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Growth of semipolar $(10\bar{1}\bar{3})$ InN on *m*-plane sapphire using MOVPE

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We report on the growth of semi-polar InN directly on *m*-plane sapphires by metal-organic vapor phase epitaxy with different nitridation times from 45 s to 6 min. Surface morphology and crystalline orientation depended on the nitridation time. Semipolar InN with $(10\bar{1}\bar{3})$ dominant orientation was obtained at 2 min and 4 min nitridation, shorter or longer nitridation times showed additional orientations. The $(10\bar{1}\bar{3})$ InN has a roughness about 30 nm (scale size 5×5 μm^2), likely due to twinning. Low temperature photoluminescence showed emission peaks between 0.72 eV to 0.75 eV, which is slightly below the energy observed for (0001) InN.

It is well-known that polar (0001) *c*-plane III-nitride layers can produce an integrated electrostatic field in the active layer and hence exhibit spontaneous and strain-induced polarizations along *c*-growth direction. These effects are unfavourable for the radiative efficiency of light-emitting devices and laser diodes. Growth in non- and semi-polar orientations can suppress these effects. For example, non-polar InGaN/GaN grown on GaN could improve the output power and the external quantum efficiency of light-emitting diodes [1]. Furthermore, for semi-polar InN such as $(10\bar{1}1)$ and $(10\bar{1}3)$, a reduction of elastic energy density is predicted compared to (0001) InN which might be significant to InN/GaN heterostructures [2].

For the GaN material system, growth and polarity effects have been intensively investigated. However, very little is known for InN. One reason is that growth of InN is still a challenge even on (0001) *c*-plane sapphire due to a narrow growth temperature window [3, 4]. Thus, very few reports exist on growth of semi- and non-polar InN. Non-polar *a*-plane $(11\bar{2}0)$ and *m*-plane $(1\bar{1}00)$ InN have been grown on $(1\bar{1}02)$ *r*-plane sapphire and free-standing GaN using molecular-beam epitaxy, respectively [5, 6]. Metal-organic vapor phase epitaxy (MOVPE) technique was also applied to produce *m*-plane InN on *r*-plane sapphire [7]. Very recently, semi-polar InN with $(11\bar{2}2)$ dominant orientation was grown on *m*-plane sapphire using MOVPE [8]. However, to our best knowledge, there is still no report on growth of $(10\bar{1}\bar{3})$ semi-polar InN.

Generally, to grow III-nitride on sapphire, a nitridation process is employed to enhance two-dimensional growth, crystalline quality, optical properties, and to suppress metastable orientations [9–12]. For InN, the nitridation procedure was found to be important as well [13]. Also, for semi-polar GaN, the initial process of substrate nitridation was critical to control growth orientation [14].

In this letter, we first report on the growth of $(10\bar{1}\bar{3})$ semi-polar InN directly on *m*-plane sapphire in a horizontal MOVPE reactor equipped with *in-situ* spectroscopic ellipsometry (SE). The crystalline orientation and morphology of the grown InN layers were investigated using high-resolution X-ray diffraction (HRXRD) and atomic force microscopy (AFM). Low temperature photoluminescence (PL) measurements were carried out using a 25 mW laser diode as an excitation source at 405 nm and detected by a liquid-nitrogen (N_2) cooled indium antimonide (InSb) photodiode.

Experiments were performed using quarters of 2 inch *m*-plane sapphire wafer. In order to remove residual contaminations, all substrates were degreased sequentially by acetone and iso-propanol solvents at 80 °C for 10 min, and then rinsed in de-ionized water prior to growth. The reactor pressure was kept constant at 100 mbar. Trimethyl-indium

(TMI) and ammonia (NH_3) were used as precursors. The sapphire substrates were first annealed at 1050 °C in 3 l/min hydrogen (H_2) for 10 min. Then, the H_2 gas line was switched to N_2 (flow rate of 3 l/min) to nitridate the sapphire at the same temperature with additional 3 l/min NH_3 for 45 s to 6 min. After that, the samples were cooled down to 500 °C to deposit the InN nucleation layers for 20 min with 0.1 Pa TMI. For nucleation and epilayer growth, the NH_3 flux was kept at 1 l/min. Following the nucleation, during subsequent growth, the reactor temperature was ramped up to 560 °C to grow the InN epilayer for 2 hours with a TMI partial pressure of 0.19 Pa. For comparison, InN was simultaneously grown on (0001) *c*-plane sapphire. After growth, all the samples exhibited an opaque specular surface and good homogeneity.

Figure 1 shows XRD symmetric $\omega/2\theta$ scans of the InN layers grown on *m*-plane sapphire with different nitridation times. Only for 2 min and 4 min nitridation, all other InN orientations e.g. $(10\bar{1}2)$, $(11\bar{2}2)$, or $(11\bar{2}0)$ are suppressed. This is similar to the findings for semi-polar $(2\bar{1}\bar{1}2)$ and $(10\bar{1}3)$ GaN grown on *m*-plane sapphire [14].

In order to obtain the in-plane relationship, XRD ϕ-scans of the (0002) InN respect to the $(20\bar{2}4)$ sapphire were used. Figure 2 shows that the $(10\bar{1}3)$ InN axes are rotated ±90° with respect to the *m*-plane sapphire substrate. This indicates a twinning of the $(10\bar{1}3)$ with two nearly equivalent portions of the layer oriented along $[1\bar{2}10]$ and $[\bar{1}2\bar{1}0]$ directions (Fig. 2). The in-plane epitaxial relationship was determined to $[30\bar{3}\bar{2}]_{InN} \| [1\bar{2}10]_{sapphire}$ and $[\bar{1}2\bar{1}0]_{InN} \| [0001]_{sapphire}$.

For the simultaneously grown (0001) InN, we found N-polarity by X-ray photo-emission, which was in good agreement with results reported in Ref. [15]. Thus, we assume that our semi-polar InN samples also have N-terminated surface.

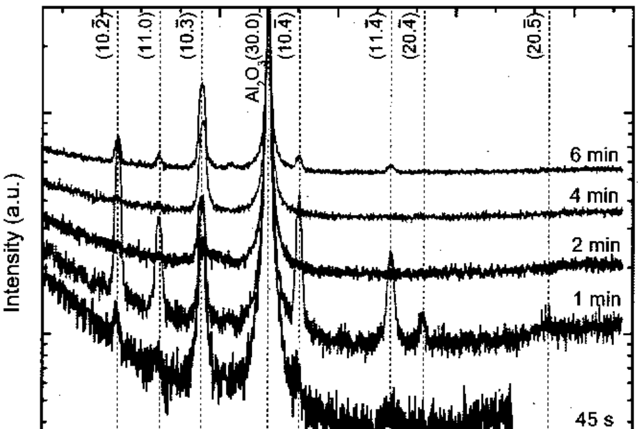

Figure 1 (online colour at: www.pss-rapid.com) XRD $\omega/2\theta$ scans of InN layers grown on *m*-plane sapphires with different nitridation times.

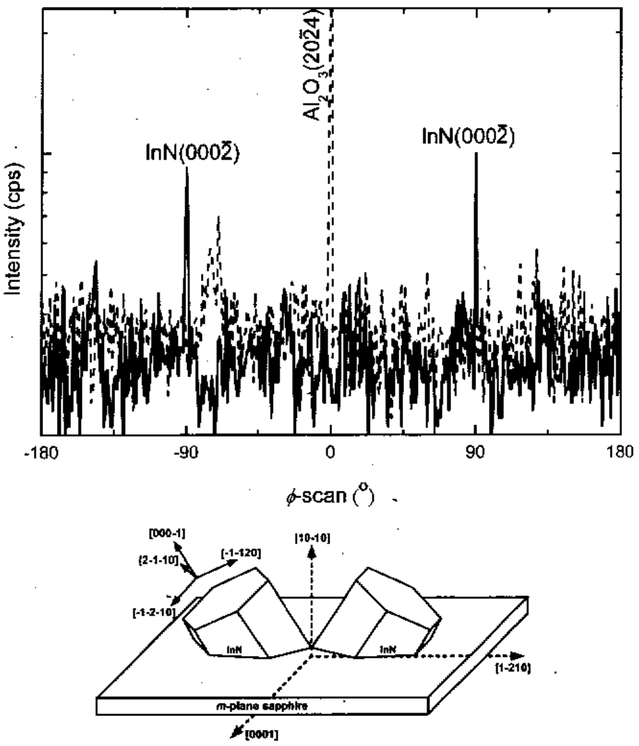

Figure 2 HR-XRD ϕ-scans of the $(10\bar{1}3)$ InN (solid line) and $(20\bar{2}4)$ sapphire (dashed line) from the InN layer grown with 2 min nitridation.

From *in-situ* SE measurements observed during and after the nitridation process, we found changes of thickness and roughness of the nitridated *m*-plane substrate surface for different nitridation times. We expect that the epilayer orientations of the grown InN rely on the bond arrangement and strain at the AlN/sapphire interface. The effects of nitridation on orientation suppression of our semipolar InN are still under investigation by using high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy (XPS).

Figure 3 shows AFM images (size 5 × 5 μm^2) after InN epilayer growth on *m*-plane sapphires with different nitridation times. All the images reveal a three-dimensional growth mode with different grain sizes and *z*-scales about 300 nm. A certain number of holes with a depth range similar to the layer thickness of about 100–200 nm was found on the surface of samples due to the coalesced islands. At 2 min nitridation, the surface morphology was smoothest with an rms roughness value of about 30 nm. The results for (0001) InN showed a similar trend at 2 min nitridation with a typical roughness of 5 nm. Interestingly, only the XRD spectra for the simultaneously grown (0001) InN samples showed metallic In.

Low temperature PL measurements at 8 K were carried out to investigate the optical properties of the grown samples (Fig. 4). For (0001) InN grown with 2 min nitridation, the blue-shifted energy can be attributed to Moss–Burstein shift because of band-filling effects [16]. The additional PL

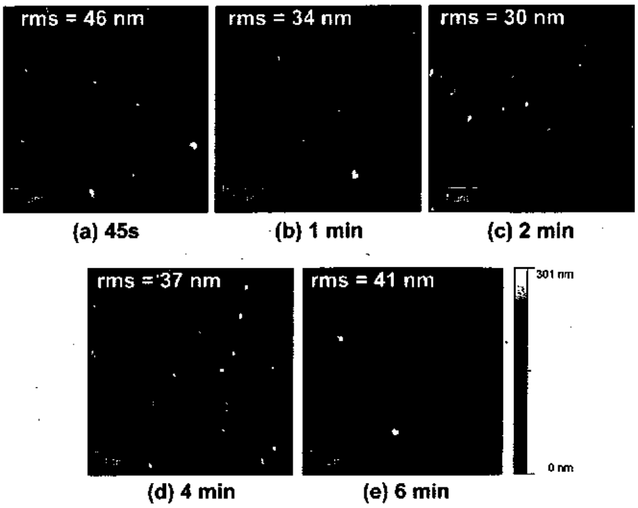

Figure 3 (online colour at: www.pss-rapid.com) 5 × 5 μm^2 AFM micrographs showing the surface of the InN grown on m-plane sapphires with different nitridation times.

shift for different nitridation times can originate from stress due to the smaller thermal expansion coefficient of InN (3.8 × 10^{-6} K^{-1}) compared to sapphire (7.5 × 10^{-6} K^{-1}), resulting in compressive stress within InN layers during the cooling down process causing the shifted luminescence emission [17, 18]. For all InN samples grown on m-plane sapphire, the PL peaks were between 0.72 eV and 0.75 eV, which is about 20–50 meV below the emission peak of (0001) InN. The redshift of PL peak energies is similar to the semi-polar (11$\bar{2}$2) [8] and non-polar (10$\bar{1}$0) InN [6]. For the (10$\bar{1}$0) InN, the redshift was attributed to basal plane stacking faults (BSFs).

A shift of PL energies can be caused by the background dopings and different grain sizes in InN layers. Since the (10$\bar{1}$3) InN samples consist of islands just near the percolation limit, the doping cannot be estimated yet.

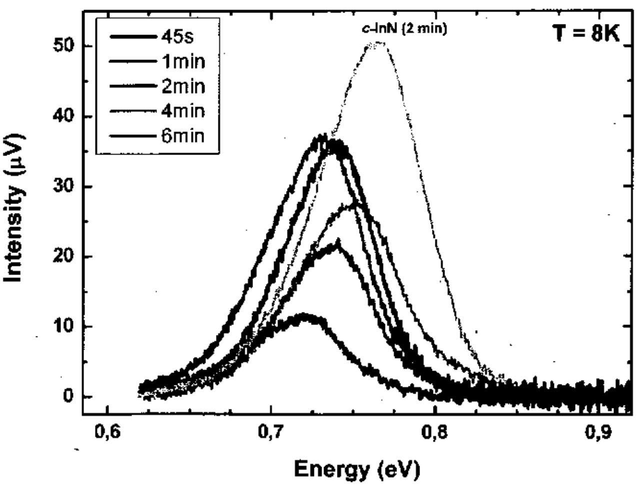

Figure 4 (online colour at: www.pss-rapid.com) Low temperature PL of the grown InN on c- and m-plane sapphires.

The average grain sizes were estimated about 50 nm to 240 nm along the [30$\bar{3}$2] direction, and from 80 nm to 310 nm along [0001] direction. We found a general trend that larger grain sizes correlate with longer wavelength emission.

The samples grown on m-plane sapphires with 2 min, 4 min and 6 min nitridation show an asymmetric broadening in the low energy range. In temperature-dependent PL, the broadening was decreasing with increasing temperature. Thus, we attributed the broadening to BSFs along [0001] direction of the grown InN on m-plane sapphire, similar to m-plane InN or a-plane GaN [6, 19]. The BSFs serving as quantum wells thus can generate phonons at lower energy.

In summary, we have studied the growth of semi-polar InN directly on m-plane sapphire substrates using MOVPE. InN grown with nitridation times of 2 min and 4 min exhibited twinned (10$\bar{1}$3) orientation and smoother morphology. Low temperature PL measurements showed main emission near 0.74 eV. The near band-edge peaks for the InN grown on m-plane sapphires showed red-shifted energies compared to the InN grown simultaneously on c-plane sapphire possibly related to BSFs overlaid with grain size distribution effects. Further characterizations are still needed to clarify the influence of nitridation procedures on orientation suppression, crystallinity, and optical properties of the InN grown on m-plane sapphires.

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