AIP Applied Physics Letters

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Citation: Applied Physics Letters **89**, 043124 (2006); doi: 10.1063/1.2243710
View online: http://dx.doi.org/10.1063/1.2243710
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/4?ver=pdfcov
Published by the AIP Publishing

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(Received 12 April 2006; accepted 6 July 2006; published online 28 July 2006)

The authors report on time-integrated and time-resolved photoluminescence (PL) of GaN nanowires grown by the Ni-catalyst-assisted vapor-liquid-solid method. From PL spectra of Ni-catalyzed GaN nanowires at 10 K, several PL peaks were observed at 3.472, 3.437, and 3.266 eV, respectively. PL peaks at 3.472 and 3.266 eV are attributed to neutral-donor-bound excitons and donor-acceptor pair, respectively. Furthermore, according to the results from temperature-dependent and time-resolved PL measurements, the origin of the PL peak at 3.437 eV is also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2243710]

One-dimensional GaN nanostructures including nanowires, nanorods, and nanotubes have recently attracted much attention because of their potential applications for optoelectronic devices in the nanoscale.[1,2] GaN nanowires have been synthesized by many different nanowire growth methods.[3–6] Among numerous nanowire synthesis methods, the metal catalyst-assisted vapor-liquid-solid (VLS) growth method has been widely employed because this technique offers easy and size-controllable growth of many semiconductor nanowires. However, since the metal catalysts used for nanowire growth may act as impurities in the nanomaterial and even a small amount of impurities in semiconductors can significantly change physical properties of the host materials, it is very important to characterize the impurities and defects in catalyst-assisted grown semiconductor nanomaterials. The effect of impurities and defects on the physical properties of host materials is also expected to increase with a reduction in the size of the materials. In addition, the unintentionally doped impurities in semiconductors make it difficult to accurately control their conductivities and optical properties. Nevertheless, the defect characterization of catalyst-assisted grown semiconductor nanowires has rarely been reported because of difficulties in elemental analysis and electrical device fabrications.[7] Meanwhile, optical characterization methods such as photoluminescence (PL) spectroscopy requiring no physical contacts are useful for defect characterization of the nanomaterials.[8] In particular, low temperature PL spectroscopy is a very sensitive and nondestructive tool for characterizing radiative defects in semiconductors.[9] Although a few papers on synthesis and PL spectra of GaN nanowires have previously been reported,[10] near-band-edge (NBE) PL peak positions from catalyst-assisted grown GaN nanowires have not been consistent with those of epitaxial thin films.[5,6] Furthermore, time-resolved PL (TRPL) spectroscopy enables the investigation of exciton lifetime, an important parameter related to defects in materials and device performance. Despite the importance of TRPL measurements, TRPL behavior in GaN nanowires has rarely been reported.[11] In this letter, we report on both time-integrated and time-resolved photoluminescent properties of GaN nanowires grown by the Ni-catalyst-assisted VLS method.

GaN nanowires were grown on a 2-nm-thick Ni layer coated $Al_2O_3(1-102)$ substrates using a low pressure metal-organic vapor phase epitaxy (MOVPE) system. For GaN nanowire growth, trimethyl–gallium (TMGa) and ammonia (NH_3) were employed as reactants and hydrogen was used as a carrier gas. Prior to GaN nanowire growth, a 2-nm-thick Ni layer was deposited on the *r*-sapphire substrates using a high vacuum e-beam evaporator, and susbsequently annealed at 800 °C for 10 min under 100 Torr in order to form Ni droplets which were used as catalytic sites for nanowire growth. During GaN nanowire growth, typical TMGa and NH_3 flow rates were 3.5 and 300 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The growth temperature was in the range of 750–850 °C.

Both time-integrated and time-resolved PL spectra of the GaN nanowires were measured in order to investigate optical properties of the nanowires and radiative recombination related to defects in the nanomaterials. The time-integrated PL (TIPL) measurements were performed at various temperatures in the range of 10–300 K with the 325 nm line of a continuous wave He–Cd laser used as an excitation source. Details of the TIPL measurements have previously been reported elsewhere.[9,12] Meanwhile, a TRPL measurement system consists of a femtosecond Ti:sapphire oscillator, a frequency tripler, and a time correlated single photon counting system employing a microchannel plate photomultiplier tube. The excitation source for TRPL measurements was a femtosecond Ti:sapphire laser laser pumped by a diode pumped neodymium-doped yttrium orthovaradate vanadate laser. The Ti:sapphire laser can provide 100 fs pulses at a repetition

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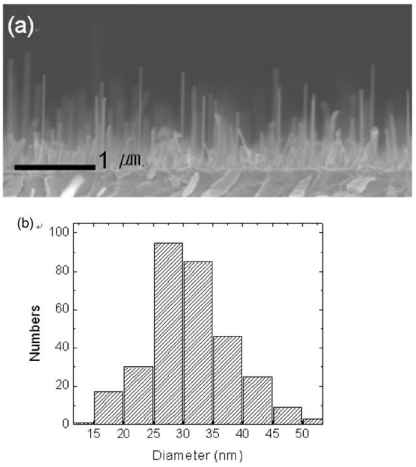

FIG. 1. (a) Scanning electron microscopic image of GaN nanowires grown on *r*-plane sapphire substrates and (b) histogram of GaN nanowire diameters. The electron microscopic image shows that GaN nanowires with a typical mean diameter (30±10 nm) of GaN nanowires are vertically aligned on the *r*-sapphire substrate.

rate of 82 MHz. Output of the femtosecond Ti:sapphire laser (Tsunami, Spectra-Physics) at 800 nm was tripled to 266 nm to serve as an excitation source for the TRPL experiments. The PL signal was confocally collected and TRPL was measured by a time correlated single photon counting system, which provides sub-10 ps time resolution with deconvolution. The resolution of TRPL spectra was 0.1 meV. All TRPL measurements in this study were carried out at 10 K.

Field emission scanning electron microscopy revealed the general morphology of GaN nanowires. Figure 1(a) clearly shows that GaN nanowires were vertically grown on *r*-plane sapphire substrates. The mean diameter of GaN nanowires was 30±10 nm and nanowire length showed wide distribution in the range of 800±300 nm, as shown in Fig. 1(b). A typical nanowire density was $1.5\times10^9/\mathrm{cm}^2$.

Defect-related NBE emissions from the GaN nanowires were investigated using low temperature PL spectroscopy. As shown in Fig. 2, a typical 10 K PL spectrum of Ni-catalyzed GaN nanowires exhibited a strong ultraviolet emission while the deep level emission at 2.2–2.5 eV, related to structural defects or impurities, was too weak to be observed. Although previous reports on PL spectra of GaN nanowires grown by catalyst-assisted methods did not show well-resolved PL peaks in NBE emission spectra,[3–6,10] the NBE emission in

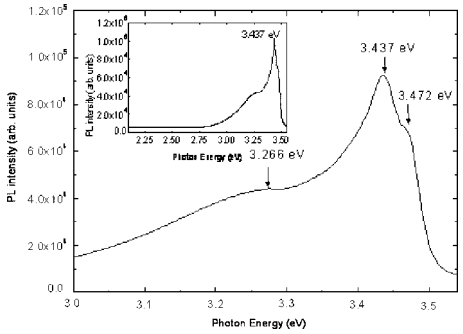

FIG. 2. TIPL spectra of Ni-catalyzed GaN nanowires at 10 K. The NBE emission was clearly resolved into three PL peaks at 3.472, 3.437, and 3.266 eV, respectively. Each dominant PL peak at 3.472 and 3.266 eV is tentatively attributed to the neutral-donor-bound excitons (I_2) and the donor-acceptor pair (DAP) recombination, respectively. The inset shows that the deep level emission is too weak to be observed.

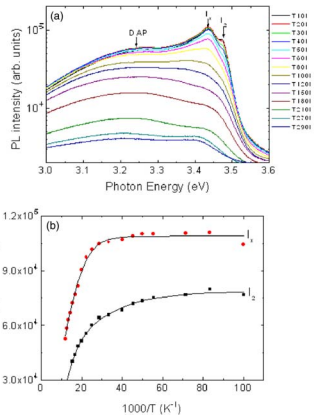

FIG. 3. (Color online) (a) Temperature-dependent TIPL spectra at various temperatures in the range of 10 K and room temperature and (b) the Arrhenius plot of the emission intensities at 3.472 and 3.437 eV under various temperatures. The emission intensities of NBE emission peaks decreased with increasing temperature, showing thermal quenching effect. From the relationship between emission integrated intensity and temperature, the ionization energies of the bound excitons were estimated to be 5.1 and 17.1 meV for the PL peaks at 3.472 and 3.437 eV, respectively.

Fig. 2 was clearly resolved into three PL peaks at 3.472, 3.437, and 3.266 eV. The PL peaks at 3.472 and 3.266 eV have previously been observed for many bulk GaN materials, attributed to neutral-donor-bound exciton (I_2) and donor-acceptor-pair (DAP) transition, respectively.[13–15]

It is also notable that the dominant emission of our GaN nanowires grown by Ni-catalyst-assisted MOVPE was observed at 3.437 eV with additional peaks at 3.472 and 3.266 eV although the dominant emission peak of GaN nanowires previously grown by other groups has previously been observed at 3.2–3.35 eV.[3–6,8] As mentioned above, the PL peaks at 3.472 and 3.266 eV are commonly observed from many epitaxial films grown by MOVPE, associated with defects presumably due to the same growth process. Meanwhile, the new PL peak at 3.437 eV is not well known for epitaxial GaN films, so it may result from Ni-related defects. No report has been made about the PL peak at 3.437 eV for high quality GaN bulk materials. Only a PL peak at 3.41 eV has been observed and tentatively attributed to strongly, localized excitons in structural defects, such as stacking faults or screw dislocations,[16] and a PL peak at 3.44 eV to neutral acceptor-bound excitons.[17,18] Since the GaN nanowires prepared in this study have not shown dislocations or stacking faults, similar to the previous report,[6,10] the PL peak at 3.437 eV is expected to result from strongly localized excitons, presumably neutral acceptor-bound excitons.

The PL peaks tentatively assigned to excitonic emissions were investigated by temperature-dependent PL and time-resolved PL measurements. As shown in Fig. 3(a), I_2 and I_x peak intensities decrease with increasing temperature and the peaks disappeared around 50 and 100 K, respectively. This thermal quenching can be explained in terms of the decomposition of bound excitons to free excitons. However, the thermal quenching rates of I_2, I_x, and DAP emission were different from each other because of different exciton ionization energies. The exciton ionization energies of I_2 and I_x of Ni-catalyzed GaN nanowires were determined by the Arrhenius plot of integrated PL intensities of the I_2 and I_x, that is, the following equation:[13]

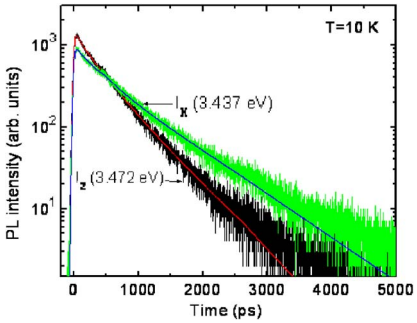

FIG. 4. (Color online) TRPL spectra of Ni-catalyzed GaN nanowires at 10 K. Each decay profile was measured at 3.472 and 3.437 eV, respectively. All decay profiles fitted well with a double exponential decay curve.

$$I = \frac{I_o}{1 + A\exp(-E_{\mathrm{fx}}/k_B T) + B\exp(-E_{\mathrm{bx}}/k_B T)},$$

where E_{fx} and E_{bx} are the ionization energy of the free exciton and the bound exciton in GaN, respectively, and A and B are coefficients. In Fig. 3(b), the solid lines are the least-square-fits to their variations. From the fits, the E_{fx} and the E_{bx} for 3.472 eV peak are determined to be 28.3 and 5.1 meV, respectively. For I_2, E_{bx} of GaN nanowires is slightly smaller than that of undoped GaN epitaxial films, 6.2 ± 1.1 meV.[18] Meanwhile, from the I_x fit, the E_{fx} and the E_{bx} for 3.437 eV peak are estimated to be 27.2 and 17.1 meV, respectively. The E_{bx} for I_x is larger than that (11 meV) of exciton bound to Mg and smaller than that (22 meV) of exciton bound to Zn.[19]

TRPL of Ni-catalyzed GaN nanowires were measured to investigate dynamics of bound excitons in GaN nanowires. Figure 4 shows the TRPL data obtained at 3.469 and 3.437 eV, which correspond to I_2 and I_x, respectively. All observed TRPL data were fitted well with a double exponential decay curve. The double exponential decay suggests that two different decay and capture processes are involved in the emission. The decay time constants of I_2 are estimated to be 197 and 526 ps. For I_x, however, the decay time constants, 252 and 816 ps, were larger than those of I_2. The decay time constants of I_x are similar to those of neutral acceptor-bound exciton in homoepitaxial thin film,[20] 800 ps, and 450 ps for Mg-doped GaN.[21]

According to the TIPL and TRPL measurements of GaN nanowires grown by the Ni-catalyst-assisted VLS method, the origin of I_x emissions should be related to the bound excitons because the I_x emission peak position and the ionization energy of the bound excitons are similar to those of acceptor-bound excitons in GaN bulk materials. This result implies that a large amount of acceptors exist in GaN nanowires. The possible acceptors in Ni-catalyzed GaN nanowires are Ni, Ga vacancy (V_{Ga}), and C. Among these possible acceptors, Ni in the form of $\mathrm{Ni}_{\mathrm{Ga}}^{2+}$ is the most probable acceptor in the GaN nanowires because Ni metal particles were used for the nanowire growth in the MOVPE reactor. So, Ni can exist in the material up to a Ni solubility limit. This is consistent with the previous report that the valence state of Ni in Ni-implanted GaN thin film is +2.[22] Furthermore, several results on transition metal implanted GaN thin film have reported that Ni incorporation enhances hole concentration.[23] Accordingly, Ni may be incorporated into the GaN nanowires and generate an acceptor state. From this point of view, the quantitative analysis of impurities in semiconductor nanowires is very important. Nevertheless, the incorporation of metal catalysts in nanowires during the VLS process has rarely been investigated. Although TEM is a very powerful technique, the limit of TEM elemental analysis is not as good as approximately 1%. Here, we demonstrate that both TIPL and TRPL measurements can be used to characterize the defects in semiconductor nanomaterials.

In summary, we performed both TIPL and TRPL measurements of GaN nanowires grown by a Ni-catalyst-assisted VLS method. Three near-band-edge emission peaks from TIPL spectra of the GaN nanowires were observed at 3.472, 3.437, and 3.266 eV, attributed to the neutral-donor-bound exciton, neutral-acceptor-bound exciton, and donor-acceptor pair peaks. From the temperature-dependent and time-resolved PL measurements, the origin of the acceptors in the GaN nanowires was considered to result from Ni catalyst metals.

This work was financially supported through the National Creative Research Initiative Project by the Korea Science and Engineering Foundations (KOSEF) and LG Electronics Institute of Technology.

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