

Catalyst-free growth of InN nanorods by metal-organic chemical vapor deposition

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We demonstrated the growth of catalyst-free InN nanostructures including nanorods on (0001) Al_2O_3 substrates using metal-organic chemical vapor deposition. As the growth time increased, growth rate along *c*-direction increased superlinearly with decreasing *c*-plane area fractions and increasing side wall areas. It was also found that desorption from the sidewalls of InN nanostructures during the InN nanorods formation was one of essential key parameters of the growth mechanism. We propose a growth model to explain the InN nanostructure evolution by considering the side wall desorption and redeposition of indium at top *c*-plane surfaces.

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1 Introduction Recently, extensive studies have been investigated on indium nitride (InN) nanoscale structures such as nanorods and nanowires for nanophotonic and nanoelectronic devices including light emitters, detectors, and high speed field effect transistors [1–4]. Compared to other semiconductor materials, InN is one of the most promising materials that exhibit narrow direct band gap at $\sim 0.65 \text{ eV}$ and superior transport properties [5–8]. However, the growth of InN nanostructures is still in immature stages due to the difficulties associated with extremely high equilibrium vapor pressure of indium and nitrogen [9]. Because of the difficulties in InN nanorod growth, most of the reported InN nanorods rely on molecular beam epitaxy (MBE) growth or catalyst-based or chlorine-assisted growth in chemical vapor deposition [10-13]. However, catalystfree InN nanorod grown by metal-organic chemical vapor deposition (MOCVD) has been rarely reported. By careful

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adjustment of growth parameters, we obtained the catalystfree InN nanorods grown on (0001) Al_2O_3 substrate by MOCVD [14]. We also investigated the effects of growth temperature on morphology of InN nanostructures, proposing that growth temperature is one of essential key parameters of nanorods formation. However, a proper mechanism for the catalyst-free InN nanorod growth has not been proposed yet. In this paper, we report that indium desorption from the sidewalls of InN nanostructures during the InN nanorods formation was an essential part of the growth mechanism of InN nanorods grown by MOCVD.

2 Experimental procedures Catalyst-free InN nanostructures were grown by MOCVD on Al_2O_3 substrate under various growth conditions. Before the growth, Al_2O_3 substrates were nitridated at 1100 °C for 3 min under ammonia ambient. During the growth, only trimethylindium

(TMIn) and ammonia (NH₃) were used as precursors for indium and nitrogen, respectively, and nitrogen was used as a carrier gas. During the growth, growth temperature of InN nanostructures was fixed at 710 °C and the growth reactor pressure was maintained at 300 Torr. The flow rates of TMIn and NH₃ were 305 standard cubic centimeter per minute (sccm) and 4 standard liter per minute (slm), respectively, and V/III ratio was kept at 25 000. InN growth was made under N-rich condition. We varied the growth times to understand the growth mechanism of InN nanorods. After the growth, the morphologies of InN nanostructures were examined by using field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), trasmission electron microscopy (TEM), and X-ray diffraction (XRD).

3 Results and discussions

3.1 Evolution of InN nanorods InN was grown at 710 °C with different growth times. The development of InN nanostructures toward InN nanorods can be understood from the time evolution of InN nanostructures. Figure 1 shows low magnification (top) and the high magnification (center) plan-view FE-SEM images, and simplified schematic illustration (bottom) of the InN nanostructures at each stage. An obvious time-dependent morphological transition of InN was observed. At first, InN hexagonal islands with small pits were grown on the Al₂O₃ substrate. It is well known that when the growth is carried out at high temperatures, the InN islands can grow in large hexagonal shape with small density due to the enhanced surface diffusion of indium atoms [15].

Figure 2 shows three-dimensional AFM images of InN nanostructures for (a) 1 min and (b) 5 min. Small pits were already formed at the initial stage of growth, even growth time was as short as 1 min. After 5 min growth, the number and depth of pits increased. The pit formation at initial stage is thought to be related with thermal desorption at energetically unstable regions like crystalline defects in nuclei of InN. One of the highly probable candidates is threading dislocation. Several papers reported 109- 10^{10} cm⁻² threading dislocation densities in InN/Al₂O₃ heteroepitaxial system [16–18], and the pit density in our sample was $\sim 6 \times 10^{10}$ cm⁻². Those two values are comparable to support the close relationship between pits and threading dislocations. As growth time increased, small pits got bigger and at the same time islands were coalesced. Pits exhibited hexagonal shapes, implying that the crystallographic etching of wurtzite InN occurred. The chemical etching results of III-nitrides also showed the anisotropic etching behavior at the dislocation site [19-21]. When growth time was increased to 40 min, bigger pits coalesced with each other, forming nanowalls as shown in Fig. 1(c). They became longer and laterally thinner with increasing growth time by thermal desorption. InN nanowall structure was obtained until 45 min growth. For the longer time growth, the morphology of InN was changed from nanowall to nanorod structure. When the growth time was 60 min, vertical $\{10-10\}$ facets appeared at side walls. Finally, InN nanorods were formed with hexagonal facets as shown in Fig. 1(d). In our previous report, we revealed that our InN



Figure 1 (online color at: www.pss-a.com) Low magnification (top) and the high magnification (center) FE-SEM images of InN nanostructures, and the simplified schematic illustration (bottom) with different growth times of (a) 10 min, (b) 20 min, (c) 40 min, and (d) 60 min. Shape of nanostructures evolves from pitted nanoislands to nanowalls and finally to nanorods.





Figure 2 (online color at: www.pss-a.com) Three-dimensional AFM images of InN nanostructures with different growth time for (a) 1 min and (b) 5 min. Note the pit formation on the *c*-plane surface of islands already started even in the sample of 1 min growth. After 5 min growth, the number of pits increased and the depth of pits increased further.

nanorods were crystalline, and it was grown along $\langle 0001 \rangle$ direction with $\{10\overline{1}0\}$ facets [14].

3.2 Analysis Figure 3 shows FE-SEM images of the surface of the InN nanostructures with different growth times of (a) 10 min, (b) 20 min, (c) 40 min, and (d) 60 min and the processed images for the calculation of *c*-plane area fraction. High magnification plan-view FE-SEM images shown in Fig. 1 (center) were used again for the calculation of *c*-plane area fractions. The red colored area shown in right side of Fig. 3 shows the processed images of *c*-plane area. Table 1 shows the calculated *c*-plane area fractions. For the calculation, three different points were analyzed and averaged. The average *c*-plane area fractions were 94.49, 69.14, 46.05, and 24.85% for (a) 10 min, (b) 20 min, (c) 40 min, and (d) 60 min samples, respectively. A decrease rate of approximately 2% per minute was obtained for *c*-plane area fraction.

The growth rates of InN nanostructures were analyzed. As shown in SEM images of Fig. 4, InN nanostructures varied with growth times. It was shown that the shape of nanostructures evolved from pitted nanoislands to nanowalls and finally to nanorods. The length of nanostructures were 0.15, 0.25, 2, 3.5, and 8 μ m, for growth time for (a) 10 min, (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min, respectively. Changes in length and *c*-plane area fraction



Figure 3 (online color at: www.pss-a.com) FE-SEM images of the surface (left) and the processed images for calculation of c-plane area fraction (right) of InN nanostructures with different growth times for (a) 10 min, (b) 20 min, (c) 40 min, and (d) 60 min.

of InN nanostructures with growth time are shown in Fig. 5. c-plane area fraction of the 80 min sample could not be measured since most of nanorods were tilted and it was not possible to image c-planes of nanorods at same time.

We observed the length of InN nanostructures increased superlinearly as the growth time increased. The growth rate (shown as the slope of length vs. time graph) was accelerated with decreasing *c*-plane area fraction. Furthermore, by considering the length and *c*-plane area fraction, the total side wall areas of InN nanostructures can be calculated (not shown here) by assuming that nanostructure had vertical side walls. Side wall area increased drastically as growth time increased. If we assume that the nanostructure is in the shape of circular rods with radius *r*, the top surface area is $2\pi r^2$, and the sidewall area is $2\pi r \cdot h$, where *h* is the height

| Tal | ble | 1 | <i>c</i> -pl | ane | area | fraction | (%) | of | InN | nanostructures |
|-----|-----|---|--------------|-----|------|----------|-----|----|-----|----------------|
|-----|-----|---|--------------|-----|------|----------|-----|----|-----|----------------|

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| | 10 min | 20 min | 40 min | 60 min | |
|---------|--------|--------|--------|--------|--|
| A | 94.95 | 71.83 | 48.91 | 24.88 | |
| В | 97.29 | 68.68 | 47.59 | 27.83 | |
| С | 91.22 | 66.92 | 41.65 | 21.80 | |
| average | 94.49 | 69.14 | 46.05 | 24.85 | |



Figure 4 Cross-section SEM images of InN nanostructures with different growth times for (a) 10 min, (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min.

of nanostructure as shown in Fig. 6. Hence the side wall area scales with square root of top surface area. While the *c*-plane area fraction decreased from 94.49% (10 min growth) to 24.85% (60 min growth), side wall area increased by $\{(24.85)^{1/2} \times 3.5\}/\{(94.49)^{1/2} \times 0.15\}$, which is approximately 12.

If the InN nanostructure growth is limited by mass transport as in usual MOCVD case, the growth rate would be linearly proportional to growth time. However, the growth rate observed in this experiment is superlinear. It is speculated that an additional flux might have been added from the nanostructure itself, and the flux increased with



Figure 5 (online color at: www.pss-a.com) Changes in length (circles) and *c*-plane area fraction (squares) of InN nanostructures with growth time.



Figure 6 (online color at: www.pss-a.com) Assuming the nanostructure is in the shape of circular rods with radius *r*, the top surface are is $2\pi r^2$, and the sidewall area is $2\pi r \cdot h$, where *h* is the height of nanostructure. Nanostructure had vertical side walls.

growth time. We speculate that the indium desorption is very crucial in this study. In order to confirm that desorption and re-deposition of indium atom really occur, we prepared two different InN nanostructures as shown in Fig. 7. Figure 7(a) and (b) shows the growth procedures for the two samples, Fig. 7(c) and (d) show the cross-section and plan-view FE-SEM images of those samples. After the growth, the ammonia flow was maintained to suppress the decomposition of nitrogen. After the InN 40 min growth at 710 °C, samples were cooled down with different procedures. Sample A was cooled down to room temperature (RT) under ammonia ambient after the growth at 710 °C as shown in Fig. 7(a). Sample B was cooled down to RT under ammonia ambient after 10 min anneal at the growth temperature without TMIn flow. The inset images are plan-view SEM images of each sample. Sample A shows nanowall structure, which is similar to Fig. 1(c). However, sample B shows the drastic changes in morphology after the 10 min anneal. It shows the tapered morphology with widened top area.

Such observation clearly shows that desorption of indium atoms can occurred and the desorbed atoms can migrate to the top surface. This phenomenon is thought to be related to the relatively high growth temperature we used. In the case of InN film growth by MOCVD, most experiments have been done in the temperature range from 550 to $650 \,^{\circ}C$ [22–24]. However, we used relatively high growth temperature of 710 $^{\circ}C$ compared to most experiments conducted by other groups. Several research groups reported that relatively high growth temperature [25, 26], however, a proper explanation was not given. In next section, we proposed a simple growth model to explain the evolution of InN nanorods involving indium desorption from nanostructure side walls and re-deposition at top *c*-planes.

3.3 Growth model To understand the growth mechanism of InN nanorods, it is important to note that the evolution of InN nanostructure may involve desorption and





Figure 7 (online color at: www.pss-a.com) Growth procedures (top) and corresponding cross-section FE-SEM images (bottom) of the two different samples grown at 710 °C for 40 min with different cool-down conditions. (a) After the InN growth at 710 °C, sample A was cooled down to RT under ammonia ambient. (b) Sample B was cooled down to RT under ammonia ambient after 10 min anneal at the growth temperature without TMIn flow. (c and d) Cross-section SEM images for samples A and B, respectively. The inset images are plan-view SEM images of each sample. Note the drastic changes in morphology of nanostructures after the 10 min anneal under ammonia ambient without TMIn flow. Desorption of InN and re-deposition at upper part of the nanostructures is evident, implying that InN desorption is significant.

re-deposition of indium atoms at relatively high growth temperatures. It is well accepted that the growth temperature controls both desorption and diffusion of the indium atoms [27].

To address evolution of InN nanorods, a growth model based on experimental facts should be formulated. In Fig. 8, we proposed a growth model simplifying atomic movement as fluxes in real space. J_{in} , a flux of adsorption indium atoms from direct incorporation and J_{out} , a flux of desorbed indium atoms from sidewall desorption are shown. Indium atoms supplied from metal organic source preferentially incorporate on top surface of nanostructures [10, 28]. On the other hand, desorbed atoms from sidewall of InN nanostructures diffuse to the top surface along *c*-direction. Concentrations profiles of indium along the nanostructure growth direction and the corresponding J_{in} and J_{out} are plotted in right side of Fig. 8. It shows that concentration of indium can be enhanced at top c-plane surface of InN nanostructures. Growth rate along c-direction will be accelerated by increased concentration near the top growth front. This is in good agreement with the experimental results that nanostructure growth rate increased with growth time. Since the total side wall area of InN nanostructures increased superlinearly with growth time, the growth enhancement from the desorption of InN



Figure 8 (online color at: www.pss-a.com) Simplified growth model showing fluxes in real space and concentration of indium atom. J_{in} and J_{out} represent a flux of adsorbed indium atoms from direct incorporation and a flux of desorbed indium atoms from sidewall desorption, respectively. J_{in} and J_{out} are assumed to be constant. Ideal concentrations of indium atoms caused by J_{in} and J_{out} are shown in right side.

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nanostructures will also increase superlinerly with growth time. We already showed that the *c*-plane area fraction of InN nanostructures decreases linearly with growth time. The superlinear behavior of InN nanostructure growth rate with time is attributed to the addition of indium flux due to the decomposition of InN side walls.

4 Conclusions In conclusion, we reported the growth mechanism of catalyst-free InN nanorods on (0001) Al_2O_3 substrates using MOCVD. The evolution of the InN nanorods can be observed based on the analysis of time-dependent morphological transition of InN nanostructures. Shape of InN nanostructures evolves from pitted nanoislands to nanowalls and finally to nanorods. The evolution of InN nanorods from nanostructures was explained by simplified growth model which is shown atomic movement of indium atom. When InN nanostructure was grown, desorbed indium atoms from sidewall can be re-incorporated to the top surface.

As a result, indium atoms from sidewall desorption contribute to evolution from pitted nanoislands to nanowalls and finally to nanorods.

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References

- X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, Nature 409, 66 (2001).
- [2] V. Davydov, A. Klochikhin, R. Seisyan, V. Emtsev, S. Ivanov, F. Bechstedt, J. Furthmüller, H. Harima, V. Mudryi, J. Aderhold, O. Semchinova, and J. Graul, Phy. Status Solidi B 229, R1 (2002).
- [3] Y. L. Chang, Z. Mi, and F. Li, Adv. Funct. Mater. 20, 4146 (2010).
- [4] E. Calleja, J. Grandal, M. Sanchez-Garcia, M. Niebelschutz, V. Cimalla, and O. Ambacher, Appl. Phys. Lett. 90, 262110 (2007).
- [5] T. Stoica, R. Meijers, R. Calarco, T. Richer, E. Sutter, and H. Luth, Nano Lett. 6, 1541 (2006).
- [6] A. G. Bhuiyan, A. Hashimoto, and A. Yamamoto, J. Appl. Phys. 94, 2779 (2003).
- [7] S. J. Pearton, B. S. Kang, B. P. Gila, D. P. Norton, O. Kryliouk, F. Ren, Y. W. Heo, C. Y. Chang, G. C. Chi, W. M. Wang, and L. C. Chen, J. Nanosci. Nanotechnol. 8, 99 (2008).

- [8] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Auger, III. E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. 80, 3967 (2002).
- [9] T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, Appl. Phys. Lett. 81, 1246 (2002).
- [10] Y. L. Chang, F. Li, A. Fatehi, and Z. Mi, Nanotechnology 20, 345203 (2009).
- [11] S. Vaddiraju, A. Mohite, A. Chin, M. Meyyappan, G. Sumanasekera, B. W. Alphenaar, and M. K. Sunkara, Nano Lett. 5, 1625 (2005).
- [12] I. Shalish, G. Seryogin, W. Yi, J. M. Bao, M. A. Zimmler, E. Likovich, D. C. Bell, F. Capasso, and V. Narayanamurti, Nanoscale Res. Lett. 4, 532 (2009).
- [13] Y. S. Won, Y. S. Kim, O. Kryliouk, and T. Anderson, Appl. Phys. Express 1, 124002 (2008).
- [14] M. H. Kim, K. Chung, D. Y. Moon, J. M. Jeon, M. Kim, J. Park, Y. Nanishi, G. C. Yi, and E. Yoon, J. Nanosci. Nanotechnol. 11 (2011), to be published.
- [15] H. Wang, D. S. Jiang, J. J. Zhu, D. G. Zhao, Z. S. Liu, Y. T. Wang, S. M. Zhang, and H. Yang, Semicond. Sci. Technol. 24, 5 (2009).
- [16] Y. Nanishi, Y. Saito, and T. Yamaguchi, Jpn. J. Appl. Phys. Part 1 42, 2549 (2003).
- [17] E. Dimakis, J. Z. Domagala, A. Delimitis, P. Komninou, A. Adikimenakis, E. Iliopoulos, and A. Georgakilas, Superlattices Microstruct. 40, 246 (2006).
- [18] R. L. Woo, L. Gao, N. Goel, M. K. Hudait, K. L. Wang, S. Lodambaka, and R. F. Hicks, Nano Lett. 9, 6 (2009).
- [19] D. A. Stocker, E. F. Schubert, and J. M. Redwing, Appl. Phys. Lett. 73, 18 (1998).
- [20] P. Visconti, K. M. Jones, M. A. Reshchikov, R. Cingolani, H. Morkoc, and R. J. Molnar, Appl. Phys. Lett. 77, 27 (2000).
- [21] H. Cho, J. Hong, T. Maeda, S. M. Donovan, C. R. Abernathy, S. J. Pearton, R. J. Shul, and J. Han, J. Electron. Mater. 27, 915 (1998).
- [22] T. Araki, Y. Saito, T. Yamaguchi, M. Kurouchi, Y. Nanishi, and H. Naoi, J. Vac. Sci. Technol. B 22, 2139 (2004).
- [23] R. Intartaglia, B. Maleyre, S. Ruffenach, O. Briot, T. Taliercio, and B. Gil, Appl. Phys. Lett. 86, 142104 (2005).
- [24] Z. X. Bi, R. Zhang, Z. L. Xie, X. Q. Xiu, Y. D. Ye, B. Liu, S. L. Gu, B. Shen, Y. Shi, and Y. D. Zheng, Mater. Lett. 58, 3641 (2004).
- [25] A. G. Bhuiyan, A. Hashimoto, and A. Yamamoto, J. Appl. Phys. 94, 1 (2003).
- [26] J. C. Lin, Y. K. Chang, W. H. Lan, W. R. Cheng, W. J. Lin, Y. C. Tzeng, H. Y. Shin, and C. M. Cang, Opt. Mater. 30, 517 (2007).
- [27] B. Schewnzer, L. Loeffler, R. Seshadri, S. Keller, F. F. Lange, S. P. DenBaars, and U. K. Mishra, J. Mater. Chem. 14, 637 (2004).
- [28] S. D. Carnevale, J. Yang, P. J. Phillips, M. J. Mills, and R. C. Myers, Nano Lett. 11(2), 866 (2011).