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The structural and optical properties of InN nanodots grown with various V/III ratios by metal–organic chemical vapor deposition

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Abstract

Self-assembled InN nanodots have been prepared at 650 °C with various V/III ratios from 500 to 30 000 by metal–organic chemical vapor deposition (MOCVD). It is found that the dot density and morphological size as well as the optical properties all display drastic changes at V/III = 12 000. Generally, denser and smaller InN nanodots with higher emission energy and narrower linewidth were obtained when growth was conducted at V/III ratios slightly lower than 12 000 as compared to those at higher V/III ratios. The physical properties of our MOCVD-grown InN nanodots are sensitive to the surface structure and the morphology is very similar to molecular beam epitaxially grown GaN and InN films, which may be used as a guide to optimize the InN growth.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The InN compound has recently attracted much attention, attributed largely to its narrow direct bandgap energy of ∼0.65 eV [1]. This material, if alloyed with other III-nitrides, is very promising for various optoelectronic device applications, such as light-emitting diodes and solar cells [2], operating from near-infrared to deep-ultraviolet. To date, regardless of growth challenges, particularly high thermal instability and high dissociation rate, good quality InN films with emission energy and background carrier concentration as low as 0.65 eV and $\sim 1 \times 10^{17}$ cm^{-3} and room-temperature Hall mobility exceeding 3500 cm^2 V^{-1} s^{-1} [3] have been achieved using molecular beam epitaxy (MBE). Moreover, it is demonstrated that the physical properties of MBE-grown InN [4], similar to MBE-grown GaN [5] and AlN [6], correlate closely with their surface structure and morphology, which in turn depend crucially on the input In/N ratio and growth temperature. Consequently, the growth diagrams have been built up and used to search for the step-flow-like growth feature in order to achieve high InN film quality.

Nevertheless, such a growth diagram has not yet been reported for InN grown by metal–organic chemical vapor deposition (MOCVD). In this study, by extending the input V/III ratio to low values, two clear growth regimes were observed in our MOCVD-grown InN nanodots in terms of dot density and morphological size. More interestingly, we also found appreciable differences in their optical properties. The emission peak energy and linewidth changed abruptly from 0.760 to 0.746 eV and from 48 to 68 meV, respectively, at the boundary of the growth regimes.

2. Experimental details

A series of InN dot growths were performed on 1 μm thick GaN epilayer on (0001) sapphire substrates at 650 °C with a growth time of 15 min using a low pressure 200 mbar MOCVD. We used trimethylindium (TMIn) and ammonia (NH_3) as source precursors and N_2 as the carrier gas. To

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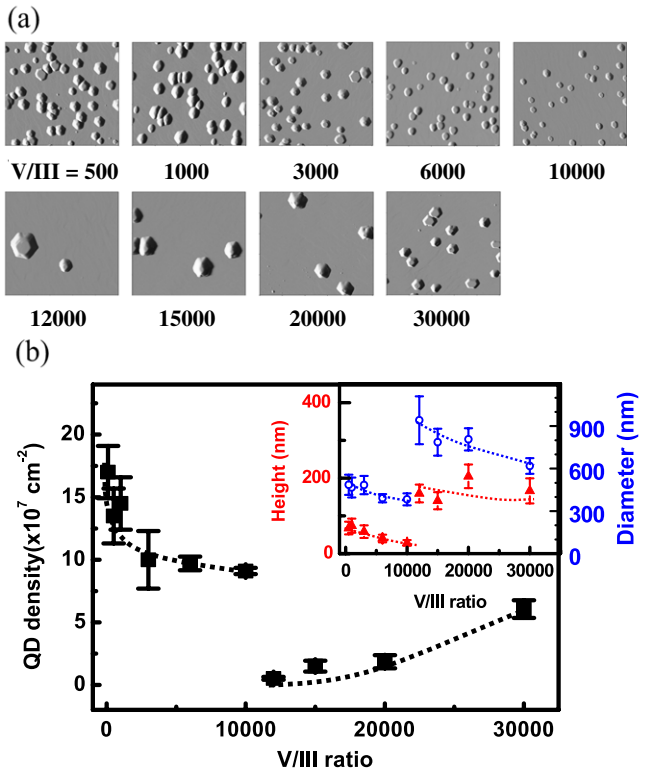

Figure 1. (a) AFM images ($10 \times 10\ \mu m^2$) and (b) dot density of InN nanodots as a function of V/III ratio. Inset of (b) shows the variations of dot diameter (○) and height (▲) versus V/III ratio.

examine the V/III ratio effects, the NH_3 flow rate was adjusted from 2.01×10^3 to 1.21×10^5 μmol min^{-1} while keeping the TMIn flow rate fixed at 3.99 μmol min^{-1}, resulting in a variation of the V/III ratio from 500 to 30 000. After the deposition, atomic force microscopy (AFM) was employed to probe the surface morphologies and dot densities using the tapping mode. PL measurements were performed at 13 K by using the 488 nm line of an Ar^+ laser as an excitation source. The luminescence signals were dispersed by a 0.5 m monochromator and detected by a liquid-nitrogen-cooled extended InGaAs detector using the standard lock-in technique.

3. Results and discussion

In figures 1(a) and (b), we show the morphological images and dot densities of the InN nanodots at different V/III ratios. The inset in figure 1(b) shows the relevant variations of their height and diameter. It is obvious that the InN dot growth can be divided into two growth regimes as revealed by both the dot density and morphological size. For samples grown at V/III ratios lower than 12 000, the surfaces were found to be covered by lots of small InN nanodots, whereas sparser and larger dots were observed at high V/III ratios. The obtained dot density decreases slowly from 1.7×10^8 to 9.1×10^7 cm^{-2} with increasing V/III ratio up to 10 000. Further increasing the V/III ratio, however, causes a sharp drop of dot density to 5.2×10^6 cm^{-2}, in conjunction with simultaneous abrupt changes in their height and diameter, from 28 to 159 nm and

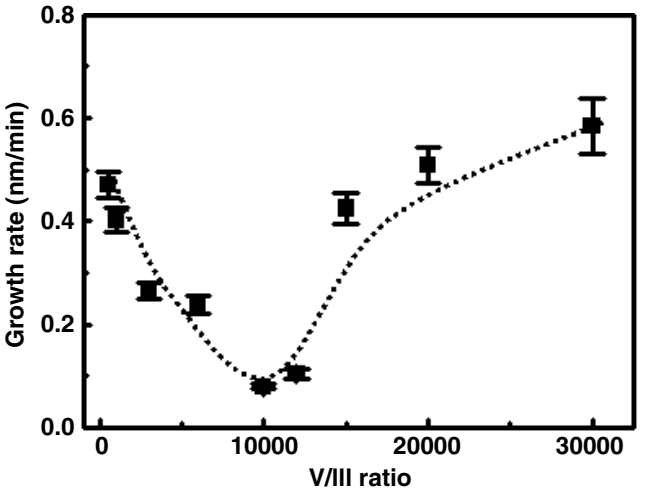

Figure 2. Growth rate of InN nanodots versus V/III ratio.

383 to 941 nm, respectively. Nevertheless, in the high V/III ratio regime the increasing V/III ratio does not bring further significant change in their surface structure, but the dot density increases steadily with a gradual decrease in dot size.

Since the growth rate is one of the major factors that controls the dot density, we thus deduce the total dot volume, and hence the growth rate, for each sample according to the AFM results. The variation of growth rate versus V/III ratio is plotted in figure 2. Unlike the monotonic decrease in growth rate with increasing V/III ratio reported by Maleyre *et al* [7], we observed an unanticipated result. Here growth rate is decreased initially at low V/III ratios and starts to grow when the V/III ratio is exceeding 12 000. As far as the dot density N is concerned, it can be expressed as a function of growth rate R by

$$N \propto (R/D_0)^p \exp(E^*/kT) \tag{1}$$

in accord with the standard nucleation theory [8], where D_0 is the diffusion prefactor of decisive surface adatoms that governs the island growth, k is the Boltzmann constant, T is the temperature, E^* is the effective diffusion energy barrier for surface adatom and scaling exponent $p = i/(i+2)$, in which i is the critical cluster size (in number of atoms) to provide nuclei for stable island formation. The derived exponents for low and high V/III ratios are 0.77 and 0.79, respectively. The nearly identical exponents imply clearly that the trends of descending and ascending dot density in the low or high V/III ratio regime is mainly due to the change of growth rate, regardless of the occurrence of discontinuity in dot density at a V/III ratio of 12 000. Moreover, from the exponents we can attain the critical cluster size of our InN island growth, which is ~8 for all our samples, independent of the flow rate of NH_3. The above finding indicates that the incorporation of more N atoms under an N-rich ambient does not necessarily convert the In clusters into more stable nuclei; this means that the critical clustering size at the initial stage is determined primarily by the adsorbed In atoms alone for InN dot growth.

On the other hand, the discontinuity in dot density at V/III = 12 000 can be inferred from the diffusivity of surface adatoms. According to equation (1), the less is the

diffusion capability of adatoms, the higher is the resulting island density. Thus, the immediate change in dot density can be considered to stem from an abrupt change of adatom diffusivity, owing simply to the replacement of decisive surface adatoms, i.e. the lowest mobility of adatom that governs the island formation. This can be explained as follows. It has been reported that the surface morphology and relevant electrical and optical properties of group III-nitrides are highly sensitive to the input molar V/III ratio, and the growth in general can be characterized into three regimes, one N-rich, and two metal-rich regimes, classified as intermediate and droplet regimes [4–6]. From the morphological viewpoints and the V/III ratios employed here, we thus assigned our InN dot growths as N-rich and In-rich intermediate growth regimes for high and low V/III ratios, respectively. The In-droplet growth regime is tentatively precluded because no droplets are observed on the surfaces of all our samples.

Regarding the III-nitride growth, the metal adatoms are known to have low surface mobilities under N-rich conditions, whereas the N adatoms become the limiting surface diffusion adatoms under metal-rich conditions [9]. Such a growth characteristic is conceivably the primary reason responsible for the distinct change of dot density and morphological structure attained in our InN nanodots. Moreover, the fact of higher dot densities at low V/III ratios together with ∼17 times difference in dot density at the transition region both suggest the diffusivity of active N adatoms under In-rich conditions is considerably lower than that of In adatoms under N-rich conditions. This agrees well with the observation in GaN, in which the diffusion of N adatoms is reported to be several orders of magnitude slower than that of Ga [9].

Figure 3(a) shows the PL spectra of InN samples measured at 13 K. These samples exhibit emission peaks around 0.739–0.762 eV, well above the commonly accepted bandgap energy of 0.65 eV. This implies that the samples all possess large background electron concentrations that alleviate the Fermi energy in the conduction band and cause a significant blueshift in PL energy. The PL integral intensity normalized to the total dot volume is also plotted in figure 3(b) as a function of the V/III ratio. A general trend is observed in which relatively low intensity with nearly unchanged value results under the N-rich growth regime, whereas a stronger intensity but with large variation is obtained under In-rich growth conditions. The optimal InN PL intensity occurs at V/III = 3000. More appealing results can be observed in figure 3(c) which reveals the peak energy and linewidth versus the V/III ratio. Both of them show sudden changes at the growth boundary, i.e. V/III ratio = 12 000. The emission peak energies of samples grown at low V/III ratios (In-rich growth regime) lie around 0.760 eV, nearly independent of the V/III ratio; in contrast, those grown at high V/III ratios (N-rich growth regime) exhibit lower emission energies, spanning from 0.746 to 0.739 eV, with about 14 meV difference at the boundary between different growth regimes. Such an abrupt change of emission energy with growth regime has also been reported by Yao *et al* in MBE-grown InN films, although their emission energies appear to be higher in the N-rich growth regime [10].

Concerning the linewidth, the narrowest value of ∼48 meV occurs in the V/III range of 6000–10 000, which

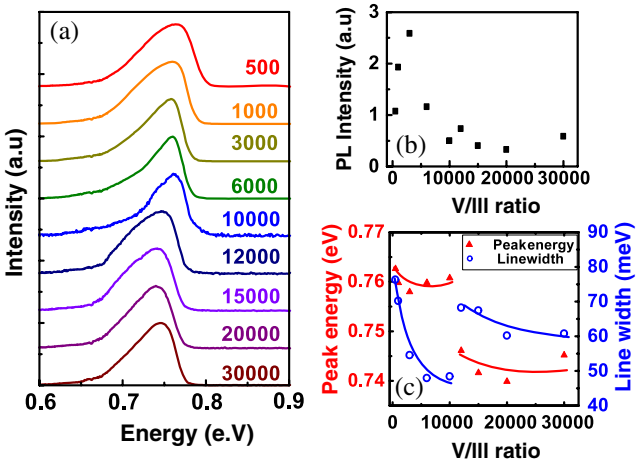

Figure 3. (a) Normalized 13 K PL spectra, (b) integral PL intensity and (c) their PL peak energy (▲) and linewidth (○) of InN nanodots grown at various V/III ratios.

jumps abruptly to 68 meV at a V/III ratio of 12 000. Outside this region, the linewidth tends to rise considerably at even lower V/III ratios, while a gradual decrease with increasing V/III ratio is observed in a higher V/III ratio growth regime. The above results suggest that the optimum InN dot growth at 650 °C by MOCVD takes place under a slightly In-rich growth condition, a situation similar to the MBE-grown GaN and AlN films [4, 5].

The concurrent variations of both PL peak energy and linewidth at the growth boundary seem to imply that the native point defects causing the optical transitions in these two growth regimes are different. Due to the highly degenerate features and small effective mass, the optical transition for our InN nanodots grown under slightly In-rich conditions is considered to involve primarily degenerate electrons in the conduction band and localized holes in the band-tail states of the valence band. These tail states are caused by potential fluctuation as a result of the presence of a large density of charged donors, most likely the nitrogen vacancies or their complexes, which are formed favorably in heavily n-doped InN materials [11]. On the other hand, when the growth moves to the N-rich regime, an additional recombination path occurs, as shown by the appearance of a low-energy shoulder located at about 40 meV below the main peak in the PL spectra of the high V/III ratio samples. This low-energy shoulder has been assigned by Arnaudov *et al* and Klochikhin *et al* to the recombination of electrons with deep acceptors in n-type InN material [1, 12]. The existence of such acceptors not only compensates the electrons in the conduction band, giving rise to reduced emission energy, but also bringing a broadening of the PL linewidth. The likely candidate for this deep acceptor is the In vacancy [13, 14]. This can be attributed to the 'dry surface' nature of InN grown under N-rich conditions, as proposed by Gallinat *et al* [6], where no metallic In adlayer is present on the growing surface to prevent desorption of the topmost In-terminated atoms, leaving non-negligible In vacancies in the epilayer, in particular when the growth was conducted at 650 °C, a temperature very close to the complete desorption temperature of In from liquid In, 675 °C [4].

4. Conclusion

In summary, we have found that both the structural and optical properties of InN nanodots grown by MOCVD at 650 °C are closely related to each other and show high sensitivity to the input V/III ratio. In a general respect, two growth regimes with a dividing V/III ratio of 12 000 were observed. Denser and smaller dots were found on the surfaces of samples grown at V/III ratios below 12 000, whereas sparser and larger dots were formed at high V/III ratios. Additionally, we also found the PL spectra behave differently in the two growth regimes. For InN nanodots grown at high V/III ratios, the luminescence appears to be much broader and has lower emission energy as compared to those prepared at V/III ratios just slightly below 12 000. It is worth mentioning that at the growth boundary there are exhibited distinct changes in terms of the dot density and size as well as optical properties. The corresponding PL peak energy and linewidth vary sharply from 0.760 to 0.746 eV and 48 to 68 meV, respectively. We ascribe such phenomena to the presence of deep acceptors in those high V/III ratio samples, such as the In vacancies. They give rise to additional transitions for broadening the emission spectrum accompanied by the reduced peak energy, due to the compensation by degenerate electrons in the conduction band.

Acknowledgments

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