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Optical properties of functionalized GaN nanowires

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The evolution of the optical properties of GaN nanowires (NWs) with respect to a sequence of surface functionalization processes is reported; from pristine hydroxylated to finally, 3-mercaptopropyltrimethoxysilane (MPTMS) functionalized GaN NWs. Photoluminescence, Raman, stationary, and time-resolved photoluminescence measurements were applied to investigate the GaN NWs with different surface conditions. A documented surface passivation effect of the GaN NWs induced by the MPTMS functionalization is determined based on our characterization results. A hypothesis associated with the surface band bending and the defect levels near the band edges is proposed to explain the observed experimental results. © 2011 American Institute of Physics. [doi:10.1063/1.3552919]

I. INTRODUCTION

Research on semiconductors nanowires (NWs) exposed to surface functionalization has drawn a great amount attention due to the increasing interest in organic/inorganic integrated systems for sensing and energy applications.^{1–3} Among these materials, GaN is a technologically important material for optoelectronic as well as high-temperature and high-power electronic devices because of its favorable optical and electrical properties.⁴ Furthermore, GaN exhibits good chemical stability as well as bio-compatibility, fulfilling the substantial requirements for bio-applications.^{5,6} Meanwhile, NWs possess a large surface-to-volume ratio while maintaining the direct conduction pathway, which is quite unique and can be advantageous as building blocks for next generation devices. As reported earlier, the surface dominates and significantly impacts the photoconductivity,^{7,8} mechanical,⁹ and electromechanical¹⁰ properties of GaN NWs at a scale far beyond the quantum confinement regime. The direct conduction pathway is essential for the NW-based field-effect-transistor sensors as they can serve as both the signal transducer and the transmitter.¹¹ Perhaps owing to the significant amount of surface atoms, the analyte close to the surface of the NWs can serve as an effective gate voltage that alters the depletion width and consequently alters the measured current passing through the NW.

It should be noted that an additional mediator (for example, organosilanes with functional groups) is required for the capabilities of further immobilization and sensing the functional moieties.^{11,12} Interestingly, from a microscopic point of view the mediator interacts strongly with the surface of the semiconductor via covalent bonding.¹³ The surface possesses distinct characteristics compared to the bulklike interiors and consequently alters the exhibiting properties of the semiconductor. A more pronounced effect can be expected

in the NW case which can be rationalized by the significant amount of surface atoms on NWs. However, the interaction of the sensitive surface and the mediator is inadequately addressed in the literature. Therefore, it is of great importance to analyze the effect of mediating molecules on the properties of the GaN NWs.

In this report, we present experimental results of the optical characterization on GaN NWs from the pristine stage followed by a sequence of chemical treatments to achieve MPTMS-GaN NWs. Our results clearly demonstrate surface passivation effects caused by the MPTMS, as revealed from the Raman spectra, stationary photoluminescence (sPL), and time-resolved photoluminescence (TR PL). The surface-sensitive optical properties of the GaN NWs and dual functionalities of MPTMS could be essential to develop a label-free optical sensing platform.¹⁴

II. EXPERIMENTS

The GaN NWs were grown on Ni-precoated Si substrates by a tube-furnace chemical vapor deposition system.¹⁵ The NWs range from 5–10 μm in length and are 25–130 nm in diameter. The axial orientation of the GaNNWs is [100] which is perpendicular to the polar surface of the hexagonal GaN crystals. For the surface hydroxylation process, the pristine GaN NWs sample was immersed in a water solution containing 0.52 M nitric acid and 0.12 M sulfuric acid at room temperature for one hour. The MPTMS-functionalization of the GaN NWs is achieved by immersing the hydroxylated GaN NWs samples into a methanol solution containing MPTMS with different concentrations for an additional 1 h. The concentrations of MPTMS employed in this report are 0.357 M, 0.714 M, and 1.171 M.

Both room temperature (RT) and low temperature (LT) sPL experiments were done by using a continuous 266 nm laser as the excitation source with a power of 20 mW. The emission was collected and detected by a TRIAX monochromator equipped with a 600 gr/mm grating and a

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liquid-nitrogen-cooled back-thinned charge coupled device. The Raman measurements were done by means of a Horiba LabRAM HR800 system with a He-Ne laser at 632.8 nm for the excitation. The TR PL experiments were excited at 266 nm generated by a frequency tripled Ti-sapphire laser. The pulse width of the excitation is 200 fs and the repetition rate is 75 MHz. The emission was collected and subsequently dispersed by a 0.3 m spectrometer. A streak camera (Hamamatsu Photonics A1976_01) was used to achieve the collected emission with a time resolution of 10 ps.

III. RESULTS AND DISCUSSION

The GaN NWs are 25–130 nm in diameter, allowing us to exclude the contribution from quantum confinement effects if any deviation from the bulk properties is observed. Prior to the functionalization of MPTMS, the pristine GaN NWs were subjected to a hydroxylation process (forming OH-GaN NWs) in order to create more—OH reactive sites for further condensation reaction with MPTMS. Thus, three different types of GaN NWs; pristine GaN NWs, OH-GaN NWs, and MPTMS-GaN NWs, were compared in our experiments. Scanning electron microscopic observations of the pristine [Fig. 1(a)] and post-treated GaN NWs reveal that the GaN NWs are robust and our chemical functionalization processes do not cause visible damage to the GaN NWs. Representative RT-sPL spectra ([Fig. 1(b)] show that only a broad emission band centered about 3.39 eV is observed from all samples. The absence of the yellow band emission (~ 2.2 – 2.5 eV) indicates a small amount of deep-level impurities and defects and suggests good crystalline quality of the studied GaN NWs.¹⁶ For an improved statistical analysis, the emission profiles from seven selected spots were recorded on the studied sample. All measurements were done by measuring the same seven spots before and after the surface treatment of the sample. According to our scanning electron microscope investigations, the spot size of the excitation laser covers approximately 50 NWs in each spot. The mean value and the standard deviation of the peak energy, peak width, and the integrated intensity were estimated from the recorded spectra. This statistical approach provides a general picture of the surface functionalization and minimizes individual features from different NWs. Considering the fact that surface states, carrier concentrations, impurities, and defects can vary in every single NW, the PL can be different from one NW to another NW, causing inhomogeneities in the fine structures.

The RT-sPL of the pristine GaN NWs appears at a lower energy than reported for the free exciton emission in strain-free GaN (~ 3.42 eV).¹⁷ This phenomenon implies the existence of lower-energy-level transitions involved in the recombination process and/or surface band bending since both cases will lead to a red-shifted emission peak. The luminescence properties are found to be improved following the sequence of surface treatments described above by showing: (1) a blue-shift of the PL peak [Fig. 2(a)], (2) a reduced emission bandwidth [Fig. 2(b)], and (3) an increased emission intensity [Fig. 2(c)]. Such an improvement in the emission properties justifies a prosperous surface passivation of

FIG. 1. (Color online) (a) Scanning electron microscopy images of pristine GaN NWs used in this study, and (b) representative RT sPL spectra of GaN NWs after different surface treatments.

the GaN NWs. For the OH-GaN NWs, the emission peak energy is blue-shifted and exhibits a smaller standard deviation for the peak energies and the FWHM compared to pristine GaN NWs. The improved homogeneity can be due to the fact that the hydroxylation process modifies the inhomogeneous native surface defects become a more uniform form by covering the surface of the GaN NWs with OH groups. NWs possessing more similar surfaces will give rise to a reduced deviation in the PL properties of this NW population. Further improvement is achieved in the next step of MPTMS-GaN NWs and accordingly indicates a positive outcome of the surface passivation effect induced by MPTMS.

FIG. 2. Statistics of RT-PL results of GaN NWs with different surface conditions. (a) The PL peak energy, (b) the FWHM of the emission band, and (c) the integrated PL intensity normalized to the excitation intensity for different surface modifications. Error bars shown in all graphs are the statistical standard deviations obtained from seven different measured samples.

However, it is intriguing to mention that the results of the MPTMS-GaN NWs at the highest concentration of MPTMS (C_{MPTMS}) are disputable. The emission intensity decreases and the FWHM increases for the highest C_{MPTMS} . These observations imply the coexistence of two counteracting effects induced by the MPTMS-modification: On one hand, the surface-passivation by MPTMS leading to a blue-shift and narrowing of the emission and on the other hand, the MPTMS-coverage behaves like a photon-absorbing layer. Excess MPTMS during the surface-modification process could result in the formation of agglomeration leading to a reversed effect as surface modifier.¹⁸ Photoluminescence excitation (PLE) spectra of MPTMS-GaN NWs shown in Fig. 3 are consistent with the strong absorption band suggested at 4.6–4.8 eV,¹⁹ in which the intensity is corrected with the C_{MPTMS} absorption band.

The Raman spectra (Fig. 4) measured at RT also supports the argument for the surface passivation effect induced by the functionalization of the MPTMS. Raman peaks centered at 556, 567, 665, and 728 cm^{-1} can be clearly observed. Except for the broad band at 665 cm^{-1} , all other peaks are in good agreement with the active Raman modes in the wurtzite GaN crystal and can be indexed to the vibration of $E_1(\text{TO})$, $E_2(\text{high})$, and $A_1(\text{LO})$ modes for 556, 567, and 728 cm^{-1} , respectively.^{20–22} The origin of 665 cm^{-1} may be associated with intricacies since the group theory predicts no Raman active mode around this energy range.^{20–22} The 665 cm^{-1} band is believed to be correlated with the density of defects and is consequently assigned to the disorder-activated Raman scattering (DARS).²² The relative intensity of the DARS and the FWHM of E_2 decrease with the sequence of our experimental process, indicating that the functionalization of MPTMS reduces the density of defect-related disorders and consequently improves the quality of the GaN NWs.

Further PL measurements performed at low temperature on GaN NWs with different surface conditions are shown in Fig. 5. The observed predominant emissions are at 3.47,

FIG. 3. (Color online) PLE spectra of pristine GaN NWs and MPTMS-GaN NWs with various C_{MPTMS} . The arrow indicates a strong absorption band at 4.6–4.8 eV, correlated with the MPTMS-functionalization. The spectrum corresponding to the pristine GaN NWs has been multiplied by a factor of 8.

FIG. 4. (Color online) The representative RT Raman spectra of GaN NWs at different stages. The relative intensity of DARS with respect to the E_2 and the FWHM of E_2 are shown in the inset graph.

3.43, 3.28, and 3.19 eV, which are commonly observed in bulk GaN and epitaxial films with the exception for the 3.43 eV, i.e., the I_d band.¹⁶ These emissions are assigned to the recombination of the neutral donor bound exciton (D^0X) at 3.47 eV, the donor-to-acceptor pair (DAP) emission at 3.28 eV, and the longitudinal-optical phonon (LO) replica of DAP (DAP-LO) at 3.19 eV, respectively. As for the effects of the MPTMS, three observations should be noted: (1) the reduction of the high energy tail, (2) the narrowing of the D^0X peak (from ~ 35 to ~ 12 meV), and (3) the enhancement of the I_d . The D^0X emission is a characteristic emission of unintentionally doped n-type GaN and its FWHM is associated with the crystalline quality, strain, and donor concentration in the material. The presence of high-energy tails in GaN NWs has been proposed to be associated with the native surface-oxide induced states.²³ The elimination of the high-energy tail together with the narrowing of the D^0X emission clearly indicates a quality improvement of the GaN NWs, and hence supports our previous claim of the effective surface-passivation role of MPTMS. Conversely, the origin of the ~ 3.43 eV (I_d) emission is not conclusive, since the

FIG. 5. (Color online) Low-temperature (5 K) PL spectra of GaN NWs at different stages. The spectra are normalized to the intensity of the D^0X peak.

emissions at 3.41–3.43 eV can be associated with extended defects, which are most likely stacking faults.^{24,25} However, it is known that NWs possess a much lower density of defects compared to their bulk counterparts. The low density of extended defects is unlikely to give rise to the prominent I_d emission observed in the NW case. From our results, the I_d becomes the dominant emission after the hydroxylation and it also exhibits a blue-shift after MPTMS-functionalization. The surface-sensitive nature of the I_d emission combined with the significant surface-to-volume ratio of the NWs is manifested by the considerable effect of the surface treatments. The I_d emission is therefore considered to be associated with unknown radiative defects close to the surface region. The I_d emission intensity is reduced by a significant density of surface states in the pristine GaN NWs and subsequently regained owing to the induced surface passivation effect. There are reports suggesting that the origin of the I_d emission is an acceptor-bound exciton in Ni-catalyzed GaN NWs as the Ni atoms/clusters can diffuse and be incorporated into GaN, serving as an acceptor.²⁶ The interpretation of the I_d emission being an acceptor-bound exciton cannot be excluded, since the presence of the bound exciton can be seen as a quality indicator in GaN. The improved quality caused by the surface passivation is consistent with the regaining of the I_d emission. However, our results are not sufficient to identify the origin of the I_d emission and require further experimental work.

In addition, TR PL was also applied to investigate the dynamic behavior of the excited carriers. The lifetime of the excited carriers can be estimated by fitting the decay with the equation:

$$I(t) = \sum_{n=1} A_n e^{-t/\tau_n}$$

where A_n represents the relative weight of different decay components and τ_n represents the corresponding lifetime of each component. The observed decay curves (Fig. 6) of the D^0X and the I_d emission exhibit nonexponential decay behaviors, meaning that the $n \gg 1$ for different recombination channels involved in the system and are accordingly difficult to compare with other results. As has been reported earlier, a more sophisticated analysis has been carried out in order to obtain a more complete understanding of the transient behavior.²⁷ For the sake of simplification and a general understanding, we assume that: (1) The NW is a geometric combination of the bulk core encapsulated by a surface shell, and (2) the nonradiative recombination is mainly associated with the surface shell, while the radiative recombination is due to the bulk.²⁸ It is known that the recombination processes associated with the nonradiative transition will exhibit a shorter measured decay time than pure radiative ones. As a consequence, one could conclude that the pristine NWs, possessing the highest density of active nonradiative surface defects should have the shortest measured decay time among the three compared here. The decay time is expected to become longer as the number of active surface defects is reduced along with the sequence of our

FIG. 6. (Color online) Normalized time-resolved PL spectra of the D^0X (3.472 eV) and the I_d (3.43 eV). The spectra of the I_d are shifted for clarity. Inset: magnified views of the time delay in the 100–500 ps window. The results are plotted with a logarithmic y-axis of intensity decay and a linear x-axis of time delay, as the half-lifetime of excited carriers can be obtained by estimating the slope of the decay curves.

experimental procedures. The estimated decay times of the D^0X (I_d) obtained by fitting the slopes of each decay curve (Fig. 6, inset) increases from 35 (71) ps for pristine GaN NWs, to 72 (164) ps for OH-GaN NWs, and to 127 (186) ps for MPTMS-GaN NWs. The observed evolution of the decay time clearly reveals the suppression of the nonradiative “fast” component and can be understood by the induced surface passivation effect, consistent with the suggested surface passivation effect of the GaN NWs as justified by the PL and Raman measurements. It should be noted that the observed decay times of the pristine GaN NWs in the present work is shorter than the earlier reported values (197 ps for D^0X and 252 ps for I_d).²⁶ These shortened decay times could be due to the high-pressure growth employed, which results in more imperfection in these GaN NWs compared to other reported work.²⁶

To explain our results, a modulation of the surface band bending caused by the surface modifiers is suggested to play a key role in the luminescent behavior (Fig. 7). Assuming that our system is analogous to a conventional n-type semiconductor; the conduction-band-minimum (CBM) and valance-band-maximum (VBM) would bend toward the vacuum level near the surface region owing to the Fermi-level pinning.²⁹ Especially for nanostructures based on polar semiconductors such as GaN, the band bending is expected to be significant. The irregularities in coordination and stoichiometry can break the crystal symmetry and compositional

FIG. 7. (Color online) Schematic illustration of the proposed surface band bending conditions of the GaNNWs with respect to different surface conditions to explain the observed results: (a) pristine GaN NWs, (b) OH-GaN NWs, and (c) MPTMS-GaN NWs.

fluctuations caused by the instability of the surface atoms. For example, oxygen is known to be associated with various defect levels and can also form an alloy with GaN ($\text{GaO}_x\text{N}_{1-x}$) depending on the level and the distribution of the incorporated oxygen.^{30–32} The expectation of significant density of surface defect states and a broad energy distribution rather than well defined energies are reasonable owing to the uncontrollable surface conditions. The surface band bending and the nonradiative surface defects will lead to the capture of carriers and consequently the generation of a surface depletion region with a subsequent reduction of the PL efficiency.³³ The deteriorated optical properties of pristine GaN NWs as characterized above [Fig. 7(a)] are therefore not surprising. The surface-hydroxylation process modifies the surface of the GaN NWs with OH groups. The OH groups possess a high electron density and can be treated as partially-charged particles close to the depleted surface of the GaN NWs, and thus reduce the surface potential accordingly [Fig. 7(b)]. Surface defect states with energy levels close to the CBM and VBM become inactivated and thus the emission energy becomes blue-shifted [Fig. 2(a)]. However, the overall emission intensity does not significantly increase, indicating the existence of efficient nonradiative channels. MPTMS, having a free thiol group, is suggested to be a soft donor.³⁴ The donorlike characteristic of MPTMS tends to have the electron close to the surface of the GaN NWs and consequently results in further reduction of the surface band bending. At this stage, the density of surface defect states that mediate the nonradiative recombination is significantly reduced, as suggested by the comprehensive improvement of the optical properties as observed in all of our measurements [Fig. 7(c)]. Our results clearly demonstrate that the functionalized mediator, MPTMS, can effectively passivate the surface of the GaN NWs and consequently improve the optical properties as demonstrated by all different characterization techniques including Raman, steady-state, and time-resolved PL. Further theoretical calculations are required to determine how the mediator reduces the surface potential and/or shifts the energy of surface defect states.

IV. CONCLUSION

The impact of the post surface treatments on the optical properties of the GaN NWs is reported. MPTMS, which is commonly applied as a mediator to link the organic/biomolecule and the inorganic semiconductor, is found to

effectively passivate the surface of GaN NWs. A modulation of surface band bending caused by the post surface treatment is proposed to account for the variation of the optical characteristics. Our results highlight the dominating role of the surface of the NWs to the optical properties. The surface functionalized GaN NWs can be useful for sensing applications.

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