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Growth of wurtzite InN on bulk In₂O₃(111) wafers

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A single phase InN epitaxial film is grown on a bulk In₂O₃(111) wafer by plasma-assisted molecular beam epitaxy. The InN/In₂O₃ orientation relationship is found to be (0001) || (111) and [1100] || [112]. High quality of the layer is confirmed by the small widths of the x-ray rocking curves, the sharp interfaces revealed by transmission electron microscopy, the narrow spectral width of the Raman E_2^h vibrational mode, and the position of the photoluminescence band close to the fundamental band gap of InN. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4761985>]

Among the group III-nitrides, InN is considered as the most attractive candidate for high-speed and high-power electronics due to its narrow band gap, small effective mass, and large electron saturation velocity.¹ Despite its evident potential, direct integration of InN into electronic devices remains challenging. The low thermal stability and consequently high dissociation rate of InN create a number of difficulties strictly limiting the maximal growth temperature.^{2–4} In addition, heteroepitaxial InN layers grown on common substrates suffer from the high density of extended defects, often considered as a source of a high residual carrier concentration and a mobility far below their maximal predicted values.⁵ InN has been predominantly grown on buffered sapphire, Si, and SiC wafers.^{6,7} In all these cases, the in-plane lattice mismatch $\Delta a/a$ between InN and the template is significantly larger than 10%. Recently, we demonstrated InN films grown on bulk ZnO substrates where $\Delta a/a$ is reduced to 8.89%.⁸ The drawback of InN/ZnO heterosystem is the chemical instability of the interface. The chemical reaction between InN and ZnO leads to the formation of different phases including In₂O₃ inclusions in the substrate and voids, as well as high doping by ZnO dissociation and subsequent O incorporation, a process which becomes more pronounced at higher growth temperature.⁸ To this end, a direct growth of InN on body centered cubic (bcc) In₂O₃ is of obvious interest. In addition, the lattice constants of bcc-In₂O₃ ($a = 10.117 \text{ \AA}$)⁹ and wurtzite InN ($a = 3.5365 \text{ \AA}$)¹⁰ are related by a factor of 4 with a mismatch of $\approx 1\%$ in the (111) crystallographic plane. This coincidence lattice makes bcc-In₂O₃ an interesting alternative substrate for InN. There have been several reports on epitaxial films of cubic In₂O₃ employed as intermediate layers for the growth of zinc-blende and wurtzite InN on sapphire.^{11–13} However, only recently In₂O₃ has been synthesized in the form of bulk single crystals at the Leibniz-Institut für Kristallzüchtung.¹⁴

Here, we present a study of the structural and optical properties of InN directly grown on a bulk bcc-In₂O₃(111) wafer focusing on interface-related phenomena.

The samples are prepared in a molecular beam epitaxy (MBE) system custom-built by CreaTec equipped with standard solid-source effusion cells and a Veeco rf plasma source providing active nitrogen. $5 \times 5 \times 0.3 \text{ mm}^3$ slices of a bulk single-crystal bcc-In₂O₃(111)¹⁴ are used as substrates. After chemo-mechanical polishing, the In₂O₃(111) wafers show a flat and featureless surface morphology with a mean roughness of 0.22 nm over $10 \mu\text{m}^2$. After degreasing in chemical solvents, the substrates are mounted with In to a Si wafer used as a sample holder. InN layers are deposited at a substrate temperature of $350 - 450^\circ\text{C}$ measured by a thermocouple placed behind the sample holder. Nominally, slightly N-rich conditions with a N/In flux ratio of ≈ 1.05 and an absolute N flux of 0.62 monolayer/s are selected in order to avoid accumulation of In droplets on the film surface. Here, we focus on a specific $1 \mu\text{m}$ -thick sample grown at 400°C with a nitridation of the wafer for 30 s at the growth temperature to induce the formation of InN analogously to the conversion of Al₂O₃ to AlN by nitridation. High-resolution x-ray diffraction (XRD) measurements are conducted with Cu $K\alpha_1$ radiation using a Philips X-Pert MRD diffractometer equipped with a four-crystal Ge(220) monochromator and a channeling Ge(220) three-reflection analyzer. Raman spectra are taken at 300 K in a $z(x,-)$ z backscattering configuration (z is parallel to the c -axis) with the 632.8 nm line of a He-Ne laser as excitation source. Room temperature photoluminescence (PL) is excited with the 643 nm emission from a laser diode and detected with an InSb photodiode. The PL spectra are corrected for the response of the setup. Cross-sectional samples for transmission-electron microscopy (TEM) are prepared by plan parallel mechanical polishing down to a sample thickness of about $10 \mu\text{m}$ followed by ion milling with a Gatan PIPSTM under liquid nitrogen cooling. TEM is performed in an aberration corrected FEI TITAN 80-300.

In₂O₃ crystallizes in rhombohedral and cubic phases. The cubic phase has the bixbyite structure with the space group Ia $\bar{3}$. The unit cell contains 32 In atoms and 48 O

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FIG. 1. bcc-In₂O₃ bixbyite structure: (a) Ideal undistorted parent crystal structure; (b) side view of the (111) surface. Dashed lines separate stoichiometric trilayers; (c) top view of the (111) surface formed by a stoichiometric trilayer. Thin solid lines illustrate the 4:1 coincidence lattice of InN(0001) relative to In₂O₃(111).

atoms. This complex crystal structure can be understood as a distorted version of a hypothetical parent crystal in which the In atoms define a simple fcc lattice and the O atoms occupy all the tetrahedral interstitial sites. The distortion in bixbyite arises because one fourth of these O atoms are missing, forming an ordered-vacancy crystal structure. Figure 1(a) depicts a conventional unit cell of the undistorted parent crystal with every fourth O missing.

Each of the 48 O atoms in the In₂O₃ unit cell has approximately tetrahedral coordination to four In neighbors (one on the 8b site and three on the 24d sites). Hence, all In-O bonds are approximately oriented along the four {111} directions. The consequence of this arrangement is that In₂O₃ is naturally organized into stoichiometric trilayers stacked along the {111} directions, as shown in Fig. 1(b). This stacking is analogous to the stoichiometric double layers of zinc-blende semiconductors and suggests that the surface formed by cleaving along the dashed planes in Fig. 1(b) leads to a reasonable approximation of the real In₂O₃ (111) surface. This surface is remarkably well matched—in symmetry, atomic spacing, and surface chemistry—to wurtzite InN (0001). Figure 1(c) shows a top perspective view of one complete trilayer. The topmost layer consists of under-coordinated O atoms, shown as large red spheres. These form a nearly planar, nearly hexagonal lattice in 1:1 registry with the atomic layers of bulk InN (0001). The registry is incomplete, however, because the 1/4 O vacancies intrinsic to bulk In₂O₃ are also present (open red circles) on this stoichiometric In₂O₃(111) surface. The fate of these surface vacancies during the deposition of InN is an interesting open question with potentially important consequences for growth.

The XRD data of the sample under investigation are summarized in Figure 2. The $\omega - 2\theta$ scan is dominated by the In₂O₃ 222 and InN 0002 reflections. ϕ -scans recorded across the 10 $\bar{1}$ 2 InN [Fig. 2(b)] and 440 In₂O₃ [Fig. 2(c)] reflections provide the in-plane epitaxial relationship between wurtzite InN and cubic In₂O₃ as InN [1 $\bar{1}$ 00] || In₂O₃ [11 $\bar{2}$] in agreement with the above discussion. No other orientations or phases of InN are detected in extended texture maps (not shown). The full width at half maximum (FWHM) of rocking curves recorded in symmetric and quasi-symmetric (skew) geometry across the on-axis 0002 and off-axis 10 $\bar{1}$ 2 reflections are 570 and 674 arcsec, respectively.

These values are comparable with the best values reported for InN epitaxial layers grown by MBE.^{7,8}

Raman spectra acquired from the top and backside of the sample, as well as a reference spectrum of the In₂O₃ wafer, are shown in Fig. 3. Consistent with the selection rules for the wurtzite structure, the spectrum of the InN layer exhibits E_2^h and $A_1(\text{LO})$ phonon modes located at 492 cm⁻¹ and 592 cm⁻¹, respectively, [Fig. 3(a)]. The spectral width of the E_2^h mode of about 3.4 cm⁻¹ confirms the high degree of lattice perfection demonstrated by XRD. Figure 3(b) displays the spectrum excited from the backside and thus reveals properties of InN in the region close to the interface InN/In₂O₃. In addition to the vibrational modes of bcc-In₂O₃ at 367, 497, and 630 cm⁻¹ [see Fig. 3(c) for In₂O₃ reference], the spectrum contains a broad feature close to the $A_1(\text{LO})$ phonon mode of InN. A similar feature [or $L^-(q_D)$ mode] assigned to plasmon-related excitation, in addition to a low-frequency coupled plasmon LO-phonon mode [$L^-(q_0)$] at about 445 cm⁻¹, has been recently detected in heavily *n*-type doped InN layers grown on ZnO.¹⁵ The presence of plasmon-related excitations in the interface region and their absence close to the surface layer clearly suggest an inhomogeneous distribution of the electron density along

FIG. 2. XRD data of the InN layer grown on bulk bcc-In₂O₃(111): (a) $\omega - 2\theta$ scan. (b) and (c) ϕ -scans recorded at the 10 $\bar{1}$ 2 and (440) reflections of wurtzite InN and cubic In₂O₃, correspondingly.

FIG. 3. Normalized Raman spectra acquired in backscattering geometry from: (a) the sample surface, (b) backside, and (c) reference spectrum of the In_2O_3 wafer. Excitation with a 632.8 nm line of a He-Ne laser; (d) PL spectrum recorded at room temperature.

the growth direction of the sample. Here, the charge carriers are mainly concentrated in the interface region, whereas the top part of the layer has a moderate doping level. Indeed, room temperature PL measurements on the sample reveal the peak position of the PL band at 0.660 eV with a FWHM of only 98 meV [Fig. 3(d)]. Both the position of the PL peak in the proximity of the fundamental band gap of InN, as well as its moderate spectral width, indicate a low electron density in the region away from the interface.¹⁶

In order to get further insight into the origin of carrier accumulation at the interface, the sample is studied by TEM. Selective area electron diffraction patterns acquired at the interface confirm the InN/ In_2O_3 in-plane orientational relationship as $[1\bar{1}00] \parallel [11\bar{2}]$. Figure 4(a) shows a high-resolution TEM image demonstrating an abrupt and atomically flat interface between InN and In_2O_3 . In the filtered image [Fig. 4(b)], a one-to-one correspondence of the lattice planes of InN and In_2O_3 is evident. In fact, the lattice mismatch between InN and In_2O_3 in the (111) crystallographic plane of about 1% implies that adjacent misfit dislocations are separated by more than 100 atomic planes as confirmed by these micrographs. The InN epilayer itself has high crystalline quality, as already indicated by XRD and Raman spectroscopy. On the other hand, the TEM study evidences formation of isolated nano-size inclusions inside the In_2O_3 substrate (not shown here and under further structural investigation). Similar inclusions were already found in the case of InN grown on ZnO and were attributed to chemical reactions occurring at the interface.⁸ Analogously to this case, the interface reaction observed in the present study is probably also accompanied by an incorporation of O donors into the InN film, which would explain the high electron density revealed by Raman spectroscopy.

In conclusion, InN films are epitaxially grown on bulk $\text{In}_2\text{O}_3(111)$ by plasma-assisted molecular beam epitaxy. The InN/ In_2O_3 orientation relationship is found to be $(0001) \parallel (111)$ and $[1\bar{1}00] \parallel [11\bar{2}]$ resulting in an effective lattice mismatch between the layer and wafer of about 1%. The high

FIG. 4. (a) High-resolution TEM image of the interface between InN and In_2O_3 substrate taken along the $[11\bar{2}0]$ direction of InN. The inset is a magnification of the image showing the regular structure of the interface. The image was taken using conditions providing for amplitude contrast of the materials. (b) Inverse FFT filtered representation of (a) done using reciprocal vectors $(1\bar{1}00)$ and $(1\bar{1}0)$ for InN and In_2O_3 , respectively.

quality of the sample is confirmed by means of x-ray diffraction, TEM and Raman spectroscopy. Results of the optical spectroscopy show that the high electron concentration detected at the InN/ In_2O_3 interface decreases with the layer thickness on a $1\ \mu\text{m}$ -scale. Although the origin of this accumulation layer, as well as the structure of the interface, require further investigation, it is already clear that $\text{In}_2\text{O}_3(111)$ can be considered as a promising substrate for the growth of wurtzite InN.

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