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Catalytic synthesis and photoluminescence of gallium nitride nanowires

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Abstract

Single crystalline wurzite GaN nanowires were successfully synthesized on the NiO catalyzed alumina substrate through a simple thermal chemical vapor deposition method. The mixture of Ga and GaN powder was used as the source material of Ga for synthesizing GaN nanowires. The diameter of nanowires ranged 50–60 nm and the length was about hundreds of micrometers. The nanowires were single crystal with hexagonal wurzite structure. The peaks of Raman spectra of GaN nanowires appeared broadened and asymmetric compared with those of bulk GaN. PL spectra under excitation at 325 nm showed a strong emission at 3.315 eV from near band-edge transition and a broad weak emission at 2.695 eV related to deep level defects.

1. Introduction

Gallium nitride (GaN), which possesses direct wide-bandgap of 3.4 eV at room temperature, has attracted much interests due to its blue or ultraviolet emission properties [1–3]. In addition, GaN exhibits high thermal conductivity and little radiation damage, suggesting its applications to high power and high temperature microelectronic devices. Up to now, many research groups have extensively studied a synthesis, microstructure and physical properties of GaN [4,5]. In recent years, GaN nanowires have arrested great attentions due to their unique physical properties and potential applications in GaN nanowire-based electronic devices [6,7]. Several techniques have been developed for synthesizing GaN nanowires including arc discharge [8], pyrolysis [9], laser ablation [10], and chemical vapor deposition (CVD) [11–15]. Among these various methods, CVD is the most promising method for the controlled and selective growth of GaN nanowire. Many efforts involving CVD process have been made for the large-scale synthesis of high-quality GaN nanowires. Especially, there were some reports for the growth of GaN nanowires by a direct reaction of GaN powder or Ga metal with flowing NH_3 [16–19].

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In this Letter, we report large-scale synthesis of single-crystalline high-quality GaN nanowires using a simple thermal CVD method. The mixture of Ga metal and GaN powder was effective source for growth of high quality GaN nanowire. The microstructure and optical properties of GaN nanowires were also investigated.

2. Experimental

An alumina substrate (10 mm $\times$ 5 mm in size), on which NiO catalyst nanoparticles were evenly distributed, was employed for the growth of GaN nitride nanowires. In a typical process, a nickel nitrate/ethanol solution (concentration 0.01 M) was dropped onto the surface of alumina substrate and dried in air. The catalyzed substrate was put downward on the top of a quartz boat loaded with the mixture of Ga/GaN powders (Ga: 99.999%, GaN: 99.99%, Sigma–Aldrich, Ga:GaN = 1:1 (volume ratio)). The vertical distance between the Ga/GaN mixture source and the catalyzed alumina substrate was about 3–5 mm. The substrate was transferred to a tube furnace, which had been degassed under vacuum condition and purged by argon. The temperature was increased to preset reaction temperature (1000 °C) at a rate of 35 °C/min and kept at the preset reaction temperature for 60 min under a constant flow of NH_3 (flow rate: 500 sccm). After reaction, the substrate surface appeared a deposit of white-colored material. The as-deposited products were characterized by scanning electron microscopy (SEM) [Hitachi S-4700 field-emission scanning electron microscope], high-resolution transmission electron microscopy (TEM) [Hitachi H-9000 NAR], energy-dispersive X-ray spectroscopy (EDX) [Hitachi S-4700], and X-ray diffraction (XRD) [Rigaku DMAX PSPC MDG 2000]. The PL spectra were excited with a 325 nm line of a He–Cd laser and measured at various temperature using a closed cycle He refrigerator operating from 10 K to room temperature. Raman scattering was performed in the near backscattering geometry using 514.5 nm line of an Ar^+ laser with a power of 20 mW. The scattered radiation was analyzed with a double monochromator and detected with liquid nitrogen cooled charge coupled device.

3. Results and discussion

Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) measurement indicate that the products are hexagonal wurzite GaN as shown in Fig. 1. XRD analysis shows that GaN nanowires have clear peaks at 2θ values of 32.37, 34.52, and 36.86, revealing a high crystalline structure.

SEM observations reveal that the products deposited on the alumina substrate consist of a large

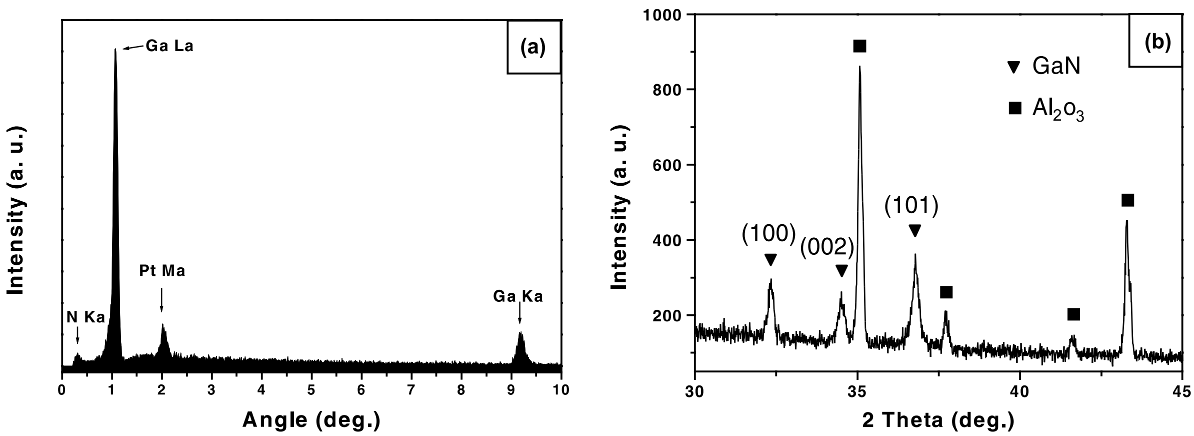

Fig. 1. EDX and XRD spectra of GaN nanowires synthesized on an alumina substrate. (a) EDX spectrum; (b) XRD spectrum.

quantity of randomly distributed nanowires in Figs. 2a,b. The nanowires have a length up to hundreds of micrometers and a diameter ranged from 50 to 60 nm. The GaN nanowires possess fairly straight morphology and also have a clean surface without any particles. The detailed geometrical morphologies are shown in Figs. 2c,d.

Fig. 3 shows HRTEM image of a GaN nanowire, showing a typical lattice image and an electron diffraction pattern of nanowire. The selected area electron diffraction (SAED) pattern confirms that nanowires are single-crystallite wurzite structure consistent with XRD result. No defect was observed in the lattice image of nanowires by HRTEM analysis, revealing the high-quality crystal lattice. The growth direction of the GaN nanowire is [1 0 0] as shown in Fig. 3.

In our experiment, NiO catalyst plays a key role for the fabrication of high-quality GaN nanowires during thermal CVD process. Omission of catalyst leads to the deposition of only amorphous materials on alumina substrate. It is well known that transition metal-oxide nanoparticles, such as NiO, CoO, and FeO, have catalyst effect on the nanowire growth in the VLS process, which are similar to that of metal catalyst [16]. Other groups reported the successful synthesis of GaN nanowires

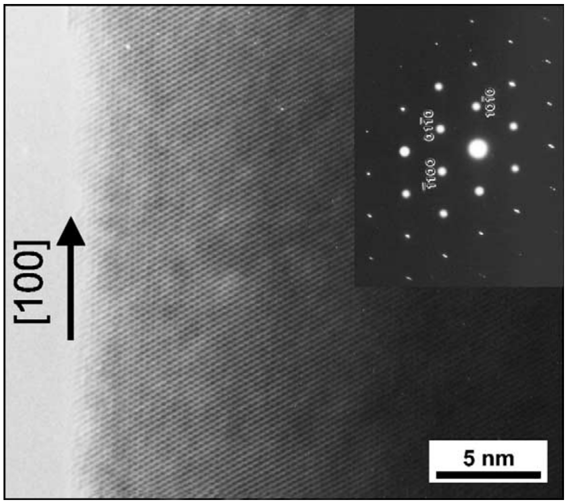

Fig. 3. HRTEM image of a wurzite GaN nanowire. Inset gives electron diffraction pattern recorded along $\langle 0001 \rangle$ zone axis, showing [1 0 0] growth direction.

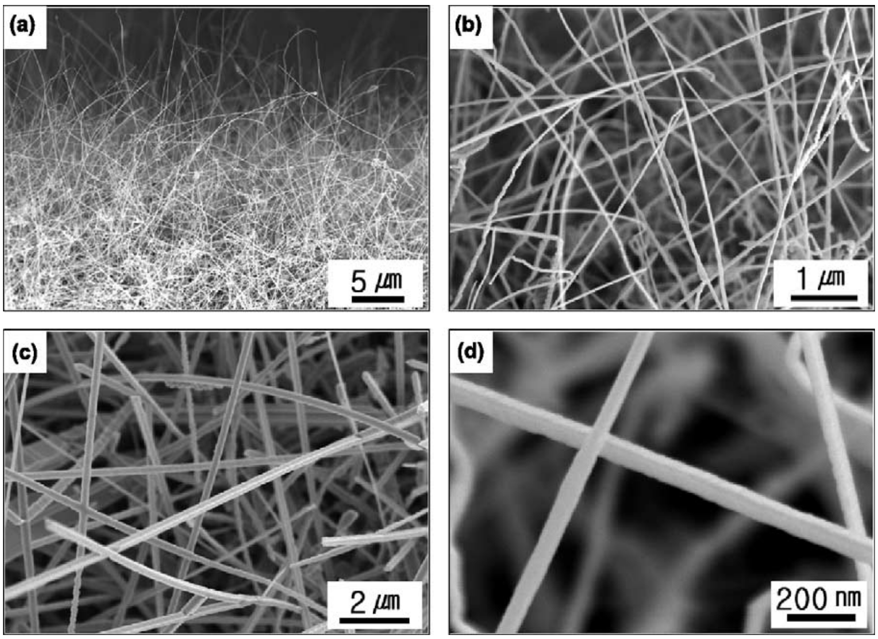

Fig. 2. SEM images of GaN nanowires. (a and b) SEM images showing a large quantity of nanowires deposited on an alumina substrate. (c and d) Magnified SEM images revealing geometrical morphology of nanowires.

using direct reaction of Ga or GaN source with NH_3. In our experimental conditions, however, we could find that only some amorphous products were deposited on the substrate when either Ga or GaN was individually used in the source material. On the other hand, large-scale production of high-quality GaN nanowires was realized when the mixture of Ga and GaN powder was used to Ga source. It is worthy to mention that similar phenomena was observed in the case of the synthesis of GaP nanowires on alumina substrate using the mixture of Ga/GaP powder as a source material [20]. Further detail study is necessary to explain that the mixture source of Ga and GaN powder would be of advantage to inducing of one-dimensional growth of GaN nanowire.

The Raman spectrum of GaN nanowires exhibits only A_1(TO), E_1(TO), and E_2 modes at 531, 560, and 566 cm^{-1}, respectively, as shown in Fig. 4. The peaks appear broadened and asymmetric, which can be explained by size confinement effect and internal stress. The absence of longitudinal optical (LO) phonons could be attributed to special angle between the wave vector of photons and axis direction [1 0 0] of wurzite GaN nanowires in the near backscattering geometry (actually all of nanowires nearly lying on the substrate). In the case of GaN epilayers grown along the *c*-axis using MOCVD, phonons of $E_2, A_1(LO)$, and E_1(LO) modes are normally observed due to the symmetry selection rule for the wurzite crystal, i.e. C_{6v} symmetry group [21]. The frequency of E_2 mode observed in our GaN nanowires is lower than those observed in epilayers grown on sapphire substrate or bulk crystal. It is known that the frequency of E_2 mode shifts to higher value with biaxial compressive stress within epilayers by $\Delta\varpi = 6.2\sigma$, where the biaxial compressive stress σ is in GPa [22]. The lower value of E_2 mode in comparison with 568 cm^{-1} of bulk crystal demonstrates that the synthesized GaN nanowires perhaps have partly tensile stress near the surface of nanowires; the magnitude of the stress estimated from the frequency shift of the E_2 mode is 0.322 GPa.

Photoluminescence (PL) of GaN nanowires was investigated using a He–Cd laser excitation at 325 nm, as shown in Fig. 5. In PL spectra, asymmetry broad emission (around 3.315 eV) is associated with the near band-edge transition and a broad weak emission band (centered around 2.695 eV) is related to deep level defects. The broadband-edge related peak exhibits a full-width at half maximum (FWHM) of 446 meV at room temperature but the near band-edge PL peak narrows to 322 meV of FWHM at low temperature of 12 K. The weak emission band, which is associated with deep level defects, quenches at lower temperature, leaving only the near band-edge PL peak.

In summary, large-scale GaN nanowires were successfully synthesized by employing the mixture of Ga and GaN species onto catalyzed alumina substrate under ammonia ambient. The GaN

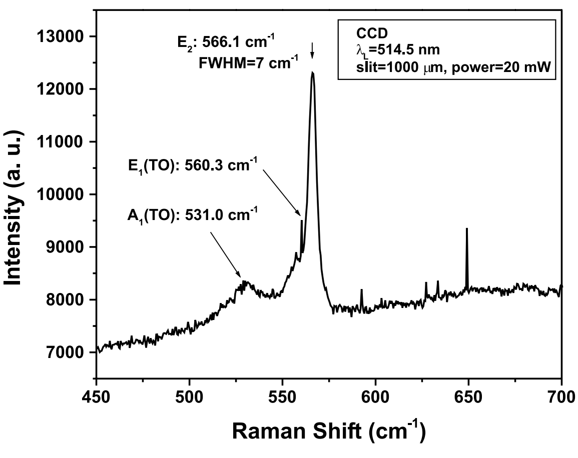

Fig. 4. Raman spectrum of GaN nanowires.

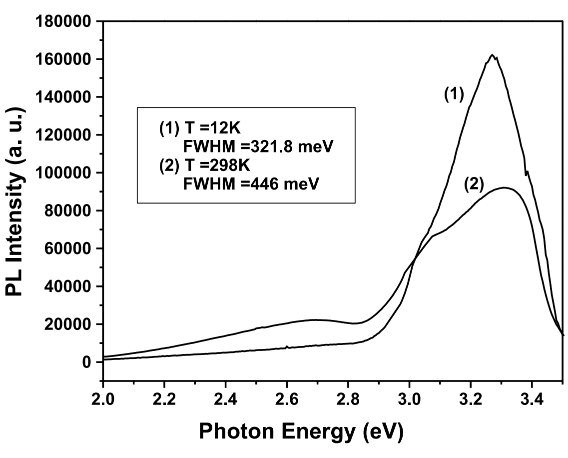

Fig. 5. Photoluminescence spectrum of GaN nanowires.

nanowires have the diameter ranged of 50–60 nm and the length up to hundreds of micrometers. The GaN nanowires indicate hexagonal wurzite single crystals with high crystallinity. Our results demonstrate that the mixture of Ga and GaN powder is more effective source for growth of large-scale synthesis of high-quality GaN nanowires.

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