Morphological and luminescent characteristics of GaN dots deposited on AlN by alternate supply of TMG and NH₃

Yu-Li Tsai^a, Jyh-Rong Gong^{b,*}, Tai-Yuan Lin^c,
Hsia-Yu Lin^d, Yang-Fang Chen^d, Kun-Ming Lin^a

^aDepartment of Materials Science and Engineering, Feng Chia University, Taichung 407, Taiwan, Republic of China

^bInstitute of Opto-Mechatronics, National Chung Cheng University, Chiayi 621, Taiwan, Republic of China

^cInstitute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202, Taiwan, Republic of China

^dDepartment of Physics, National Taiwan University, Taipei 106, Taiwan, Republic of China

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Abstract

GaN dots were deposited on AlN underlayers by alternate supply of trimethylgallium (TMG) and ammonia (NH₃) in an inductively heated quartz reactor operated at atmospheric pressure. Various growth parameters including deposition temperature, TMG admittance and pulse time between TMG and NH₃ exposures were proposed to investigate the influence of growth parameters on the size distribution of GaN dots. It appears that GaN dots with uniform size distribution can be achieved under certain growth conditions. Based on the study of atomic force microscopy (AFM), high deposition temperature was found to be in favor of forming large GaN dots with small dot density. Decrement of TMG flow rate or reduction in the number of growth cycle tends to enable the formation of GaN dots with small dot sizes. The results of room temperature (RT) cathodoluminescence (CL) measurements of the GaN dots exhibit an emission peak at 3.735 eV. A remarkable blue shift of GaN dot emission was observed by reduced temperature photoluminescence (PL) measurements.

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1. Introduction

Group III-nitride compound semiconductors have received great attention due to their wide band gap nature and applicability in high brightness light-

emitting devices such as laser diodes (LDs) [1] and light-emitting diodes (LEDs) [2]. Currently, two-dimensional (2D) multiple quantum well (MQW) structures are used to serve as the active layer in most of the above-mentioned devices. It has been reported that replacement of the 2D-MQWs with smaller dimensional structures such as zero-dimensional dots

* Corresponding author.

allow to improve the LD performances including threshold current density reduction, spectral linewidth decrement and low temperature sensitivity [3,4]. Such improvements in device operation are attributed to the enhanced quantum efficiency of the device. The nanoscale III-nitrides were also observed to show interesting physical phenomena such as biexcitonic transition [5] which has been proposed as a potential optical transition for achieving quantum dot lasers.

Meanwhile, most of the GaN (or InGaN) dots were grown by metalorganic vapor phase epitaxy (MOVPE) [6,7] or molecular beam epitaxy (MBE) [8,9]. Few reports have focused on the preparation of GaN dots by the alternate supply approach which has been considered as a promising deposition technique for low-dimensional structures due to the merit of migration enhancement of the adatoms [10,11]. A separation in the admittance of TMG and NH_3 was previously reported to be helpful in depositing high quality GaN films on (0 0 0 1) sapphire substrates and on Si substrates [12]. Accordingly, the implementation of alternate supply of precursors for the growth of GaN

dots is of great interest from practical and academic viewpoints.

In this paper, we report the result of the growth of GaN dots on AlN by alternate supply of TMG and NH_3 under various growth conditions. It was found that a reduced admittance of TMG either by a decrement in TMG flow rate or by a reduction in the number of growth cycle tends to be in favor of forming small-sized GaN dots.

2. Experimental procedures

Growth of GaN dots was conducted by exposing the AlN film-coated (0 0 0 1) sapphire substrate alternatively to TMG and NH_3 fluxes carried by purified H_2 gas in an inductively heated quartz reactor operated at atmospheric pressure. The manner of introducing TMG and NH_3 into the reaction chamber has been described elsewhere [12]. In this investigation, various growth parameters including deposition temperature, TMG flow rate, number of growth cycles, and substrate

Fig. 1. 2-D and 3-D AFM images of GaN dots prepared on 0.3 μm thick AlN underlayers at 950 $^{\circ}\text{C}$ with the TMG admittances being 0.045 μmol (a and b), 0.09 μmol (c and d) and 0.54 μmol (e and f).

rotation speed per growth cycle were proposed to investigate the influence of the growth conditions on the size and distribution of the GaN dots. Typically, the TMG and NH_3 flow rates were controlled in a range of 4.80–38.39 $\mu\text{mol}/\text{min}$ and 0.2 mol/min, respectively. (0 0 0 1) Sapphire substrates were solvent-cleaned first, followed by hot etched in an $\text{HCl}/\text{H}_3\text{PO}_4$ (3:1) solution for 5 min, rinsed with deionized water, and blow-dried with N_2 gas before loading. The (0 0 0 1) sapphire substrate was deposited with a low temperature (LT)-AlN buffer layer first, followed by the growth of a 0.3 μm thick AlN underlayer at 1050 $^\circ\text{C}$ with a final deposition of GaN dots at a temperature range of 900–1050 $^\circ\text{C}$. The substrate rotation speed per growth cycle in this study was controlled to be in the range of 2.4–3.0 s.

As grown GaN dots were characterized by a Digital Instrument (DI) NS4 scanning probe microscope (SPM) operated under AFM mode to reveal their size and distribution. The luminescent properties of GaN dots were investigated by RT CL measurements using a JEOL/JSM6500 scanning electron microscope (SEM) under an acceleration voltage of 5 kV and the temperature-dependent PL studies using the 266 nm excitation of a diode pumped laser.

3. Results and discussion

Fig. 1(a–f) is the 2-D and 3-D AFM images, 3 $\mu\text{m} \times 3 \mu\text{m}$ in scanning area, showing the surface morphologies of GaN dots prepared on 0.3 μm thick AlN underlayers at 950 $^\circ\text{C}$ with different TMG admittances. In this case, Fig. 1 represents the surface morphologies of GaN dots with the TMG admittances being 0.045 μmol (a and b), 0.09 μmol (c and d) and 0.54 μmol (e and f). The estimation of TMG admittance is based on the TMG flow rate and the exposure time of substrate to TMG flux. The AFM image of GaN dots exhibits a close-packed dot arrangement rather than the discrete dot arrangement [13]. The discrete GaN dots were previously reported to be grown on AlN at reduced temperatures and were considered as the consequence of Stranski-Krastanov (S-K) growth in which a strained two-dimensional wetting layer is formed first followed by a three-dimensional growth [13]. It is believed that surplus TMG admittance and elevated growth temperature

Fig. 2. Plots of (a) GaN dot size and (b) GaN dot density as functions of TMG admittance.

may have resulted in the close-packed configuration of GaN dots in this study.

The result of AFM observations also reveals the effect of TMG admittance on the dimension of GaN dots. Fig. 2(a and b) shows plots of GaN dot size and GaN dot density as functions of TMG admittance, respectively. As shown in Fig. 2(a), the diameter and height of GaN dots appear to ramp up with the TMG admittance. An average GaN dot diameter of ~ 51 nm can be prepared at 950 $^\circ\text{C}$ with TMG admittance being 0.045 μmol . In this case, a 0.045 μmol of TMG admittance can be achieved by a two-growth-cycle deposition under a TMG flow rate of 4.8 $\mu\text{mol}/\text{min}$. It is evident that decrement of the TMG admittance is in favor of forming GaN dots with small diameter and reduced height. The GaN dot density was also found to be affected by TMG admittance. As shown in Fig. 2(b), GaN dot density reduces considerably from $2.4 \times 10^{10} \text{ cm}^{-2}$ to

Fig. 3. AFM images of GaN dots prepared on 0.3 μm thick AlN underlayers at (a) 900 $^{\circ}\text{C}$ and (b) 1000 $^{\circ}\text{C}$ with a TMG flow rate of 9.6 $\mu\text{mol}/\text{min}$ and at (c) 950 $^{\circ}\text{C}$ and (d) 1050 $^{\circ}\text{C}$ with a TMG flow rate of 38.39 $\mu\text{mol}/\text{min}$.

$1.1 \times 10^{10} \text{ cm}^{-2}$ when TMG admittance increases. The reduction in GaN dot density is attributed to the growth of GaN dots and the coalescence of the nearby GaN dots into bigger ones at elevated temperatures.

The influence of growth temperature on the size and density of GaN dots was also found to be prominent in this work. Fig. 3(a–d) shows the AFM images of GaN dots, $3 \mu\text{m} \times 3 \mu\text{m}$ in scanning area, prepared on 0.3 μm thick AlN underlayers at different growth temperatures. In this case, Fig. 3(a and b) represents the surface morphologies of GaN dots prepared at 900 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$, respectively, with a TMG flow rate of 9.6 $\mu\text{mol}/\text{min}$ under a substrate rotation speed of 3 s per growth cycle. Fig. 3(c and d) shows the surface morphologies of GaN dots prepared at 950 $^{\circ}\text{C}$ and 1050 $^{\circ}\text{C}$, respectively, with a TMG flow rate of 38.39 $\mu\text{mol}/\text{min}$ under a substrate rotation speed of 3 s per growth cycle. It appears that the average diameter of GaN dots shows strong depen-

dence on the deposition temperature. In addition, the GaN dot density was also observed to decrease considerably when the growth temperature increases. The nature of temperature-dependence of GaN dot size and GaN dot density has previously been reported in the GaN dots prepared by MBE [13] and MOCVD [14] techniques. It is believed that the surface diffusion velocities of the Ga adatoms on the grown surface are greatly enhanced at elevated growth temperatures. In this way, GaN dots having smaller sizes tend to coalesce into bigger ones at high deposition temperature, and the coalescence of GaN dots also enable the reduction of GaN dot density.

In this investigation, various TMG admittances were also proposed by changing the substrate rotation speed to reveal the influence of TMG admittance on the morphology of GaN dots. However, AFM observations show that an increment of substrate rotation speed tends to form GaN dots with poor

Fig. 4. RT CL spectrum of the GaN dot having an average dot diameter and an average dot height of 51 nm and 15 nm, respectively.

morphology and uniformity. The reduction of effective surface migration paths of Ga adatoms caused by the increase of substrate rotation speed is considered to deteriorate the quality of GaN dots.

Fig. 4 shows the RT CL spectrum of GaN dots having an average dot diameter and an average dot height of 51 nm and 15 nm, respectively. In this spectrum, a dominant emission peak at 3.735 eV was observed. The quantum confinement effect of GaN dots is clearly demonstrated by this emission which shows a much higher emission energy than the bandgap energy of a bulk GaN. It is not clear at this point why GaN dots having an average diameter of 51 nm and an average height of 15 nm also exhibit such a remarkable quantum confinement effect. However, the close-packed nature of the GaN dots, in this study, could generate a large number of close contact areas between adjacent GaN dots. Previous report indicates that the surface diffusion length of Ga in GaN is of the order of ~ 0.7 nm at 950°C [15]. In current investigation, at a growth temperature of 950°C , the surface diffusion of Ga could possibly enable the formation of localized GaN necking areas having dimensions of 1–2 nm [16] because of the coalescence of adjacent GaN dots. Thus, the large blue shift of 0.3 eV above the band gap energy of a bulk GaN observed in the RT CL spectrum of this study is tentatively attributed to the quantum confinement effect at GaN necking areas. More works are required to elucidate this issue.

Temperature-dependent PL measurements of the GaN dots were also performed in this study. Fig. 5(a

Fig. 5. (a) Temperature-dependent PL spectra of the GaN dots measured at a temperature range of 10–110 K and (b) a plot of GaN dot PL emission energy versus measurement temperature.

and b) shows the PL spectra of the GaN dots measured at reduced temperatures of 10–110 K and a plot of the PL emission energy of GaN dots versus measurement temperature. In this case, the diameter and height of GaN dots are the same as those described in Fig. 4. It appears that a decrement in the measurement temperature tends to result in a blue shift of the PL emission energy of the GaN dots. As shown in Fig. 5(b), the PL emission energy of the GaN dots shifts from a value of 3.924 eV at 110 K to a value of 3.974 eV at 10 K. Over the temperature range of 300 to 10 K, the result of luminescent characterization of GaN dots in this study indicates that the blue shift in PL emission energy of GaN dots is ~ 240 meV which is much larger than the blue shift in the near band edge PL emission energy of a bulk GaN (~ 60 meV). It is believed that temperature change tends to induce larger variations of atomic spacings inside a nanoscaled GaN

dot than that inside a bulk GaN. Accordingly, the effect of measurement temperature on the PL emission energy of GaN dots is stronger than that on the near band-edge PL emission energy of a bulk GaN. This explains the prominent influence of PL measurement temperature on the blue shift of the emission of GaN dots.

4. Conclusions

We report the influence of growth parameters on the characteristics of GaN dots deposited on AlN by alternate supply of TMG and NH_3 . Based upon the AFM observations, GaN dot diameter and density were found to be affected considerably by various growth parameters including deposition temperature, TMG flow rate, number of growth cycles, and substrate rotation speed per growth cycle. RT CL measurements of the GaN dots having 51 nm in dot diameter and 15 nm in dot height show a dominant emission peak at 3.735 eV. Temperature-dependent PL data show that apparent blue shift in the emission of GaN dots occurs when temperature decreases.

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