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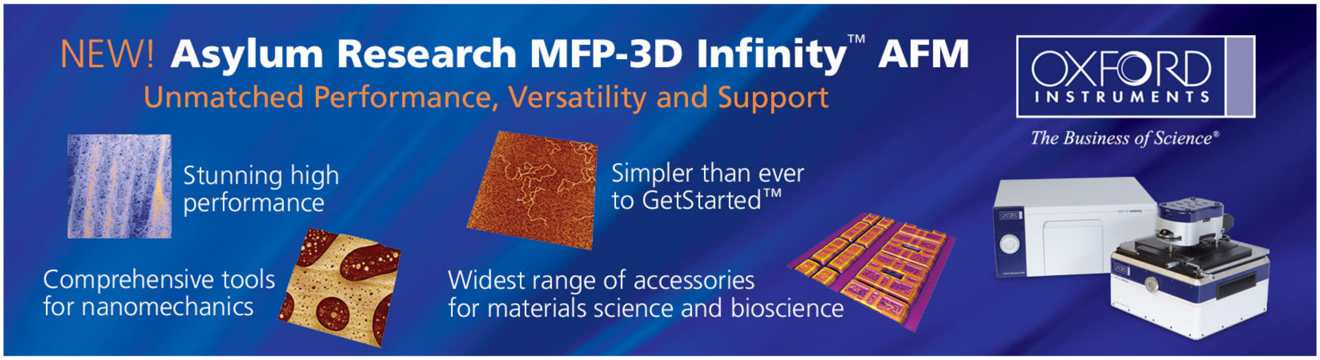

Impacts of ammonia background flows on structural and photoluminescence properties of InN dots grown on GaN by flow-rate modulation epitaxy

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Structural and photoluminescence (PL) properties of InN dots grown on GaN by metal organic vapor phase epitaxy using the flow-rate modulation technique, and their dependence on growth conditions, were investigated. An ammonia (NH_3) background flow was intentionally supplied during indium deposition periods to control the kinetics of adatoms and hence the morphology of InN dots. Samples prepared under lower NH_3 background flows generally exhibit narrower and more intense PL signals peaked at lower emission energies. The authors point out that the NH_3 background flow is an important parameter that controls not only the nucleation process but also the emission property of InN dots. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2425038]

Indium nitride (InN) has attracted much attention in recent years due not only to its superior electronic transport properties,[1] such as high theoretical mobility and large drift velocity, but also to the recent revision of its band gap energy to ~0.7 eV.[2–4] This discovery further spans the spectral range of III-nitride materials into near infrared, covering the wavelength range for telecommunications applications. High crystalline quality InN films have been obtained by a number of growth techniques in the past few years, including molecular beam epitaxy (MBE) (Ref. 5) and metal organic vapor phase epitaxy (MOVPE).[6] Recent progress has also shown that nanometer-scale InN dots with controllable size and density can be formed on GaN surface during the initial stage of heteroepitaxial growth using MBE (Refs. 7–9) or MOVPE.[10,11] After proper capping with GaN, this kind of InN dots shows superior photoluminescence (PL) properties and pronounced quantum confined effects.[11] However, the growth of high-quality InN dots with tailored optical properties to act as "quantum dots" for practical applications is still of great challenge. The difficulty is believed to arise from the low growth temperature for InN due to the low InN dissociation temperature and the high equilibrium N_2 vapor pressure over the InN film.[1] This peculiar feature not only inherently restricts the temperature for growing capping layers (e.g., GaN or AlN) but also hinders the surface migrations of adatoms. A low growth temperature implies a short migration length, which means that In adatoms are less mobile to find an energetically favored site. A number of studies with respect to nucleation processes and structural properties of either MBE—or MOVPE-grown InN dots have been reported.[12,13] However, it remains less clear how the optical properties of InN dots relate to their structural properties and nucleation processes.

In MOVPE growth, a well-known technique that can achieve a lower growth temperature while keeping high crystalline quality is the flow-rate modulation epitaxy (FME).[14] Due to the alternative supply of group-III and group-V sources in FME growth, surface migrations can be considerably enhanced, which is believed to be very useful for the fabrication of nanostructures. In this letter, structural and PL properties of FME-grown InN dots on GaN, and their dependence on growth conditions, were investigated. During the FME growth of InN dots, an NH_3 background flow was intentionally supplied in addition to the alternating precursors. By tuning the NH_3 background flow, it is possible to control the kinetics of In adatoms and hence the morphology of InN dots. PL investigations further reveal the information about intrinsic properties of InN dots prepared under different growth conditions. We point out that the NH_3 background flow is an important parameter that controls not only the nucleation process but also the emission property of InN dots.

Samples in this study were grown on sapphire (0001) substrates in a MOVPE system using trimethylgallium (TMGa), trimethylindium (TMIn), and ammonia (NH_3) as source precursors. After nitridation of the substrate at 1120 °C, a thin GaN nucleation layer was first grown at 520 °C, followed by the growth of a 1-μm-thick undoped GaN buffer layer at 1120 °C. After the growth of GaN buffer layers, the substrate temperature was then reduced to 600 °C to grow InN dots. The gas-flow sequence of FME consists of four steps in one cycle: a 20 s TMIn flow period, a 20 s NH_3 flow period, and two 10 s purge periods intervened in between. The TMIn and NH_3 flow rates are 150 and 18 000 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. During TMIn flow periods, an NH_3 background flow was intentionally supplied throughout the growth. A series of samples using different NH_3 background flow rates r_0, ranging from 0 to 10 000 SCCM, has been grown. The growth of InN dots was completed by a total of six cycles for all samples. For comparison purpose, we have also prepared a sample of InN dots by the conventional MOVPE growth mode with continuous flows of 10 000 SCCM NH_3 and 150 SCCM TMIn for 120 s at the same growth temperature of 600 °C. Surface morphologies,

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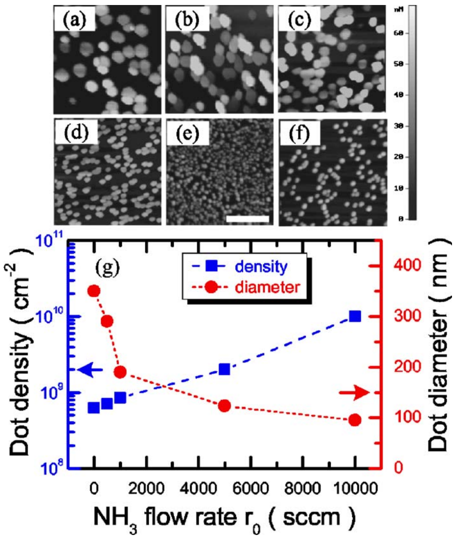

FIG. 1. (Color online) AFM micrographs of InN dots grown by FME with different r_0: (a) 0 SCCM, (b) 500 SCCM, (c) 1000 SCCM, (d) 5000 SCCM, and (e) 10000 SCCM, and (f) by the conventional growth mode. (g) The density and diameter of the InN dots as function of r_0.

sizes, and densities of InN dots were analyzed using atomic force microscopy (AFM). PL measurements were performed at 10 K using the 488 nm line of an Ar$^+$ laser as an excitation source. The luminescence signals were dispersed by a 0.5 m monochomator and detected by a liquid-nitrogen-cooled extended InGaAs detector (with a cutoff wavelength at 2.05 μm) using the standard lock-in technique.

Figure 1 shows AFM micrographs of InN dots grown by FME with different NH$_3$ background flow rates (r_0) ranging from 0 to 10 000 SCCM [Figs. 1(a)–1(e)] and by the conventional growth mode [Fig. 1(f)]. The dot density and average diameter as function of r_0 are plotted in Fig. 1(g). As r_0 was increased from 0 to 10 000 SCCM, the dot density increased from 6.2×10^8 to 1.0×10^{10} cm^{-2}, whereas the average base diameter decreased from 350 to 95 nm. Comparing the dot density and size to those obtained by conventional growth mode [indicated by arrows in Fig. 1(g)], FME growth under low NH$_3$ background flows ($r_0<1000$ SCCM) generally yields much larger and less dense dots. This can be attributed to the enhanced surface migration of In adatoms in low NH$_3$ ambience during the deposition of In species.[15,16] As more NH$_3$ are injected during TMIn periods, surface migration of In adatoms is considerably hindered due to the exposure to a highly N-rich ambience, leading to higher dot densities and smaller dot sizes.

Apart from the dot size and density, their shape also changes with the NH$_3$ background flow. Figure 2 gives line profiles across typical InN dots grown by FME with different r_0 [Figs. 2(a)–2(e)] and by the conventional method [Fig. 2(f)]. In order to represent the typical dot size in each case, we have selected the dot having based diameter and height very close to their average values. In general, FME-grown InN dots under low NH$_3$ background flows reveal a mesa shape, or more precisely, a truncated hexagonal pyramid with a flattop and faceted sidewalls. The aspect ratio (i.e., height-to-diameter ratio) for the case of $r_0=0$ is found to be $\sim1/8$. Such a low aspect ratio indicates that the lateral growth rate is at least a few times (~8) faster than the vertical one. With the increasing NH$_3$ background flow, the mesa-type dots gradually evolved to lens-shaped dots without clear faceting.

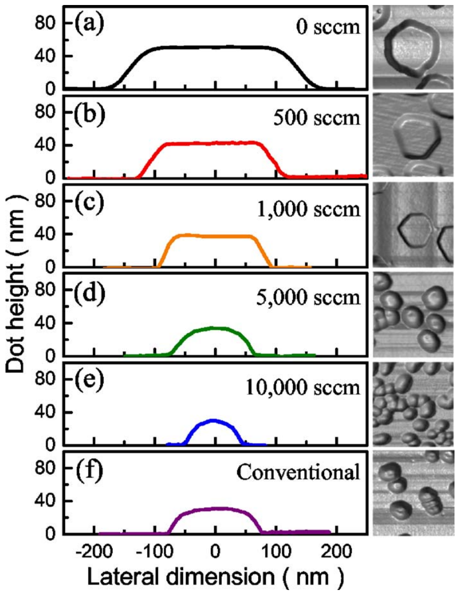

FIG. 2. (Color online) Line profiles across typical InN dots grown by FME with different r_0: (a) 0 SCCM, (b) 500 SCCM, (c) 1000 SCCM, (d) 5000 SCCM, and (e) 10000 SCCM, and (f) by the conventional method. The AFM micrographs shown on the right are the corresponding morphologies in an area of 500×500 nm^2.

Furthermore, the aspect ratio also increases remarkably to $\sim1/3$ as the r_0 reaches 10 000 SCCM. As for InN dots grown by conventional MOVPE, the dot shape is also lens-shape-like, with an aspect ratio of about $\sim1/5$.

The above observations clearly demonstrate the impact of the NH$_3$ background flow on the kinetics of adatoms during the nucleation of InN dots. Indeed, reducing the NH$_3$ background flow during In deposition periods not only leads to a longer migration length of In adatoms but also prevents the In adatoms from moving uphill to island tops, due to the preferential formation of In-terminated surface on the InN island tops under such In-rich conditions. As a consequence, In adatoms tend to nucleate at the edge of InN dots, yielding a faster lateral growth rate than the vertical one and hence mesa-type islands with lower aspect ratios. On the contrary, when a high NH$_3$ background flow was used, the exposure to a highly N-rich ambience not only hinders the surface migration of In adatoms, but also tends to form N-stabilized surfaces on islands tops. This facilitates uphill transfer of In adatoms to island tops, due possibly to the lower chemical potential thereon, leading lens-shaped dots with a significantly higher aspect ratio.

The effect of the NH$_3$ background flow on PL properties of InN dots is shown in Fig. 3. The PL spectra shown in Fig. 3(a) were measured at 10 K under an excitation power density of ~0.15 kW/cm^2. All samples exhibit near-infrared emission bands in the range of 0.7–0.9 eV. Since the dot sizes are still too large to produce pronounced quantum size effects, differences in peak energy between samples are mainly due to variations of the electron concentration in InN dots. With the decreasing NH$_3$ background flow, a redshift of peak energy can be clearly seen. This implies that the NH$_3$ background flow is an important parameter for controlling the electron concentration of InN dots. To give a quantitative estimation, we have further employed a line shape model considering "free-to-bond" radiative recombination to analyze the PL spectra.[17] Since our main interest in modeling aims at finding the Fermi energy (E_f) and the relative elec-

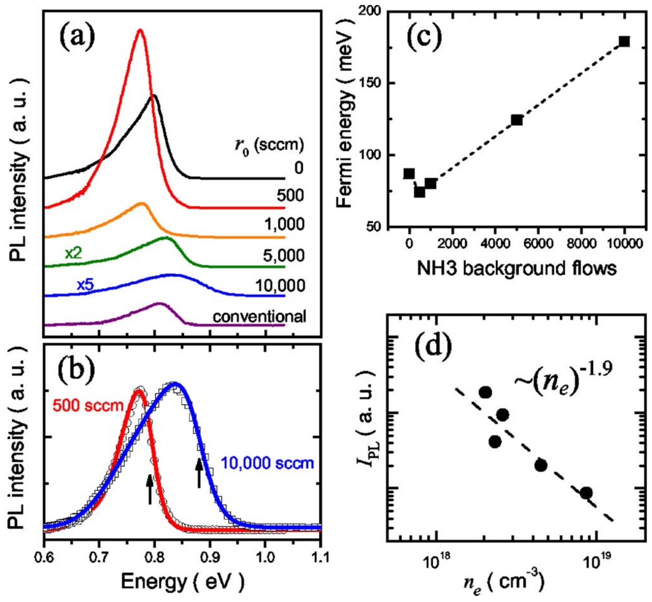

FIG. 3. (Color online) (a) PL spectra measured at 10 K under the same excitation condition. (b) The measured PL spectra and the calculated line shapes for samples with r_0=500 and 10000 SCCM. (c) The deduced Fermi energy relative to the conduction band edge as a function of r_0. (d) Correlation of the estimated electron concentration n_e with the integrated PL intensity I_{PL}.

tron concentration (n_e) in different samples, the model was further simplified by assuming a deltalike function for the distribution of photogenerated holes near the valence band edge, so that the shape of emission band can be approximated by the electron energy distribution in the conduction band. As illustrated in Fig. 3(b), the simplified model reproduces our PL spectra very well. The fitted band gap values are in the range of 0.69–0.72 eV, in good agreement with the value reported in literature.[17] In Fig. 3(c), the deduced E_f was lowered from 179 to 74 meV as r_0 was decreased from 10 000 to 500 SCCM. If the electron effective mass was chosen to be $0.07m_0$,[17] the change in E_f corresponds to a reduction of n_e from 8.6×10^{18} to 2.0×10^{18} cm^{-3}. This seems to imply that more donor-type impurities, most likely the hydrogen, may be incorporated under a high NH_3 background flow. On the other hand, we noted that the emission property of InN dots is getting worse when further changing the NH_3 background flow from 500 to 0 SCCM. This fact suggests that another mechanism governs the source of electron concentration in InN dots grown under such an NH_3-free condition for the deposition of In species. For the growth of InN at 600 °C, the decomposition of InN is significant, while the desorption of In is still negligible.[18] If the amount of active nitrogen is insufficient, N atoms are expected to desorb rapidly from InN during the TMIn flow periods, probably in the form of N_2 molecules, resulting in the accumulation of metallic In on the surface. This may facilitate the formation of nitrogen vacancies and/or metallic In droplets, leading to degraded optical quality.

Besides, we also found a general correlation between the PL intensity (I_{PL}) and the deduced carrier concentration n_e. In Fig. 3(d), we can see that the I_{PL} decreases with the deduced n_e as a power function $\sim(n_e)^{-1.9}$. This is a stronger dependence than for a dominant Auger recombination $\sim(n_e)^{-1}$.[19] Therefore, we conclude that the PL efficiency increases not only due to the reduced electron concentration but also to the reduced nonradiative centers with the decreasing *n*-type background. The maximum PL intensity occurred at r_0=500 SCCM, which is about ~40 times higher that at 10 000 SCCM and is still ~ eight times higher than those prepared by conventional MOVPE growth mode. Such an improvement in PL efficiency provides a new approach to the fabrication of high optical quality InN dots for practical applications.

In summary, structural and PL properties of FME-grown InN dots grown on GaN and their dependence on growth conditions were investigated. By tuning the NH_3 background flow during deposition periods of In species, it is possible to control the kinetics of adatoms and hence the morphology of InN dots. Samples prepared under lower NH_3 background flows generally exhibit narrower and more intense PL signals at lower emission energies. We point out that the amount of NH_3 background is very important not only to the morphology but also to the emission property of InN dots.

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