neither theoretically or experimentally. However, the bandgaps are fairly similar,^{2,11–17} which increases the probability for a type II alignment. In a type II structure, a transition from spatially indirect at lowest temperatures to spatially direct transitions at elevated temperatures could give rise to a blueshift in the PL spectra with increasing temperatures. Nevertheless, more experiments are still needed to clarify the origin of the S-shaped behavior in zb-InN.

In summary, the growth of zb-InN films on *r*-plane sapphire is achieved by inserting an interlayer by means of a proper substrate nitridation. The orientation relationship for zb-InN film on sapphire along its surface normal is zb-InN(200)∥*r*-Al₂O₃(1102) and that along the in-plane direction is zb-InN[011]∥*r*-Al₂O₃[0221]. The differences in PL peak energy and the absorption edge are 68 and ~140 meV, respectively, between the w-InN and zb-InN films with similar levels of carrier densities. Furthermore, even the low-carrier-density InN microcrystals¹⁶ show a higher PL peak energy than the zb-InN film with somewhat higher carrier density. Our results have further supported that zinc-blende structured nitride semiconductors indeed have lower bandgaps than their wurtzite counterparts.^{12,13}

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