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Effect of N_2 flow rate on growth and photoluminescence properties of GaN nanorods grown by using molecular beam epitaxy

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We have studied the effect of N_2 flow rate on the structural and optical properties of GaN nanorods grown on (111) Si substrates by radio-frequency plasma-assisted molecular-beam epitaxy. The hexagonal shape nanorods with lateral diameters from 80 to 190 nm with increasing N_2 flow rate from 1.1 to 2.0 sccm are obtained. However, the ratio of length (thickness) and compact region increases with increasing N_2 flow rate up to 1.7 sccm and then saturate. From the photoluminescence, free exciton transition is clearly observed for GaN nanorods with low N_2 flow rate. And the PL peak energies are blue-shifted with decreasing diameter of the GaN nanorods due to size effect. Temperature-dependent photoluminescence spectra for the nanorods with N_2 flow rate of 1.7 sccm show an abnormal behavior like “S-shape” with increasing temperature.

Ⅰ. Introduction

One-dimensional structures (nanowires or nanorods) of nanometer-scale gallium nitride are known to have great prospects in fundamental physical science and novel technological applications [1,2]. Because of the large band gap and structural confinements of nano structures, for example, the fabrication of visible and UV optoelectronic devices with relatively low power consumption is potentially feasible [3,4]. These studies mainly focused on zero-dimensional quantum dot and two-dimensional quantum well structures, while investigation of one dimensional structure nanometer-scale GaN could enable unique opportunities in understanding fundamental concepts underlying the observed electronic, optical, and mechanical properties of materials. Semiconductor quantum wires can confine excitons as in quantum dots and also exhibit other interesting phenomena, such as exciton diffusion. Recently, it is reported that dislocation-and strain-free GaN materials can be obtained by forming nano-scale structures, such as columnar structures [5,6] and pyramidal hillocks [7]. For the past several years considerable effort has been placed on the synthesis of nanowires using laser ablation [8], template synthesis and catalytic synthesis of GaN nanorods[9], sublimation of GaN powder under a flowing ammonia atmosphere [10], and direct reaction of metal Ga vapor with flowing ammonia [11]. Among them, the recent development of self-assembled nanorods formed on silicon [12,13] and sapphire [12,14] substrates at an unprecedented pace makes them promising due to their extremely high quality and relatively easy size controllability.

In this study, we report the effect of N_2 flow rate on growth and optical properties of self-assembled GaN nanorods formed on Si(111) substrates grown by radio-frequency (rf) plasma assisted molecular beam epitaxy (PAMBE). Field emission high resolution

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scanning electron microscopy (HRSEM) was adapted to study the formation and structural properties of the nanorods. In order to study the optical properties of the GaN nanorods, we carried out temperature-dependent photoluminescence (PL) measurements.

Ⅱ. Experiments

The samples used in this study were grown on Si (111) substrates without any buffer layer by using rf-PAMBE. The Si substrates were degreased and etched with HF. A reconstructed (7×7) reflection high energy electron diffraction (RHEED) pattern was obtained for the Si substrate after thermal treatment for 30 min at 1000℃. After deoxidation the temperature was decreased to 900℃ and GaN nanorods were deposited for 3 hours. All GaN nanorods were grown at the same temperature under different III/V ratios. We have already reported the growth condition of the GaN nanorods by varying Ga flux and growth time with a fixed N_2 flow rate [15,16]. The rf-plasma power was kept constant at 350 W during the growth. The Ga flux was fixed and nitrogen flow rates were varied from 1.1 to 2 sccm. All the procedures were carried out under N-rich conditions. The formation of the GaN nanorod was confirmed by high- resolution field emission scanning electron microscope (FESEM). The optical properties were studied by temperature-dependent photoluminescence (PL) measurements. The 325-nm line of a He-Cd laser was used as an excitation light source for the PL measurement.

Ⅲ. Results and discussion

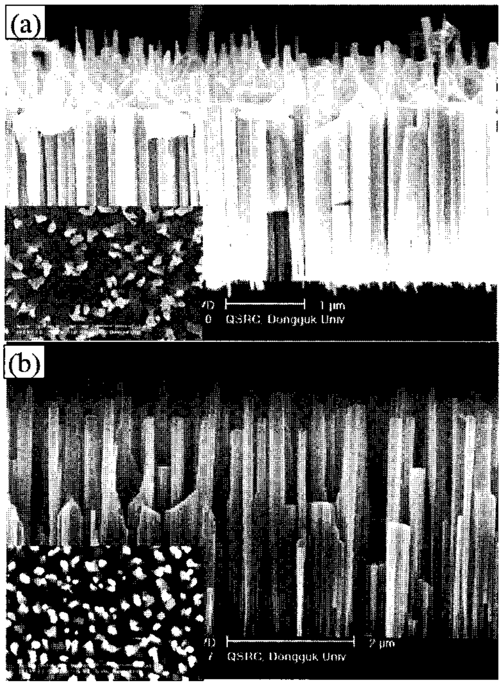

Figure 1. FESEM micrograph images of GaN nanorods grown on Si(111) substrates with different N_2 flow rate; (a) 1.1 sccm and (b) 1.7 sccm. The insets of each figure present the plan- view images and all the scale bars are 1μm.

Figure 1(a) and (b) show the cross-sectional HRSEM images for the GaN nanorods with N_2 flow rate of 1.1 and 1.7 sccm, respectively. These nanorods are aligned along the (0001) direction. As shown these figure, the nanorods were formed by two layers, that is, one is nanorods and the other is compact region. In the case of low N_2 flow rate, the compact region becomes more dominant than the nanorod region. The insets show top views of the nanorods. The average diameter and density of the hexagonal GaN nanorods vary from 80 to 190 nm and 3.0×10^{8} cm^{-2} to 7.8×10^{8} cm^{-2} respectively.

Figure 2(a) represents the summarized results of diameter and density of the GaN nanorods as a function of N_2 flow rate. The diameter and density are linearly increased with the increasing N_2 flow rate. If the N_2 flow rate increases more, the nanorods and compact region will be merged like the epitaxy layer. Figure 2(b) shows the summarized results of the length (thickness) for the nanorods and the compact region. With increasing N_2 flow rate, the length of nanorods slightly increases, while the that of compact region slightly decreases. Inset shows the ratio of the nanorod and compact region. When the N_2

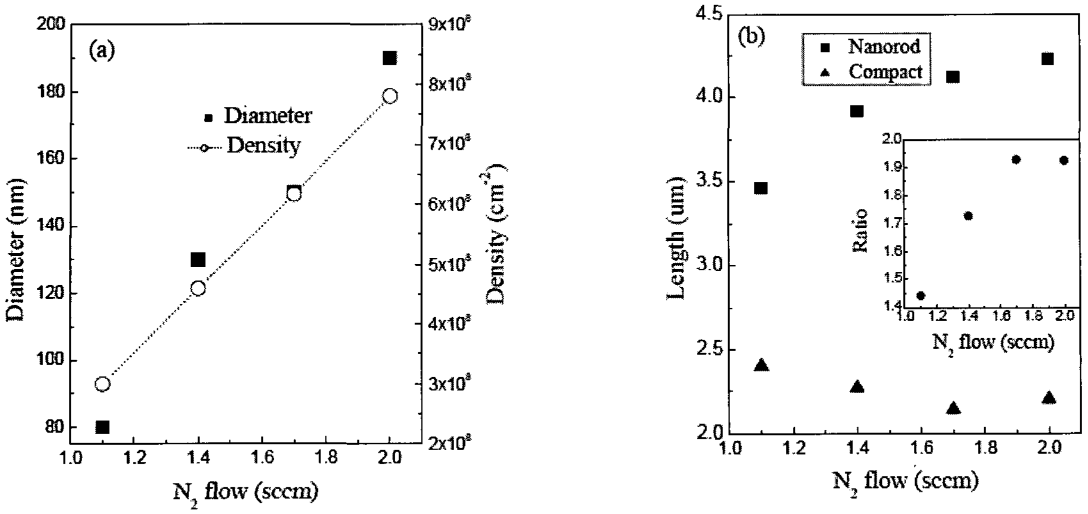

Figure 2. (a) Average diameter and density of nanorods as a function of N_2 flow rate. (b) The average length of nanorods and compact region. Inset shows the ratio of the nanorods and compact region.

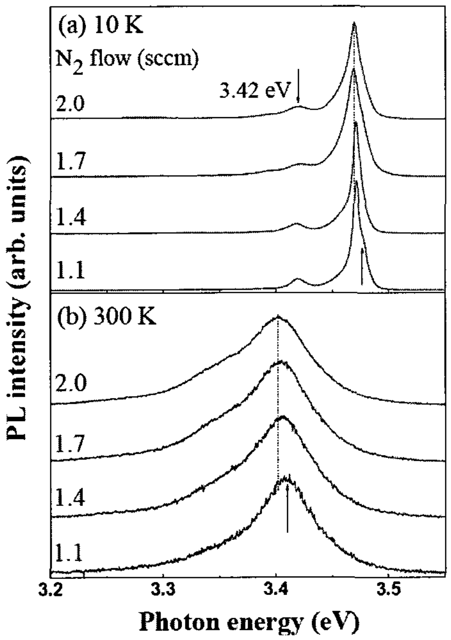

Figure 3. Photoluminescence spectra of the nanorods with different N_2 flow rate (a) 10 K and (b) 300 K.

flow rate reachs 1.7 sccm, the ratio of the nanorod and compact region becomes constant.

Figure 3(a) and (b) show the PL spectra of GaN nanorods with different N_2 flow rate at 10K and 300K, respectively. An emission line around 3.478 eV at the high energy side, strong emission line near 3.47 eV, and weak emission line around 3.42 eV are observed at 10K. The PL peak positions of the main emission line (3.47 eV) is assigned to donor bound exciton (denoted as D^0X or I_2). The full width at half maximum (FWHM) is less than 10 meV, which indicates high quality GaN nanorods. The FWHMs of the main emission line are narrowed with decreasing N_2 flow rate. And the emission line near 3.478 eV corresponds to free exciton (FX). With decreasing N_2 flow rate, the FX emission line more is clearly showed, that is, when the N_2 flow rate is 1.1 sccm, an additional peak appears at a high energy of 3.47 eV. However, all the peaks are strongly overlapped. In order to obtain the peak position and intensity accurately, we have reconstructed the spectrum by using a Gauss- Lorentzian line shape function and a multi peak analysis was done (not shown here). From the PL spectra, the peak positions are blue-shifted with decreasing diameter of the GaN nanorod. These results show clearly strong radial confinement of excitons in the nanorods. These observations are consistent with the quantum confinement effect in the one-dimensional nanorods [17]. Though the smallest diameter of ~80 nm is still larger to compared with Bohr radius, the quantum confinement effect could be occurred in the diameter of less ~140

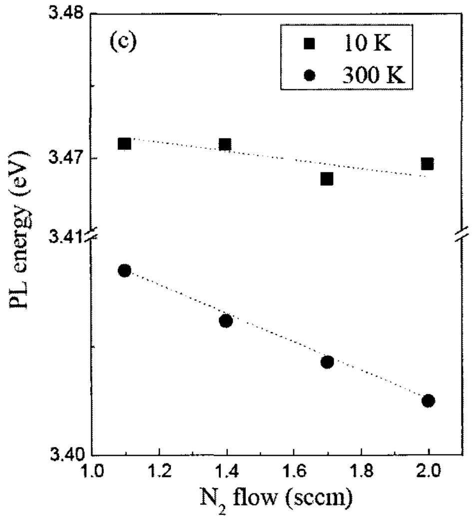

Figure 4. Photoluminescence position for the donor bound exciton (D^0X) at 10 K and free exciton (FX) at 300 K.

nm [16]. The PL peak position of the emission about 3.42 eV comes from structural defects at the column/substrate interface and the values agree well with the reported values by Calleja et al [18].

The peak positions of the main emission lines at 10 and 300K are represented to Fig. 4. The peak positions of the main emission line related to D^0X at 10K are almost independent of samples with maximum energy difference of only 1.5 meV. In the case of FX transition, however, the maximum energy differences at 10K and 300K are about 8 meV and 6 meV, respectively. This means that the size of nanorods affects the PL transition.

Figure 5(a) and (b) show temperature-dependent PL spectra of the nanorods taken from 10 to 300K with samples of N_2 flow of 1.1 and 1.7 sccm, respectively. The peak intensity- and position- variation of the FX and the D^0X emission line are clearly shown with increasing temperature. And the intensity of FX peak relative to D^0X peak changes as the temperature increases. The intensity of the D^0X peak decreases abruptly, while that of the FX peak decreases slowly. In the case of sample with N_2 flow rate of 1.7 sccm, in particular, the temperature-dependence PL spectra show abnormal properties like the "S-shape" behavior in the peak position with increasing temperature. As shown in Fig. 5(b), the peak position shows sequential red-shift, blue-shift, and red-shift with increasing temperature. With increasing temperature up to 150K an initial dramatic decrease (44.3 meV) in PL peak energy was observed. Then the PL peak energy was almost constant or slightly blue-shift in the temperature range of 150~250K.

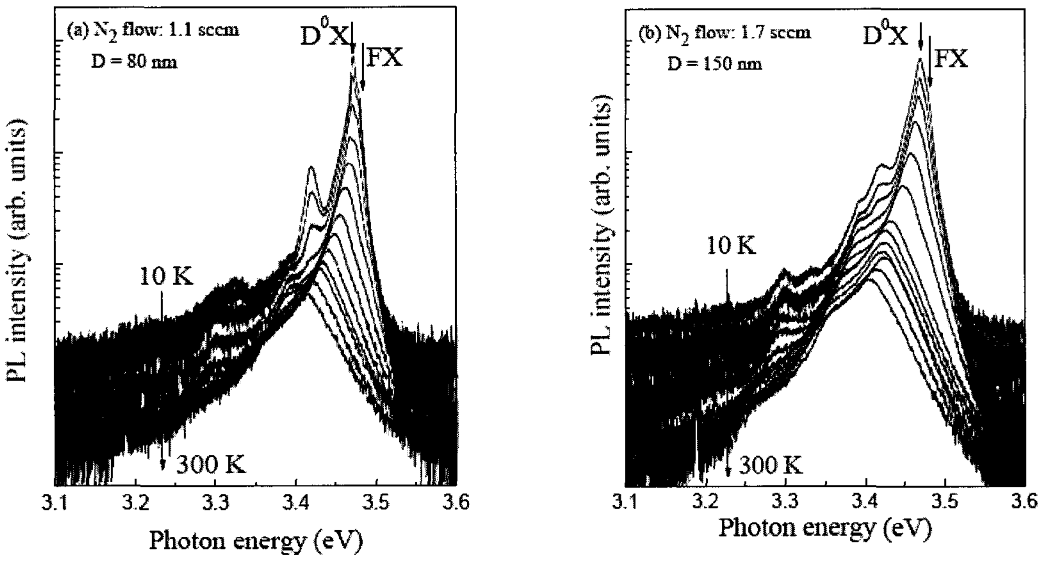

Figure 5. Temperature-dependent photoluminescence spectra of the GaN nanorods with different N_2 flow rate (a) 1.1 sccm and (b) 1.7 sccm.

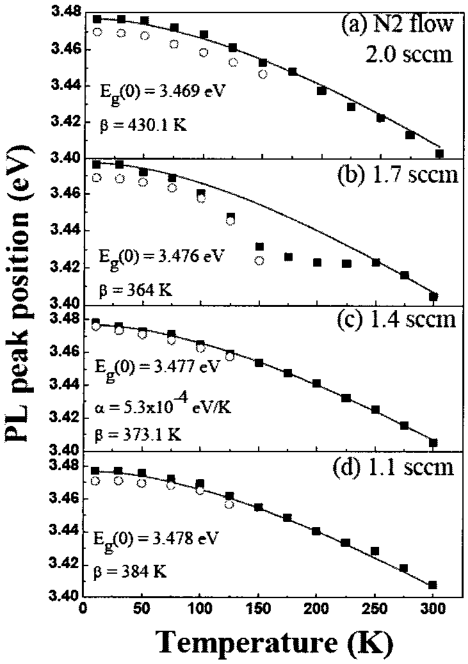

Figure 6. PL peak position of the free excitonic transition with different diameters. The solid lines are the least-square fitted curves following the Varshni's equation for the variation of the band gap as a function of temperature.

Finally, PL peak energy decrease again with increasing temperature above 250K. A similar behavior has been reported previously for the temperature-dependent PL emission energy shift in III-nitride ternary or quantum well system such as $Al_xGa_{1-x}N$ alloys [19], and InGaN/GaN multiquantum wells [20]. However, there is big difference in the behavior in that in the present work the fitted lines agree well with the measured data point in the low temperature region, while deviations are present in Ref [19,20].

Figure 6(a)~(d) show the peak positions for the D^0X and FX emission line of GaN nanorods as a function of temperature with N_2 flow rate of 1.1, 1.4, 1.7, and 2.0 sccm, respectively. The D^0X emission lines for the all samples are almost disappeared above ~150K. It is well known that the temperature-dependent energy gap follows Varshni's equation, $E_g(T)=E_g(0)-\alpha T^2/(\beta+T)$, where $E_g(T)$ is the transition energy at temperature T, $E_g(0)$ the corresponding energy at 0K, and α and β are known as Varshni's thermal coefficients and Debye temperature, respectively [21]. The best fitted values are $\alpha=5.3\times10^{-4}$ eV/K and β = 373.1K for the sample with N_2 flow rate of 1.4 sccm. These values are close to the reported ones for the free exciton transition [22]. The solid lines in Fig. 6 are obtained by least-square fitting. One of the fitting parameters, α, is fixed as 5.3×10^{-4} eV/K because the thermal coefficient should have the same values for the same material grown under the same conditions. For the sample with N_2 flow rate of 1.7 sccm, the Debye temperatures are almost the same for all samples, while the sample with N_2 flow rate of 2.0 sccm has different value (430.1K) compared to the other three samples. In this sample, a weak "S-shape" behaviors was observed. This tendency does not follow the typical temperature dependence of the energy gap transition. In the case that the diameter was below 130 nm, however, this "S-shape" behavior was not observed.

Ⅳ. Conclusions

In conclusion, we have investigated the effect of N_2 flow rate on the structural and optical properties of GaN nanorods grown on (111) Si substrates by radio-frequency plasma-assisted molecular-beam epitaxy. The diameter of hexagonal shape nanorods was varied from 80 to 190 nm with increasing N_2 flow rate from 1.1 to 2.0 sccm. From the photoluminescence, free exciton transition is clearly observed for GaN nanorods with low N_2 flow rate (small diameter of about 80 nm). And the PL peak energies are blue-shifted with decreasing diameter of the GaN nanorods due to size effect. And Temperature-dependent photoluminescence spectra for the nanorods with N_2 flow rate of 1.7 sccm show an abnormal behavior like "S-shape"with increasing temperature.

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분자선 에피택시를 이용하여 GaN 나노로드를 성장시 구조 및 광학적인 특성에 미치는 N_2의 양의 효과

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rf 플라즈마 소스가 장착된 분자선 에피택시 장비를 이용하여 Si(111) 기판위에 GaN 나노로드를 성장할 때, N2의 흐름양을 조절하여 나노로드의 구조 및 광학적인 특성을 조사하였다. N_2의 양이 1.1sccm에서 2.0sccm으로 변할 때 육각형 모양의 나노로드가 성장되었으며, 평균 직경이 80nm에서 190nm 까지 변화 하였다. 그러나 나노로드와 compact한 영역의 길이 (두께) 비는 N_2의 양이 1.7sccm 까지는 증가하지만 그 이상에서는 변화지 않았다. PL 측정으로부터, N_2의 양이 적은 나노로드에서 자유 엑시톤의 피이크가 더욱 뚜렷하게 관측되었고, 모든 PL 피이크의 위치는 직경이 적을수록 나노로드의 크기 효과에 의해서 고에너지 쪽으로 이동하였다. N_2의 양이 1.7sccm 인 시료에서는 온도에 따른 PL의 피이크의 위치가 온도가 증가함에 따라서 “S-형”의 거동을 나타내었다.

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