



Short communication

Growth of network structured carbon-doped GaN (GaN:C) nanowires using a modified metal-organic chemical vapor deposition

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ARTICLE INFO

Article history:

Received 11 July 2015

Received in revised form

14 October 2015

Accepted 15 October 2015

Available online 19 October 2015

Keywords:

Carbon-doping

GaN

MOCVD

Nanowire

Network structure

TMGa

ABSTRACT

A network structured carbon-doped GaN (GaN:C) nanowires (NWs) was formed by a modified metal-organic chemical vapor deposition (MOCVD) technique using Ga(CH₃)₃, HCl and NH₃ as precursors. The GaN:C NWs were acquired from a non-stoichiometric ratio of Ga(CH₃)₃ and HCl, and the key process is believed to be the formation of polymerized GaCl_x containing methyl groups. As-formed GaN:C NWs exhibited a hexagonal Wurtzite structure. The Ga to N elemental ratio was approximately 1:1, and the GaN:C NWs contained carbon with concentration of ~5%. The GaN:C NWs showed the blue luminescence (BL) at 2.69 eV, which was conjectured to originate from the C_N⁺–C_N⁰ transitions. The method developed in this study could produce a network structure of GaN:C NWs without using catalysts. Moreover, carbon doping was found to be one of the candidates to change the optoelectronic properties of GaN.

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Gallium nitride (GaN) is a wide band-gap semiconductor (3.4 eV) with a direct transition, strong tolerance to high energy radiation and high thermo-chemical stability [1–3]. Given their properties, GaN is commonly used in light emitting diodes (LEDs), short wavelength lasers, ultraviolet detectors, and solar cell windows in space [1,2,4]. Currently, one-dimensional GaN nanowires (NWs) have attracted considerable interest in electronic devices and display applications [5–7], because the formation of GaN NWs on the hetero-substrates can reduce the strain caused by thermal expansion and lattice mismatch. Several methods have been developed to form GaN nanostructures, such as template-assisted technique, carbon nanotube confinement technique, etc. [8–11]. Among these techniques, a metal catalyst-assisted technique is considered as the most successful method to grow GaN nanostructures. On the other hand, this method has some difficulty such as complicated process, long formation time and catalyst embedded nano-structure formation. Therefore, a simpler method for fabrication of nano-dimensional GaN is still needed. In this study, the network structures of carbon-doped GaN (GaN:C) nanowires (NWs) were fabricated on a c-axis Al₂O₃ substrate using

a modified metal-organic chemical vapor deposition (MOCVD) technique, which was controlled to allow sequential chemical reactions between reactants. The network structured GaN:C NWs were formed without using catalysts with a non-stoichiometric concentration ratio of the reactants. The characteristics of the GaN:C NWs were examined, and the formation mechanism for the network structured GaN:C NWs is proposed.

The modified MOCVD method for the formation of network structured GaN:C NWs is a hot-wall deposition technique using trimethyl gallium (Ga(CH₃)₃, TMGa), ammonia (NH₃), and hydrogen chloride (HCl) diluted in nitrogen (N₂) gas (HCl:N₂ = 1:9). The reaction chamber was made of quartz materials with 6 zone heaters, and the temperatures of the 6-zones were set and controlled separately to obtain suitable chemical reactions in each zone, as shown in Fig. 1. The sequential chemical reactions in each zone were as follows: The TMGa was decomposed in the 1st zone, volatile Ga-halides were formed in zones 2 and 3, and the GaN:C NWs were synthesized in zones 4 and 5 from the reactions between Ga-halides and NH₃. The network structured GaN:C NWs were formed on z-axis Al₂O₃ substrates located in the 5th heater-zone of the reactor, and the growth time of the GaN:C NWs was changed from 5 to 20 min to examine the formation mechanism of the GaN:C NWs. Table 1 and Fig. 1 show the experimental conditions and a

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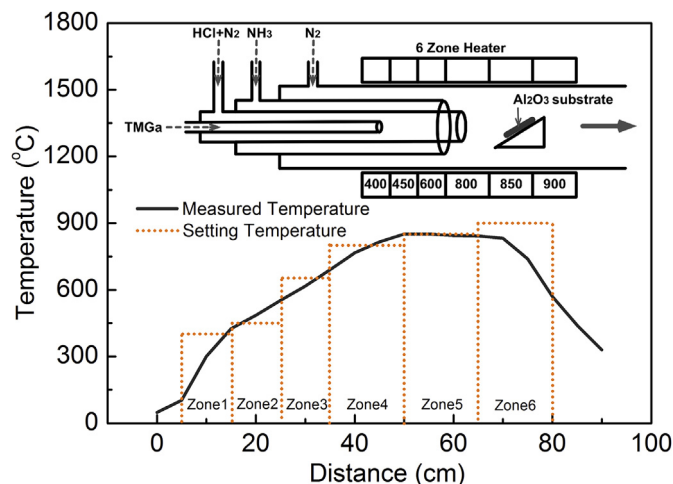


Fig. 1. Schematic diagram of the metal-organic chemical vapor deposition apparatus for the growth of the network structured GaN:C NWs and the temperature profile of the 6 zone heaters.

Table 1

Growth conditions for the network structured GaN nanowires.

Parameters	Unit	Value
Ga(CH ₃) ₃ flow rate	[sccm]	60
HCl flow rate	[sccm]	20
NH ₃ flow rate	[sccm]	220
N ₂ flow rate	[sccm]	2700
Total flow rate	[sccm]	3000
TMGa bath temperature	[°C]	5
Growth time	[min]	5–20
Deposition temperature	[°C]	850

schematic diagram of the modified MOCVD, respectively. The network structured GaN:C NWs were observed by scanning electron microscopy (SEM, Hitachi S-4100), and the structural properties of the GaN:C NWs were investigated by X-ray diffraction (XRD, PANalytical X'Pert PRO) using Cu-K α radiation. The optoelectronic properties of the network structured GaN:C NWs were examined by photoluminescence (PL) spectroscopy using a He–Cd laser with an excitation wavelength of 325 nm. Elemental analysis of the network structured GaN:C NWs was performed by X-ray photoelectron spectroscopy (XPS, ThermoFisher KA1149), and the vibrational modes of the NWs were studied by Raman spectroscopy (TII Nanofinder 30).

Fig. 2a shows the XRD pattern of the network structured GaN:C NWs formed at the growth time of 20 min. The peaks were observed at 32.5°, 34.7° and 36.9° 2 θ , respectively, which were assigned to the (100), (002) and (101) diffraction planes of hexagonal GaN with Wurtzite structure (JCPDS PDF No.74–0243). Fig. 2b shows the Raman spectrum of the network structured GaN:C NWs formed at the growth time of 20 min. The Raman peaks of network structured GaN:C NWs were observed at 242, 416, 560, 713, 1418, and 1587 cm⁻¹. The peaks at 242 and 416 cm⁻¹ were assigned to the second-order modes, which were attributed to imperfections of the crystal structure, the effects of the finite size and acoustic overtone of Wurtzite GaN [9–11]. The peaks at 560 and 713 cm⁻¹ correspond to the first-order modes [11], and the position of the peaks showed a red-shift compared to the values of 570 and 735 cm⁻¹ from bulk GaN. This shift can be explained by the size effect of nano-dimensions for the network structured GaN:C NWs. In addition, the Raman peaks centered at 1418 (D-band) and 1587 cm⁻¹ (G-

band) were attributed to amorphous carbon [12,13], suggesting that the as-formed GaN:C NWs possess a small quantity of carbon components.

Fig. 2c shows high resolution XPS spectra of Ga 3d, N 1s, O 1s, and C 1s for the network structured GaN:C NWs. The Ga 3d peak centered at 20.5 eV was shifted positively from the core level of Ga 3d (~19 eV) [14], which were attributed to energy shifts due to the formation of Ga–N bonding. The as-formed network structured GaN:C NWs possessed a large quantity of oxygen, and the oxygen bonding originated from chemical adsorption on the surface of the GaN:C NWs. Generally, the oxygen peaks ranged from 529 to 535 eV, and the peak near 529–530 eV represents the lattice oxygen, while the peak from 530 to 531.6 eV is related to chemical adsorption at the film surface [15]. The O 1s peaks in this study were observed at 531.5 eV, as shown in Fig. 2c, which indicates chemical adsorption on the surface of the GaN:C NWs. The N 1s XPS peaks exhibited an asymmetric form, and the de-convoluted peaks were positioned at 397.6 and 395.2 eV, respectively. This was confirmed by the chemical corporation between the Ga and N atoms, and the atomic ratio of Ga to N was almost stoichiometric. The GaN:C NWs also contained low concentrations of carbon components (~5%), as shown in Fig. 2c, whereas Cl elements were not detected. The C 1s peak could be numerically decomposed into two peaks using Gaussian fitting method. Decomposed peaks centered at 285 eV and 284 eV were attributed to the bonding of C–C and Ga–C, respectively. Thus, C elements would mainly be substituted into N sites in the GaN NWs, and it is conjectured that C elements act as acceptors in the network structured GaN:C NWs. In addition, the existence of C–C bonding implied that various structural defects were induced in GaN NWs.

Fig. 2d shows the PL spectrum of the GaN NWs at the growth time of 20 min. The PL spectrum exhibited three emission peaks at 2.69, 2.98, and 3.18 eV, respectively. The violet luminescence centered at 3.18 eV (FWHM: 150 meV) was assigned to the band to band transition of GaN, and the near-violet luminescence centered at 2.98 eV (FWHM: 208 meV) was attributed to near-band-gap emission of GaN [16,17]. On the other hand, the blue luminescence (BL) centered at 2.69 eV was strongly related to the C-doping in GaN NWs. Recent studies report that C_N acts as a deep acceptor with an ionization energy of 0.9 eV in GaN:C films [18–20]. Owing to this electronic property of C_N, the transition between neutral state (C_N⁰) and negatively charged state (C_N⁻), that is C_N⁰ + e⁻ → C_N⁻ process, causes a yellow luminescence (YL) at 2.14 eV [18,19]. In addition, the transition between positively charged state (C_N⁺) and neutral state (C_N⁰), that is C_N⁺ + e⁻ → C_N⁰ process, gives rise to the blue emission at 2.70 eV [20]. These results indicate the C_N deep acceptor leads to YL or BL depending on the position of Fermi energy level [17–20]. From above results, it was conjectured that the BL at 2.69 eV was originated from the C_N⁺–C_N⁰ transition in the GaN:C NWs of this study.

Fig. 3 shows SEM images of GaN NWs according to the growth times. The shape of the GaN:C NWs exhibited a chain structure of small spheres at the growth time of 5 min, and this shape grew gradually to network structured NWs with increasing growth time. This formation pattern can be explained as follows: GaCH₃ molecules were formed via the homolytic fission of methyl groups from the TMGa molecules, suggesting that these were polymerized due to the high concentration of GaCH₃ radicals. In addition, the activation energy for the decomposition of GaCH₃ molecules was higher than that of Ga(CH₃)₂ molecules [21–23]; hence GaCH₃ molecules are considered as in the meta-stable state in this case. In the 2nd and 3rd zones, the gallium halides were formed from gas phase reactions between (GaCH₃)_n and HCl, and the molecules grew gradually through these zones. In the highest temperature zones (zone 4–5), the polymerized molecules combined with each

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