Japanese Journal of Applied Physics **50** (2011) 01AE02 **REGULAR PAPER**
DOI: 10.1143/JJAP.50.01AE02

In situ Investigation of Growth Mechanism during Molecular Beam Epitaxy of In-Polar InN

Ke Wang, Tomohiro Yamaguchi, Tsutomu Araki[1], Euijoon Yoon[2], and Yasushi Nanishi[1,2]

Research Organization of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
[1]*Department of Photonics, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*
[2]*WCU Hybrid Materials Program, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea*

Received May 20, 2010; accepted September 10, 2010; published online January 20, 2011

A real-time investigation of In-polar InN growth by radio-frequency plasma-assisted molecular beam epitaxy has been conducted using laser reflection and reflected high-energy electron diffraction (RHEED). Laser reflection intensity is very sensitive to surface changes in the growth front. Clear reflection intensity changes have been observed for In-stabilized surface, In adlayer, and In droplet formation. Simultaneously, the envelope of reflection intensity variation shows interference oscillation due to the increasing InN thickness. Laser reflection intensity increases during In deposition and decreases during the following N irradiation, in contrast to RHEED intensity. *In situ* monitoring using both techniques has demonstrated complementary information on the growth front. On the basis of the observation from both techniques, the growth mechanisms and roles of the In adlayer and droplets in the InN growth are discussed.

1. Introduction

InN has been investigated extensively since the discovery of an updated band gap of about 0.65 eV.[1–3] Such a narrow band gap makes possible many potential applications in light-emitting devices spanning a much wider wavelength range and also in high-efficiency photovoltaics.[4] With its high electron mobility, up to 14000 $cm^2 V^{-1} s^{-1}$ predicted by recent theoretical calculation, InN is a promising material for applications in high-speed electronic devices and could be an ideal channel material for high-electron-mobility transistors.[5] Despite recent improvement in InN crystalline quality, mainly by the molecular beam epitaxy (MBE) technique, the growth of reliable high-quality InN is still very difficult owing to its thermal instability, low dissociation temperature, and large mismatched substrates.[6]

Usually InN epilayers grown by MBE under N-rich condition show a rough and facetted surface and low crystalline quality; however, those grown with excess In exhibit spiral hillocks with step-flow growth characteristics with In droplets forming on surfaces.[7–9] Recently, we have proposed a novel InN growth method (*in situ* In droplet elimination by radical beam irradiation (DERI)) to obtain InN films and related alloys.[10,11] Following InN growth under In-rich condition, extra nitrogen radical irradiation is used to react with the excess In droplets, which yields high-quality InN layers. Further work has shown that completely separate In and N supplies also result in high-quality InN layers. Nevertheless, the growth mechanism and roles of adsorbed In adatoms on the growth front have not been fully understood. In this work, we report the *in situ* investigation of InN MBE growth by laser reflection and reflected high-energy electron diffraction (RHEED), demonstrating that the laser reflection signal is a useful complement to RHEED. On the basis of our observation, we then analyze the growth mechanisms and discuss the roles of the In adlayer and droplets in MBE-grown In-polar InN.

2. Experimental Methods

All experiments were performed in an MBE system (EpiQuest RC2100NR) facilitated with the use of several Knudsen cells of III metals, a nitrogen plasma source (SVT Associates 6.03), and various types of *in situ* monitoring equipment. 1.7-μm-thick GaN templates grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD) were used as substrates to grow InN epilayers. A thin GaN buffer layer was grown first at 650 °C until a clear surface reconstruction pattern was observed. InN was then grown at 450 °C using the DERI method. During growth, a 660 nm red laser, a CCD camera, and a frame grabber were used to record the reflection intensity. Simultaneously, the RHEED pattern and intensity of specular and diffracted streaks were also monitored using kSA400 (k-Space Associates). In order to study the growth mechanisms, we investigated InN growth using completely separate In and nitrogen supply. When studying In adsorption/desorption processes, the GaN substrate temperature was increased up to 625 °C. In beam flux is controlled by varying the In cell temperature from 690 to 825 °C, which correspond to beam equivalent pressures (BEP) from 4.2×10^{-8} to 1.3×10^{-6} Torr. A nitrogen gas flow rate of 2 sccm and a plasma power of 150 W were used in this study.

3. Results and Discussion

We monitored the InN growth process for about 2 hours using completely separate In and nitrogen supplies. In each growth cycle, the indium supply time is 30 s and the nitrogen radical supply time is 60 s, and this supply mode is repeated for 80 growth cycles, as shown in Fig. 1. The envelope of the reflection signal has demonstrated clear intensity oscillation, which is due to the interference between the reflected laser beams from the top surface and GaN/InN interface. The damping of the intensity oscillation is due to the absorption of 660 nm laser light by the growing InN layer. The inset shows a zoom-in figure from 1550 to 3050 s covering about 16 cycles of InN growth. The upper line in the inset is the laser reflection intensity and the lower one is the RHEED intensity.

The RHEED intensity shows the exact steps as previously reported, showing firstly an abrupt decrease when the In shutter was opened, then a gradual decrease, a slow increase after closing the In shutter, and finally a quick recovery to the original intensity.[10] The laser reflection intensity shows that it is also very sensitive to surface changes and the turning points match very well with the RHEED signal, but their increase and decrease are just opposite of each other. Figure 2 shows details of one InN growth cycle. Four distinct steps can be observed in both reflection and RHEED signals. The deposition of In includes steps 1 and 2; steps 3

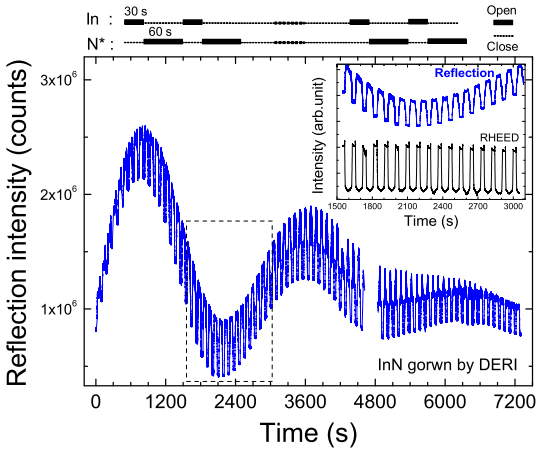

Fig. 1. (Color online) *In situ* monitoring of laser reflection intensity during InN growth with separate In (30 s) and N (60 s) supplies for 80 cycles. The inset is a zoom-in figure from 1550 to 3050 s showing both laser reflection signal and RHEED intensities.

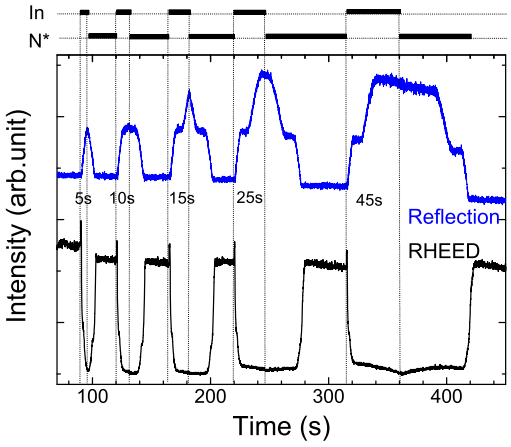

Fig. 3. (Color online) Variation of laser reflection intensity as In deposition time changes, showing that step 2 depends on the amount of In adatoms on sample surface. The RHEED signal is also included for comparison.

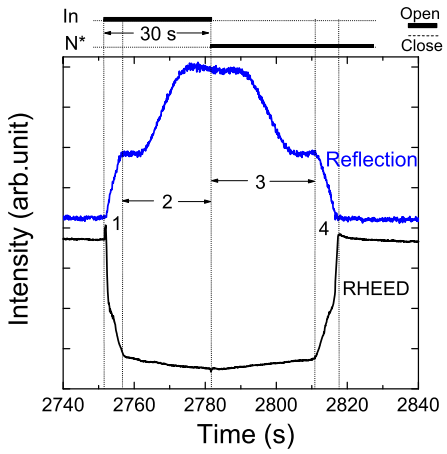

Fig. 2. (Color online) *In situ* laser reflection and RHEED intensity variation during one-cycle InN growth with separated In (30 s) and N (60 s) supplies. Four steps have been revealed. In deposition includes steps 1 and 2. Step 1 ($\sim 4.5 \pm 0.2$ s) is attributed to the deposition of two monolayers of In; step 2 shows $\sim$7 s constant level, an increase of $\sim$13 s, and a plateau of $\sim$6 s, and corresponds to In droplet formation. N radical irradiation and its reaction with In adatoms include steps 3 and 4. Step 3 is a process entailing the shrinking of In droplets on the top of the two monolayers of In, which is a reverse of step 2. Step 4 corresponds to the reaction of the two monolayers of In and a reverse of step 1.

and 4 are the reaction of the N radicals with the deposited In adatoms after In shutter is closed and nitrogen source is opened. When all In is consumed by irradiated nitrogen and the reaction is completed, RHEED intensity recovers to its initial level, and simultaneously laser reflection intensity returns back to its initial level.

Although the RHEED intensity of step 2 (and step 3) only shows a gradual decrease (increase), the laser reflection signal during this step has revealed extra information on the growth front. As can be seen in Fig. 2, after step 1, the reflection intensity in step 2 initially remains a constant for $\sim$7 s, then increases for $\sim$13 s, and finally reaches a plateau sustained for $\sim$6 s. Furthermore, the reflection feature of step 2 has been observed to change as the deposition time increases, corresponding to an increase in the amount of In adatoms on the sample surface, as shown in Fig. 3. Reflection and RHEED intensities have been recorded for five distinct InN growth cycles with various In deposition times, namely, 5, 10, 15, 25, and 45 s, as shown in Fig. 3. For an In supply time of only 5 s, almost only step 1 with its reverse (step 4) can be seen and step 2 barely appears. For 10 s of In supply, the first constant reflection level at the beginning of step 2 is observed. With further increase in In deposition time (to 15 and 25 s), step 2 shows a sharp increase after the first constant level. When the In shutter is closed at 15 s, the reflection level continuously increases, but for the 25 s In deposition it has already reached the plateau. For the 45 s In deposition, step 2 is similar to that of 25 s and the plateau lasts longer.

Therefore, the laser reflection signal is able to provide complementary information to RHEED for the *in situ* monitoring of the InN growth. The RHEED signal reveals crystalline surface structures. However, when metallic In is deposited on the surface, the RHEED intensity becomes very weak and can hardly reveal such deposition processes except an abrupt drop in its intensity. On the other hand, the laser reflection signal is very sensitive to the species and surface morphology. Consequently, a strong contrast can be seen between laser reflection and RHEED signals.

On the basis of the above observation, we now discuss the mechanisms responsible for each step. Step 1 is a very rapid process corresponding to the abrupt increase (decrease) in the reflection (RHEED) intensity within $\sim$4.5 s ($\pm$0.2 s, standard deviation of all growth cycles). We attribute this step to the deposition of monolayers of In, which has a significantly larger reflectivity than that of a bare surface. This probably corresponds to the InN surface stoichiometry change from a N-stabilized surface to an In-stabilized one and then an additional In adlayer on top of it. The amount of deposited In during step 1 can be estimated from the growth rate, which can be extracted from interference oscillations in Fig. 1. Since the 660 nm laser is normally incident, one interference oscillation corresponds to an $\sim$122-nm-thick InN layer assuming that the refractive index of InN is 2.7 at 660 nm,[12] and it consists of $\sim$30 cycles of InN growth. Therefore, the InN layer for one cycle is 4.1 nm thick. This

estimation is confirmed by *ex situ* cross-sectional SEM measurement, which shows that the entire InN layer is about 330 nm thick for 80 cycles. Since In adatoms barely re-evaporate away from the surface at such a low growth temperature, the amount of In supplied in one cycle (In opens for 30 s) is equal to the total amount of In in 4.1-nm-thick InN. Consequently, the In supply of 4.5 s in step 1 corresponds to the amount of In in 0.615-nm-thick ($= 4.5 \times 4.1/30$ nm) InN. The c lattice constant of InN is 0.570 nm and two In layers are in each unit cell. Therefore, the In coverage during step 1 is estimated to be 2.2 ± 0.2 ($= 0.615/0.570 \times 2$) monolayers, assuming that its areal density following that of InN, which is $9.17 \times 10^{14}/\mathrm{cm}^2$. Therefore, approximately two monolayers of In have been deposited during step 1.

Northrup *et al.* have reported a laterally contracted Ga bilayer model in a GaN surface, which means that the Ga–Ga lateral distance is slightly smaller than that inside the GaN lattice, and areal density is higher.[13] Such a thin metallic film has been reported to act as an efficient diffusion channel for adatoms, thereby enhancing lateral diffusion and leading to a smoother surface.[14] Distinct GaN growth regimes have been reported to be directly related to the coverage of Ga adlayers on the MBE grown GaN surface.[15,16] Similarly, the metallic In layers may also play such a role and enhance lateral diffusion during the MBE growth of InN. Therefore, reproducible high-quality InN growth can be achieved using the DERI method.[10]

Further evidence of two monolayers of In adatoms has been demonstrated when we investigated the adsorption/desorption kinetics of In adlayers at higher substrate temperatures, 570–650 °C. Figure 4 shows the laser reflection signals during In adsorption and desorption on the GaN surface at 625 °C for various beam fluxes with BEPs from 4.2×10^{-8} to 2.2×10^{-7} Torr. It is very clear that In adsorption shows two distinct processes and two steady states, similarly to the ellipsometry results reported in ref. 17. Below the critical BEP, $\sim 10^{-7}$ Torr, the reflection intensity saturates at almost the same level, the first steady state. For the lowest BEP, the reflection intensity is still slightly below the first steady state. With increasing BEP, following a sharp increase and a relatively slow increase, the reflection intensity saturates again at an obviously higher level than the first steady state. In the steady states, In deposition at a proper beam flux is expected to be balanced by its desorption. It is therefore reasonable to say that the first steady state appearing at a lower beam flux is balanced by a lower desorption rate and the second steady state appearing at a higher beam flux is balanced by a higher desorption rate.

The In desorption process proves that this is the case. We can see in Fig. 4, after the In shutter is closed, that the desorption also shows two distinct processes: an initial fast decrease from the higher steady state to the lower one; and a subsequent slow decrease from the first steady state to the original level at beginning. In both desorption processes, the slopes are surprisingly similar for different beam fluxes, namely, they are parallel to each other. This clearly reveals that the same desorption processes are happening. Therefore, the observation strongly supports that step 1 corresponds to the deposition of two monolayers of In, and the first and second In monolayers show distinct adsorption and desorption rates.

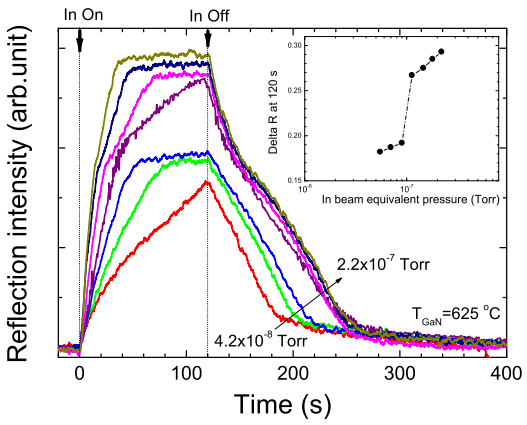

Fig. 4. (Color online) Relative reflection change during In adsorption/desorption processes under In BEP varying from 4.2×10^{-8} to 2.2×10^{-7} Torr, and with fixed deposition time (120 s) and substrate temperature (625 °C). The inset shows a relative reflection change at 120 s as a function of BEP.

As for step 2, the very slow decrease in RHEED intensity in step 2 indicates that randomly distributed and gradually growing In droplets scatter incident electrons. At first glance, it is possible that more In adlayers might have formed at the very beginning of step 2. If so, we would expect to observe a similar sharp reflectivity increase as in step 1. However, this is not the case because a constant level lasting for ~7 s has been observed at the beginning of step 2. Therefore, we attribute step 2 to In droplet formation. As mentioned before and shown in Fig. 3, the reflection signal in step 2 strongly depends on In supply time, i.e., the number of In adatoms on surface. This should be due to the increase in the size and volume and/or increasing density of In droplets, which determines the surface morphology.

We have also performed an *in situ* scanning electron microscopy (SEM) experiment to study the In deposition process and observed microscale In droplets with several minutes of In supply.[18] Although it is difficult for the *in situ* SEM to reveal nanoscale droplets, this observation has demonstrated strong evidence of *in situ* In droplet formation. Moreover, *ex situ* SEM and XRD 2θ–ω scans have also demonstrated In droplets on an InN surface grown under In-rich condition.[10]

Steps 3 and 4 show just the reverse profiles of steps 2 and 1. This reveals that the surface condition during the In adatom reaction/consumption process (In: off; N: on) is a reverse of that during In deposition, namely, two monolayers of In with shrinking droplets on a surface. The two monolayers of In are like a wetting layer and In droplets are like reservoirs to supply In atoms to maintain the two monolayers of In as it is and keep the reaction going until all the droplets are consumed. Finally, the two monolayers of In react with nitrogen radicals and are incorporated into the crystalline InN layer.

4. Conclusions

In summary, our investigation of InN MBE growth by *in situ* laser reflection and RHEED monitoring has demonstrated complementary information on the growth front. Laser

reflection intensity increases during In deposition and decreases during the following N irradiation, in contrast to RHEED intensity. We attribute the abrupt increase (decrease) in laser reflection (RHEED) intensity in step 1 to the deposition of two monolayers of In, which is followed by In droplet formation on the top, step 2, with further In deposition. During the nitrogen radical irradiation process, the surface condition revealed by laser reflection and RHEED is a reverse of that during In deposition. Further study of the adsorption/desorption kinetics of adsorbed In under various In beam fluxes has demonstrated clear evidence of two monolayers of In adatoms, revealing their distinct adsorption and desorption rates. The monolayers of In in the growth front probably plays a similar role to Ga adlayers during GaN MBE growth, which enhances the lateral diffusion and enables the realization of a smoother surface morphology.

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) through Grants-in Aid for Scientific Research in Priority Areas "Optoelectronics Frontier by Nitride Semiconductor" (18069012) and Scientific Research A (21246004), and the WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-2008-000-10075-0). KW acknowledges the support by the Japan Society for the Promotion of Science (JSPS).

1) J. 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** (2002) 3967.
2) V. Y. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmuller, H. Harima, A. V. Mudryi, J. Aderhold, O. Semchinova, and J. Graul: Phys. Status Solidi B **229** (2002) R1.
3) Y. Nanishi, Y. Saito, and T. Yamaguchi: Jpn. J. Appl. Phys. **42** (2003) 2549.
4) J. Wu, W. Walukiewicz, K. M. Yu, W. Shan, J. W. Ager, E. E. Haller, H. Lu, W. J. Schaff, W. K. Metzger, and S. Kurtz: J. Appl. Phys. **94** (2003) 6477.
5) V. M. Polyakov and F. Schwierz: Appl. Phys. Lett. **88** (2006) 032101.
6) W. L. Chen, R. L. Gunshor, J. Han, K. Higashimine, and N. Otsuka: MRS Internet J. Nitride Semicond. Res. **5S1** (2000) W3.30.
7) C. S. Gallinat, G. Koblmüller, J. S. Brown, and J. S. Speck: J. Appl. Phys. **102** (2007) 064907.
8) X. Wang, S. B. Che, Y. Ishitani, and A. Yoshikawa: Jpn. J. Appl. Phys. **45** (2006) L730.
9) C. 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** (2006) 032109.
10) T. Yamaguchi and Y. Nanishi: Appl. Phys. Express **2** (2009) 051001.
11) T. Yamaguchi and Y. Nanishi: Phys. Status Solidi A **207** (2010) 19.
12) M. Anani, H. Abid, Z. Chama, C. Mathieu, A. Sayede, and B. Khelifa: Microelectron. J. **38** (2007) 262, and references therein.
13) J. E. Northrup, J. Neugebauer, R. M. Feenstra, and A. R. Smith: Phys. Rev. B **61** (2000) 9932.
14) J. Neugebauer, T. K. Zywietz, M. Scheffler, J. E. Northrup, H. Chen, and R. M. Feenstra: Phys. Rev. Lett. **90** (2003) 056101.
15) G. Koblmüller, S. Fernandez-Garrido, E. Calleja, and J. S. Speck: Appl. Phys. Lett. **91** (2007) 161904.
16) G. Koblmüller, R. Averbeck, H. Riechert, and P. Pongratz: Phys. Rev. B **69** (2004) 035325.
17) S. Choi, T. H. Kim, S. Wolter, A. Brown, H. O. Everitt, M. Losurdo, and G. Bruno: Phys. Rev. B **77** (2008) 115435.
18) in preparation.