Structural properties of InN films grown on O-face ZnO(000(1)over-bar) by plasma-assisted molecular beam epitaxy

Citation for published version (APA):

Cho, Y., Brandt, O., Korytov, M., Albrecht, M., Kaganer, V. M., Ramsteiner, M., & Riechert, H. (2012). Structural properties of InN films grown on O-face ZnO(000(1)over-bar) by plasma-assisted molecular beam epitaxy. *Applied Physics Letters*, 100(15), [152105]. <https://doi.org/10.1063/1.3702572>

DOI:

[10.1063/1.3702572](https://doi.org/10.1063/1.3702572)

Document status and date:

Published: 01/01/2012

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Structural properties of InN films grown on O-face ZnO(000 $\bar{1}$) by plasma-assisted molecular beam epitaxy

YongJin Cho,^{1,a)} Oliver Brandt,¹ Maxim Korytov,² Martin Albrecht,² Vladimir M. Kaganer,¹ Manfred Ramsteiner,¹ and Henning Riechert¹

¹Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5–7, 10117 Berlin, Germany

²Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, 12489 Berlin, Germany

(Received 2 February 2012; accepted 23 March 2012; published online 10 April 2012)

We study the impact of substrate temperature and layer thickness on the morphological and structural properties of InN films directly grown on O-face ZnO(000 $\bar{1}$) substrates by plasma-assisted molecular beam epitaxy. With increasing substrate temperature, an interfacial reaction between InN and ZnO takes place that eventually results in the formation of cubic In₂O₃ and voids. The properties of the InN films, however, are found to be unaffected by this reaction for substrate temperatures less than 550 °C. In fact, both the morphological and the structural quality of InN improve with increasing substrate temperature in the range from 350 to 500 °C. High quality films with low threading dislocation densities are demonstrated. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3702572>]

The revision of the fundamental band gap of InN a decade ago^{1,2} has renewed the interest in this compound semiconductor, which is now believed to possess not only the smallest band gap but also the smallest effective mass and the highest electron drift velocity among the group III-nitride semiconductors. However, InN is still the least mature of the group III-nitride semiconductors primarily due to the difficulty in its synthesis. Contrary to its two relatives GaN and AlN, the metal-stable growth of InN along the cation-polar [0001] direction was found to be problematic for fundamental reasons: InN(0001) actually dissociates at temperatures below those required for the desorption of In from the growth front.³ Growth with excess In thus inevitably results in an accumulation of In on the surface and even in In inclusions in the film.⁴

Xu and Yoshikawa⁵ were the first to report that these problems can be overcome by growth along the anion-polar [000 $\bar{1}$] direction. However, InN(000 $\bar{1}$) is most frequently prepared on GaN(000 $\bar{1}$) templates themselves obtained heteroepitaxially.^{4,6–9} Obviously, these templates do not represent an ideal substrate, since they invariably exhibit a high dislocation density degrading both the structural and morphological properties of the GaN template. From this point of view, ZnO seems to be an interesting alternative substrate for InN. ZnO is isomorphic to InN with a smaller mismatch (8%) than GaN (11%). Furthermore, ZnO bulk substrates with excellent crystal quality and epi-ready Zn- as well as O-face surfaces are commercially available. Despite this fact, the growth of InN on ZnO has not been thoroughly investigated.^{10–13} A drawback of ZnO is its pronounced reactivity with InN as demonstrated in Ref. 13. At present, however, it is not clear whether a reaction between these materials can be inhibited or not.

In this paper, we study the structural properties of InN films grown on O-face ZnO(000 $\bar{1}$) substrates by molecular beam epitaxy (MBE). The impact of the substrate temperature T_S on the films' morphology and the structure of the InN/ZnO interface is investigated in detail. Moreover, we examine the microstructure of InN films of various thicknesses and show that films with low threading dislocation (TD) densities may be obtained on ZnO.

As substrates, we use epi-ready O-face ZnO(000 $\bar{1}$) wafers produced by Tokyo Denpa Co., Ltd. Atomic force microscopy (AFM) reveals a typical root-mean-square roughness of the O-face surface of 0.2–0.3 nm over an area of 25 μm^2 . High-resolution x-ray diffraction (XRD) ω scans across the (0002) and the (10 $\bar{1}$ 2) reflection exhibit a full-width-at-half-maximum (FWHM) of 27 and 50 arcsec, respectively. The InN films presented here were directly grown on the O-face ZnO (000 $\bar{1}$) surface in a MBE chamber equipped with a standard effusion cell for In and a radio-frequency plasma source for the active N species. The base pressure of the growth chamber is $< 10^{-10}$ Torr, and the chamber was maintained at $\approx 5 \times 10^{-6}$ Torr during the growth runs. All the InN films were grown under slight N excess with a N/In flux ratio of ≈ 1.2 . Two groups of samples were prepared. For group A, T_S was varied from 350 to 600 °C for the growth of InN films with the same nominal thickness of 130 nm. For group B, InN films with different thicknesses in the range from 0.172 to 2.5 μm were grown at the same T_S of 475 °C. The morphology and structural quality of the InN films were evaluated by *in situ* reflection high-energy electron diffraction (RHEED), AFM, and XRD. For studying the interface structure, scanning electron (SEM) and high-resolution transmission electron (TEM) microscopies were employed. As an optical method to characterize structural quality and to estimate the carrier concentration in the films, Raman scattering experiments were carried out at 300 K in a $z(x, -)\bar{z}$ backscattering configuration (z is parallel to the c axis) using an excitation wavelength of 482.5 nm. Samples for TEM were prepared by plan parallel mechanical

^{a)}Present address: Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands. Electronic mail: yjcho@alumni.nd.edu.

FIG. 1. RHEED patterns [(a)–(c)], AFM [(d)–(f)], and TEM [(g)–(i)] micrographs of thin InN films grown at different T_S , namely, 350 °C for the images in the left column [(a), (d), and (g)], 450 °C for those in the center column [(b), (e), and (h)], and 550 °C for those in the right column [(c) and (f)] with the exception of the sample in (i) which was grown at 600 °C. All RHEED patterns were taken along the $\langle 11\bar{2}0 \rangle$ azimuth after growth. The inset in (f) shows a bird's eye view SEM micrograph of the surface of the sample. The arrow indicates a hexagonal pit. The white box in (g) draws attention to the presence of cubic InN clearly seen in the magnified inset. The white arrows in (g)–(i) highlight the interface between InN and ZnO.

polishing down to a sample thickness of about 10 μm followed by ion milling with a Gatan Pips under liquid nitrogen cooling. TEM was performed in an aberration corrected FEI TITAN 80-300 using imaging conditions ($cs < 2 \mu\text{m}$, Gaussian focus) providing for amplitude contrast.

We first discuss the structural characteristics of the thin InN films of group A. Figure 1(a) presents the RHEED pattern of the film after growth at 350 °C. A spotty pattern is observed for this case, reflecting a three-dimensional growth as also evident from the surface morphology of this sample displayed in Fig. 1(d). The transmission pattern reveals the hexagonal structure of the InN film after growth. In the early stage of InN growth at this low temperature, however, the RHEED pattern exhibited reflections characteristic for the twinned cubic phase. Indeed, the TEM micrograph of this sample displayed in Fig. 1(g) shows the presence of the zinc-blende phase close to the interface.

For the InN films grown at higher T_S , a two-dimensional growth mode is evident from the streaky RHEED patterns with clear Kikuchi lines [Figs. 1(b) and 1(c)]. This streaky pattern starts to dominate after less than 1 nm of deposition after the initiation of growth and is sustained until the end of growth. The AFM micrographs shown in Figs. 1(d)–1(f) confirm the improvements of surface morphology with increasing T_S : The root-mean-square roughness measured by AFM on a $5 \times 5 \mu\text{m}^2$ area amounts to 4.0, 3.3, and 1.0 nm for T_S of 350, 450, and 550 °C, respectively. Despite the slight N-excess during growth, a smooth surface exhibiting atomic steps is obtained for the highest T_S [Fig. 1(f)]. At the same time, deep hexagonally shaped pits are present in these films, particularly for the one grown at the highest T_S . The inset in Fig. 1(f) shows a typical example for the cross-section of these pits and reveals that they actually originate from the InN/ZnO interface. In all cases, we observe the ZnO substrate beneath the pit to be severely disturbed.

Figures 1(g)–1(i) show cross-sectional TEM micrographs of the InN/ZnO interface as dependent on T_S . The interface is structurally and chemically abrupt for the low-temperature sample as already mentioned above [Fig. 1(g)]. For higher T_S , the cubic phase of InN close to the interface is absent, and a regular network of a -type (Burgers vector $\mathbf{b} = \langle 11\bar{2}0 \rangle / 3$) 60° misfit dislocations is present at the interface [e.g., see Fig. 1(h)]. While the interface itself remains abrupt, we observe nanoscale protrusions distributed in patches in the ZnO substrate for the samples grown at this intermediate T_S ($= 450^\circ\text{C}$) (not shown here). These protrusions are of cubic crystal structure and are chemically distinct from both InN and ZnO. Their actual nature can be analyzed for the sample grown at the T_S of 600 °C [Fig. 1(i)], where the protrusions are found to be large enough to extend throughout the cross-section. The crystal structure and lattice

FIG. 2. FWHM of the XRD ω scans across the (0002) reflection for thin InN films grown at different T_S . The line is a guide to the eye. The inset shows a symmetric XRD $\omega - 2\theta$ scan of an InN film grown at 600 °C.

constant of all protrusions examined match the ones of cubic In_2O_3 , which is consistent with the results of Shih *et al.*¹³

Figure 2 shows the FWHM of XRD ω scans across the (0002) reflection as a function of T_S (group A). Between 350 and 500 °C, the FWHM monotonically decreases, eventually reaching the value (≈ 27 arcsec) of the ZnO substrates for $T_S = 500$ °C. This improvement of the structural quality of InN despite the beginning of interfacial reactions was confirmed by Rutherford backscattering measurements (not shown here). For the highest T_S of 600 °C, an abrupt increase of the FWHM occurs. The inset in Fig. 2 depicts an XRD $\omega - 2\theta$ scan of this sample. The intensity of the In_2O_3 (222) is comparable to that of the InN (0002) reflection, suggesting that a significant volume at the interface has been transformed, as also suggested by TEM [Fig. 1(i)]. Due to this transformation of InN into In_2O_3 , the thickness of the InN layer grown at 600 °C is significantly smaller than the nominal one (130 nm). For this sample, the In_2O_3 protrusions are accompanied by voids [Fig. 1(i)] as reported previously by Shih *et al.*¹³ Despite of these voids, we still observe the formation of a well-defined film with an abrupt “interface” to both the voids and the protrusions. In atomically resolved lattice images,¹⁴ the interface is even seen to exhibit a regular array of misfit dislocations (corresponding to the 8% mismatch between InN and ZnO) directly above the voids. Moreover, the RHEED pattern recorded during the nucleation stage was free from any secondary reflections related to the formation of cubic In_2O_3 . These findings demonstrate that the reaction between InN and ZnO does not take place during nucleation, but rather after the formation of a well-defined, relaxed InN film which continues to grow unperturbed by the simultaneously occurring interface reaction. In fact, the atomically resolved lattice images¹⁴ also demonstrate that all the InN films are N-polar as expected from a nucleation on bare $\text{ZnO}(000\bar{1})$.

We next discuss the evolution of the structural perfection of InN films with thickness (group B). The films were

FIG. 3. XRD ω scans across the (0002) and $(10\bar{1}2)$ reflections for a 1.85 μm thick InN film grown at 475 °C. The grey squares display the experimental data, and the solid lines a fit using the model described in the text. The right inset shows a plan-view TEM micrograph of this sample. The red circles highlight threading dislocations. The arrow indicates the diffraction vector $\mathbf{g} = 1120$ used for imaging the dislocations. The left inset shows the evolution of the FWHM of the $(10\bar{1}2)$ ω scans with the thickness of films grown at 475 °C. The dashed line is a guide to the eye.

grown at an intermediate T_S of 475 °C, at which no significant amounts of In_2O_3 and voids are formed at the interface. Symmetric ω scans across the (0002) reflection do not show any evident thickness dependence, with an FWHM scattering around a mean value of 100 arcsec. In contrast, and as shown in the left inset of Fig. 3, the FWHM of the asymmetric ω scans across the $(10\bar{1}2)$ reflection monotonically decrease with increasing film thickness by a factor of four. This latter result implies that the density of a -type TDs continues to decrease with increasing film thickness even beyond a value of 2 μm . For InN grown on GaN templates, TD annihilation is complete at a thickness between 0.5 μm and 1 μm .^{9,15}

Since the FWHM of x-ray reflections is not determined by the dislocation density alone, but is affected also by correlations between the dislocations, we analyze the ω scans of one of these samples (with a thickness of 1.85 μm) with a model properly taking into account both of these effects.¹⁶ Figure 3 depicts both the symmetric and asymmetric XRD ω scans for this sample together with a best fit based on the model developed in Ref. 16. The densities of dislocations having a - and c -component Burgers vectors obtained from the fits are $\approx 2 \times 10^{10} \text{ cm}^{-2}$ and $\approx 2 \times 10^8 \text{ cm}^{-2}$, respectively. The former of these values is to be compared with the a -type TD density of $\approx 1 \times 10^{10} \text{ cm}^{-2}$ estimated from plan-view TEM (see the right inset of Fig. 3). The factor of two between the values derived from XRD and TEM is a natural consequence of the different spatial regions sampled by these two techniques. XRD integrates over the entire thickness of the film, and thus also reflects the high dislocation density directly at the interface and in the bottom part of the film. Plan-view TEM, in contrast, only images the dislocations contained in the upper part (at most a few 100 nm) of the film. The density of these dislocations is necessarily lower than the one averaged over depth due to the efficient annihilation of TDs occurring for the present samples (cf. inset of Fig. 3). In any case, the dislocation density measured for the present samples (the 2.5 μm -thick InN film has a TD density of $\approx 9 \times 10^9 \text{ cm}^{-2}$ according to plan-view TEM) is comparable to or lower than the lowest values reported in the literature.⁹

Figure 4 shows the room-temperature Raman spectrum of a 1.85 μm thick InN film grown at 475 °C. In accordance with the Raman selection rules for wurtzite crystals,¹⁷ the

FIG. 4. Raman spectrum of a 1.85 μm -thick InN film grown at 475 °C recorded at 300 K and with excitation at 482.5 nm.

spectrum measured in the $z(x, -)\bar{z}$ configuration exhibits clearly scattering by the E_2 and $A_1(\text{LO})$ phonon modes at 491 cm^{-1} and 585 cm^{-1} , respectively. The spectral width of the E_2 phonon line is commonly used as a measure of the structural quality, since it increases with decreasing phonon correlation length caused by lattice disorder.^{4,18,19} The narrow E_2 phonon line ($\text{FWHM} < 3\text{ cm}^{-1}$), therefore, supports our above findings concerning the excellent structural quality of our thick InN films. The observed linewidth is smaller than that of typical InN films grown on other substrates including GaN templates.^{4,18,20} In addition to the E_2 and $A_1(\text{LO})$ phonon modes, a weak peak due to scattering by the low-frequency coupled plasmon-phonon mode (L^-) is resolved at about 430 cm^{-1} .¹⁷ The observed frequency of this peak corresponds to an estimated electron density of $9 \times 10^{18}\text{ cm}^{-3}$,²¹ which is larger than that in InN films with comparable dislocation densities grown on GaN templates. The comparatively large electron density is presumably due to the interfacial reaction and the resulting incorporation of O donors in the InN films. Indeed, we have found that the electron density in the investigated InN films decreases drastically with decreasing film thickness and decreasing substrate temperature. For example, the $2.5\text{ }\mu\text{m}$ -thick InN film in the inset of Fig. 3 exhibits an electron density of about $4 \times 10^{18}\text{ cm}^{-3}$, and for samples prepared at lower T_s , the electron density drops into the 10^{17} cm^{-3} range. For these samples, we observe the band-to-band transition in room-temperature photoluminescence spectra to be at 0.66 eV ,²² i.e., close to the fundamental gap of InN.^{8,23}

Summarizing and concluding, the structural properties of InN films on ZnO are largely unaffected by the interfacial reaction between these two materials for substrate temperatures less than 550°C . At the same time, a -type TDs are found to annihilate each other efficiently even at a layer thickness exceeding $2\text{ }\mu\text{m}$, resulting in a high structural quality for films of this thickness. Despite the high chemical reactivity and the consequential degradation of the interface and unintentional donor doping, O-face ZnO(000 $\bar{1}$) hence remains an interesting substrate for InN.

The authors would like to thank Kin Man Yu for the RBS measurements, Uwe Jahn for the SEM image, and

Hans-Peter Schönherr for the maintenance of the MBE system. We are indebted to Emmanouil Dimakis for critical reading of the manuscript. Part of the work has been performed within the IAPP project SINOPE, financed by the European Union.

- ¹V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmüller, H. Harima, A. V. Mudryi, J. Adhrhold, O. Semchinova, and J. Graul, *Phys. Status Solidi B* **229**, R1 (2002).
- ²J. Wu, W. Walukiewicz, K. M. Yu, J. W. Arger III, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, *Appl. Phys. Lett.* **80**, 3967 (2002).
- ³E. Dimakis, E. Iliopoulos, K. Tsagaraki, Th. Kehagias, Ph. Komninou, and A. Georgakilas, *J. Appl. Phys.* **97**, 113520 (2005).
- ⁴T. Ive, O. Brandt, M. Ramsteiner, M. Giehler, H. Kostial, and K. H. Ploog, *Appl. Phys. Lett.* **84**, 1671 (2004).
- ⁵K. Xu and A. Yoshikawa, *Appl. Phys. Lett.* **83**, 251 (2003).
- ⁶S. V. Ivanov, T. V. Shubina, V. N. Jmerik, V. A. Vekshin, P. S. Kop'ev, and B. Monemar, *J. Cryst. Growth* **269**, 1 (2004).
- ⁷X. Wang, S.-B. Che, Y. Ishitani, and A. Yoshikawa, *J. Appl. Phys.* **99**, 073512 (2006).
- ⁸G. Koblmüller, C. S. Gallinat, S. Bernardis, J. S. Speck, G. D. Chern, E. D. Readinger, H. Shen, and M. Wraback, *Appl. Phys. Lett.* **89**, 071902 (2006).
- ⁹C. S. Gallinat, G. Koblmüller, F. Wu, and J. S. Speck, *J. Appl. Phys.* **107**, 053517 (2010).
- ¹⁰S. Ohuchi and T. Takizawa, *J. Electron. Mater.* **34**, 424 (2005).
- ¹¹T. Ohgaki, N. Ohashi, H. Haneda, and A. Yasumori, *J. Cryst. Growth* **292**, 33 (2006).
- ¹²T. Ohgaki, N. Ohashi, T. Ohnishi, H. Haneda, M. Lippmaa, and A. Yasumori, *J. Ceram. Soc. Jpn.* **115**, 414 (2007).
- ¹³C.-H. Shih, I. Lo, W.-Y. Pang, and C.-H. Hsieh, *J. Phys. Chem. Solids* **71**, 1664 (2010).
- ¹⁴M. Korytov (unpublished).
- ¹⁵V. Lebedev, V. Cimalla, J. Pezoldt, M. Himmerlich, S. Krischok, J. A. Schaefer, O. Ambacher, F. M. Morales, J. G. Lozano, and D. Gonzalez, *J. Appl. Phys.* **100**, 094902 (2006).
- ¹⁶V. M. Kaganer, O. Brandt, A. Trampert, and K. H. Ploog, *Phys. Rev. B* **72**, 045423 (2005).
- ¹⁷V. Yu. Davydov and A. A. Klochikhin, *Semiconductors* **38**, 861 (2004).
- ¹⁸M.-C. Lee, H.-C. Lin, Y.-C. Pan, C.-K. Shu, J. Ou, W.-H. Chen, and W.-K. Chen, *Appl. Phys. Lett.* **73**, 2606 (1998).
- ¹⁹A. Delimitis, P. Gladkov, Ph. Komninou, Th. Kehagias, J. Arvanitidis, S. Ves, M. Katsikini, E. Dimakis, and A. Georgakilas, *Phys. State Solidi A* **203**, 162 (2006).
- ²⁰R. Cuscó, E. Alarcoñ-Lladó, J. Ibáñez, T. Yamaguchi, Y. Nanishi, and L. Artús, *J. Phys.: Condens. Matter* **21**, 415801 (2009).
- ²¹E. Burstein, A. Pinczuk, and S. Iwasa, *Phys. Rev.* **157**, 611 (1967).
- ²²Y. J. Cho (unpublished).
- ²³C. S. Gallinat, G. Koblmüller, J. S. Brown, S. Bernardis, J. S. Speck, G. D. Chern, E. D. Readinger, H. Shen, and M. Wraback, *Appl. Phys. Lett.* **89**, 032109 (2006).