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## LETTER TO THE EDITOR

## Effects of In surfactant on the crystalline and photoluminescence properties of GaN nanowires

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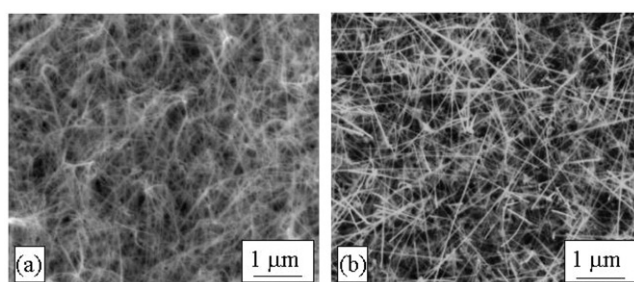
### Abstract

GaN nanowires have been grown with and without In as an additional source. The effects of In surfactant on the crystal quality and photoluminescence property of GaN nanowires are reported for the first time. X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, energy-dispersive x-ray spectroscopy, and photoluminescence measurements are employed to analyse the products. The results show that introducing a certain amount of In surfactant during the growth process can improve the crystal quality of the GaN nanowires, and enhance the photoluminescence of them. In addition, the as-prepared GaN nanowires have the advantage of being easy to be separated, which will benefit the subsequent nanodevice fabrication.

### 1. Introduction

The group-III nitride semiconductors are very important materials for many applications in the areas of optoelectronic devices and high-temperature/power electronic devices [1, 2]. One-dimensional semiconductor nanostructures possess unique electronic, optical and magnetic properties compared with the corresponding bulk materials due to the quantum confinement effect, Coulomb blockade effect, high surface to volume ratio, and so on. Various techniques have been employed to synthesize GaN nanowires and nanobelts [3–9]. Surface-active species doping has shown a significant improvement in epitaxial growth quality by manipulation of the surface free energy [10]. Among the surfactants, isoelectronic In appears to be a good

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**Figure 1.** (a) and (b) The FESEM images for NW-A and NW-B, respectively.

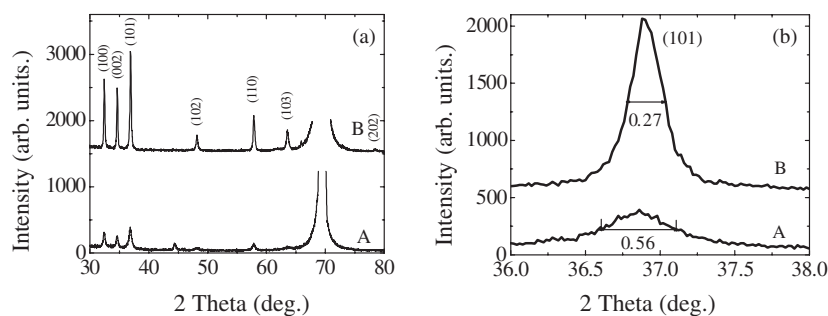
candidate for growing GaN due to its low solubility in GaN in the growth temperature range and its tendency to segregate [11–16]. It has been reported that the crystal quality as well as the optical and electrical properties of GaN films can be improved by isoelectronic In-doping with a fraction of 0.2% or less [13–16]. In this paper, we report the effects of In surfactant on the crystalline and photoluminescence (PL) properties of GaN nanowires. As far as we know, no similar work has been reported before.

## 2. Experiments

Our experiments were carried out in a specially designed two-hot-boat chemical vapour deposition system [17]. Inside a chamber, there are two horizontally placed molybdenum boats for loading the source and the substrate, respectively. The centre distance between the two boats is about 3 cm. The source-boat is close to the outlet of the  $\text{NH}_3$  gas pipe. The temperatures of the two boats could be controlled separately, and could reach as high as  $1000^\circ\text{C}$  in several minutes. For the growth of the GaN nanowires, molten Ga (99.99%) or Ga and In (99.999%) with a mass ratio near to 4:1 were used as the source, and p-Si substrates covered with a thermal evaporated 2–5 nm-thick Ni catalyst layer were used as the substrate. First the vacuum in the chamber was pumped to about  $10^{-5}$  Torr, then  $\text{NH}_3$  gas was let in at a flow rate of 50–100 sccm. When the vacuum reached about 100 Torr, the source- and the substrate-boats were heated to  $850\text{--}900^\circ\text{C}$  and  $900\text{--}950^\circ\text{C}$ , respectively, in a few minutes. The synthesis duration was about 30 min. The GaN nanowires grown with and without In as an additional source were labelled as NW-B and NW-A, respectively. The products were characterized using an x-ray powder diffractometer (XRD) (Rigaku Dmax-2000), a field emission focused ion beam system (Strata DB235) working in field emission scanning microscope (FESEM) mode, and a field emission transmission electron microscope (TEM) (Tecnai F30) equipped with an energy-dispersive x-ray spectroscopy (EDX). Low-temperature (19 K) photoluminescence (PL) measurements were carried out using a 325 nm He–Cd laser as the excitation source.

## 3. Results and discussion

Figures 1(a) and (b) show FESEM images for NW-A and NW-B, respectively. From these figures, we can see that the morphologies of NW-A and NW-B are quite different. Most NW-A are twisted and entangled, and their surfaces are not smooth. In contrast, most NW-B are much straighter with smoother surfaces. The NW-A and NW-B are usually 10–40 nm in diameter, and about several microns in length. The growth rate is about several hundreds of nanometres per minute.

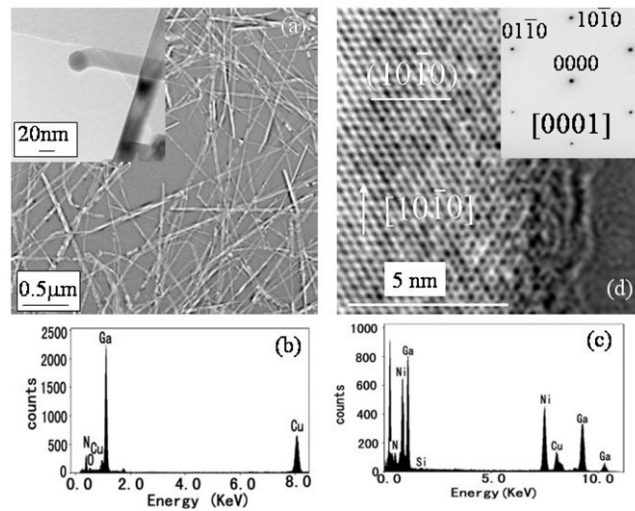


**Figure 2.** (a) The XRD patterns, with A and B taken from NW-A and NW-B, respectively; (b) magnified XRD peaks from (101) crystal planes of NW-A and NW-B. The FWHM of the XRD peaks for NW-A and NW-B are  $0.56^\circ$  and  $0.27^\circ$ , respectively.

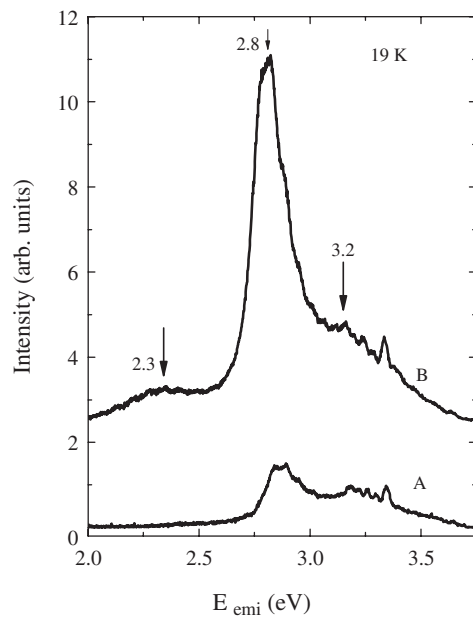
Figure 2(a) shows typical XRD patterns, with A and B taken from NW-A and NW-B, respectively. All the peaks in both samples are in good agreement with those from the GaN powder with wurtzite structure recorded on the Powder Diffraction Standards card published by the Joint Committee (JCPDS 76-0703). Compared to those from NW-A, the XRD peaks from NW-B are much higher in intensity and narrower in the full width at half maximum (FWHM). From the magnified (101) peaks of the two samples plotted in figure 2(b), we can see that the FWHM of the XRD peak for NW-A is about twice that for NW-B. These facts indicate a positive effect of In surfactant on the crystal quality of GaN nanowires. It is worth noting that because the scan step used in our x-ray diffraction measurement is not small enough to resolve the accurate peak positions of the narrower XRD peaks for NW-A, the apparent difference of the two peak positions shown in figure 2(b) does not reflect the real result. Actually, we do not expect a change in the lattice constant with In atom percentage less than 1% (to be addressed next).

For TEM analysis, the products were scraped from a substrate, dispersed in ethanol by an ultrasonic process, and then dropped onto a copper grid. The TEM images for NW-A (not presented) show they are usually not straight, and tend to entangle together. A TEM image for NW-B is shown in figure 3(a). We can see that these nanowires are well-separated, and the diameters of the nanowires are quite uniform along the growth directions. From the magnified TEM image shown in inset, we can see a nanoparticle at one end of a nanowire. The EDX data taken at the nanowire and the nanoparticle are shown in figures 3(b) and (c), respectively. From these figures, we can see that the nanowire consists of only Ga and N elements, while the nanoparticle also consists of Ni, besides Ga and N elements. The observed Cu peaks come from the copper grid. This result suggests that the NW-B synthesis process was based on the well-known vapour–liquid–solid mechanism with Ni nanoparticles working as the catalyst. No In element was detected in the EDX measurement, indicating the In atom percentage in NW-B to be below the EDX detection sensitivity of about 1%. Figure 3(d) is a high-resolution TEM (HRTEM) image of the nanowire. The inset is the corresponding selected area electron diffraction (SAED) pattern recorded along the [0001] zone axis. Miller indices as well as the nanowire growth direction (to be  $[10\bar{1}0]$ ) are labelled in the figures. The HRTEM image together with the SAED pattern demonstrates again that the GaN nanowires are single crystals with wurtzite structure.

Figure 4 shows the 19 K PL spectra, with A and B taken from NW-A and NW-B, respectively. A blue luminescence band (BL) with peak around 2.8 eV dominates both PL spectra. Two other emission bands with peaks around 2.3 and 3.2 eV can be found in the PL spectra, which are the well-known yellow luminescence, and donor-to-acceptor pair transitions



**Figure 3.** (a) A TEM image of NW-B. The inset is a magnified TEM image that shows a nanowire terminating with a nanoparticle (black) at one end; (b) and (c) the EDX data taken at the nanowire and nanoparticle, respectively; (d) an HRTEM image of the nanowire; the inset is the corresponding SAED pattern recorded along the [0001] zone axis. Miller indices as well as the nanowire growth direction are labelled in the figures.



**Figure 4.** 19 K PL spectra, with A and B taken from NW-A and NW-B, respectively.

in GaN, respectively. No band-edge emission is observed in both samples. Compared to that of NW-A, the PL intensity from NW-B is much stronger. This means there are fewer non-radiative recombination centres in NW-B. In other words, NW-B has better crystal quality.

The BL (2.7–2.9 eV) had been observed in various GaN film previously [18–21]. However, its origin is still controversial. Chen *et al* suggested the transitions between shallow donor N vacancy ( $V_N$ ) clusters and deep acceptor Ga interstitial ( $Ga_I$ ) clusters as being responsible for the BL [18]. We consider that, during our In-doped GaN nanowires growth process, In atoms tend to occupy the Ga positions. In other words, by adding extra group-III material in the source, the original near-stoichiometric ratio of group-III and group-V elements would be broken. This might cause an increase of  $V_N$  and/or  $Ga_I$  in the GaN lattice, which might give rise to the BL, or even cause the observed dominant BL after a competition of different recombination processes. Our result supports Chen *et al* in view of the origin of BL.

#### 4. Conclusions

We have synthesized single-crystal GaN nanowires with wurtzite structure via a two-hot-boat chemical vapour deposition method with and without In surfactant as an additional source. The nanowires synthesized with introducing a certain amount of In surfactant during the growth process are much straighter, with smoother surfaces, easier to separate from each other, and have much stronger BL. The positive effects of In surfactant on the crystal quality and PL property of GaN nanowires are reported for the first time.

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