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Growth mode control and micro-Raman characterization of triangular GaN nanowires in a vapor phase epitaxy process

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ABSTRACT

The synthesis of single-crystalline GaN nanowires on *c*-Al_2O_3 substrates using a vapor phase epitaxy process was studied. The GaN nanowires synthesized at a high NH_3 gas flow rate and thus with a sufficient supply of the N source grew via the vapor–solid mechanism, while those synthesized at a low NH_3 gas flow rate grew via the vapor–liquid–solid mechanism. The internal stress between the nanowires and the substrate was investigated using micro-Raman spectroscopy. The X-ray diffraction indicated that the triangular GaN nanowires have a single-crystalline hexagonal structure.

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1. Introduction

In recent years, the nitrides of third-group metals have been actively investigated in an attempt to make wide band-gap semiconductors and opto-electronic devices. Especially, GaN, a semiconductor with a high melting point and electric breakdown field, large carrier mobility and direct wide band gap, has been recognized as a promising material for blue light emitting diodes and high power electric device applications [1,2].

Studies on the fabrication and characterization of one-dimensional nanostructures such as nanowires and nanotubes have flourished in recent years, because of their fundamental importance to nanotechnology [3,4]. Especially, GaN has been used both to demonstrate new theoretical concepts and for practical applications and a great deal of attention has been accorded to them due to their unique properties and potential applications [5,6]. In this regard, the realization of high quality GaN nanostructures is very much required. There have been several reports on the generation of various architectural morphologies within the GaN system [7,8]. In spite of the remarkable progress which has been made in the synthesis of GaN nanowires, studies of their lattice dynamics and electron–phonon interaction still remain few and incomplete, whereas such research is important to understand the optical and electronic properties of devices based on nanowire structures.

In this work, the GaN nanowires were synthesized using vapor phase epitaxy (VPE) method under atmospheric pressure. We examined the influence of the NH_3 gas and Ar gas flow rates and the position of the substrate. In addition, we examined the stress between the synthesized GaN nanowires and the substrate.

2. Experimental

The GaN nanowires were synthesized using a VPE method. The starting materials were a mixture of GaN powder and Ga metal at a weight ratio of 1:1. We used an Au metal catalyst for the synthesis of the GaN nanowires, which was deposited as a thin film with a thickness of 3 nm. High purity Ar (99.999%) and NH_3 (99.99%) were introduced into the reactor as the carrier gas and reaction gas, respectively. The flow rate of Ar was fixed 1000 sccm and the NH_3 gas flow rate was varied with 300 and 50 sccm, which are called conditions A and B, respectively. After the main growth, the GaN nanowires were cooled naturally to room temperature.

The morphology of the GaN nanowires was observed using field-emission scanning electron microscopy (FESEM). The structure of the nanowires was investigated by X-ray diffraction (XRD). The micro-Raman analysis of the GaN nanowires was recorded using the 514.5 nm line of an Ar^+ laser.

3. Results and discussion

The GaN nanowires were successfully synthesized using the VPE method. Fig. 1 shows the FESEM images of the GaN nanowires obtained using synthesis conditions A and B, respectively. The diameter of the GaN nanowires increases when a higher N flow (due to the provided sufficient supply of the N source) is supplied during the growth process. We could not find any metal catalyst or metal alloy at the end of the GaN nanowires shown in Fig. 1(a). However, some metal catalyst was observed in the GaN nanowires shown in Fig. 1(b). This reveals that the

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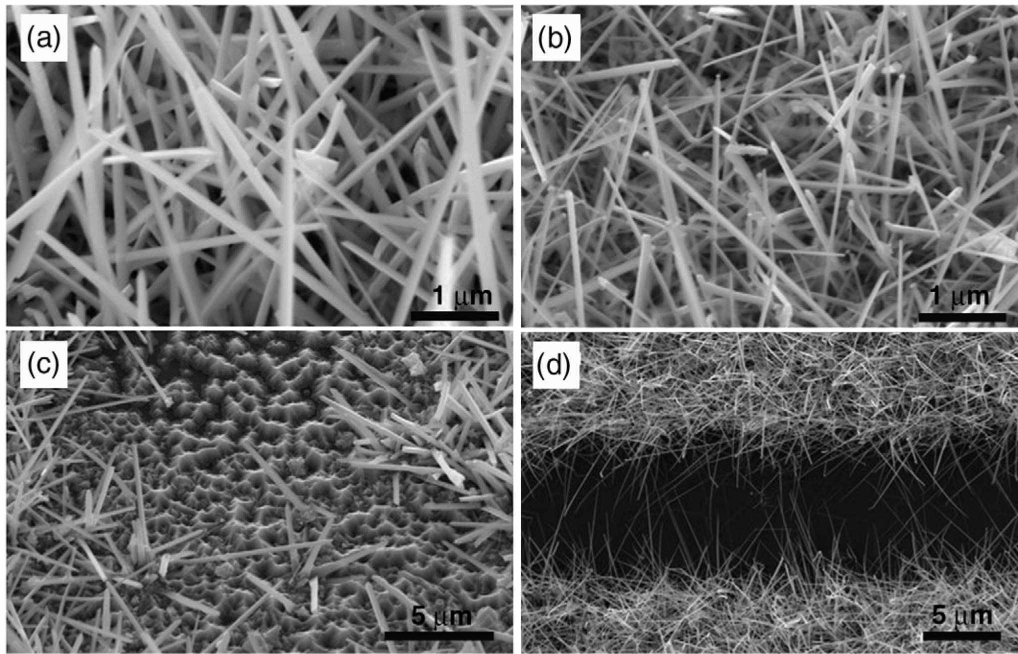

Fig. 1. FESEM images of GaN nanowires synthesized by the VPE method. (a) NH_3 gas flow rate of 300 sccm, and (b) NH_3 gas flow rate of 50 sccm. (c) No selective growth FESEM image of sample A obtained via VS mechanism. (d) Selective growth FESEM image of sample B obtained via VLS mechanism.

NH_3 gas flow rate has an influence on the synthesis behavior. Fig. 1(c) and (d) shows the FESEM images of the selective growth of the GaN nanowires obtained using synthesis conditions A and B, respectively. As shown in Fig. 1(c), when the NH_3 gas flow rate was increased, the thin film like buffer layer covered the Al_2O_3 substrate. And there are no GaN nanowires in the absent part of the metal catalyst as shown in Fig. 1(d). It was concluded that the GaN nanowires synthesized using a high NH_3 gas flow rate thus with a sufficient supply of the N source grew via the vapor–solid (VS) mechanism which was not influenced by the metal catalyst [9], while those synthesized using a low NH_3 gas flow rate grew via the vapor–liquid–solid (VLS) mechanism which was influenced by the metal catalyst [10].

Fig. 2 shows the XRD pattern used for the structural characterization of the synthesized GaN nanowires. All of the diffraction lines were indexed and identified as the hexagonal wurtzite structure, while no cubic phase was found. The peak of the synthesized GaN nanowires was sharp and the value of the full width at half maximum (FWHM) has narrow peak. The XRD analysis shows that the GaN nanowires are well-crystallized.

Fig. 3 shows the micro-Raman spectrum of the GaN nanowires synthesized using synthesis conditions A and B, respectively. The

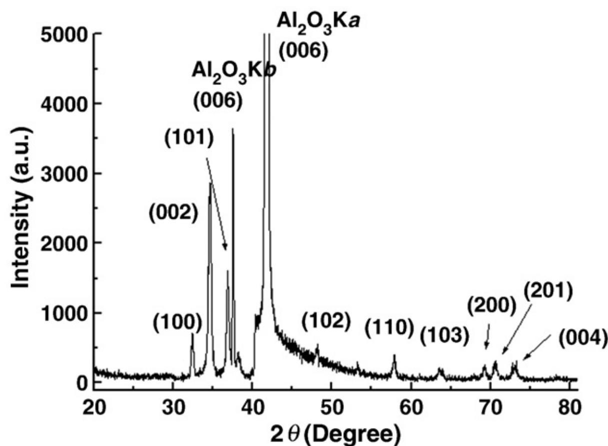

Fig. 2. X-ray diffraction pattern of GaN nanowires synthesized using condition A.

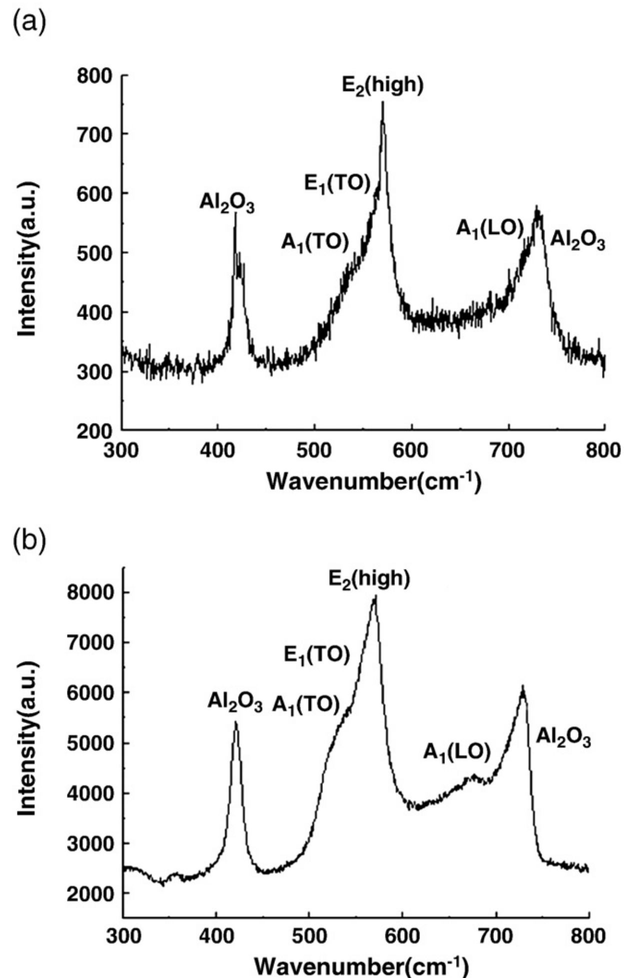

Fig. 3. Micro-Raman spectra of GaN nanowires. (a) and (b) micro-Raman spectrum of GaN nanowires synthesized using conditions A, and B, respectively.

Raman spectrum of GaN is relatively well known. The dependence of the spectrum on the sample orientation, as well as on the incident and dispersed light polarization according to the selection rules for the wurtzite structure is also well known [11]. The peaks observed in the spectrum correspond to the phonon vibration frequencies of the A_1(TO), E_1(TO) and E_2(high) Raman modes of crystalline hexagonal GaN. The E_1(TO) mode indicates the c-face of the wurtzite crystal and the E_2 mode appears to be the a-face. Generally, the Raman modes of single-crystalline GaN nanowires appear at 531, 560 and 569 cm^{-1}, respectively [12]. The three Raman modes; A_1(TO), E_1(TO) and E_2 (high) of the GaN nanowires synthesized in this study were observed at frequencies of 540, 564, and 570 cm^{-1} and of 519, 534, and 565 cm^{-1} in the case of conditions A and B, respectively. The Raman peaks of the GaN nanowires synthesized using condition A exhibit smaller shifts than those synthesized using condition B. This means that the GaN nanowires synthesized using condition A have less stress than those synthesized using condition B [8,13]. Furthermore, the line width of the E_2 (high) mode indicates the existence of atomic disorder in the nanowires [14]. The FWHM of the E_2 (high) mode for the GaN nanowires synthesized using conditions A and B were 12 and 31 cm^{-1}, respectively. Therefore the GaN nanowires synthesized using condition A have better crystallinity. This means that the thin film layer relaxes the stress between the nanowires and substrate by acting as a buffer layer.

4. Conclusion

We synthesized GaN nanowires with high quality and yield using the VPE method. We were able to conclude that the GaN nanowires synthesized using a high NH_3 gas flow rate thus with a sufficient supply of the N source grew via the VS mechanism, while those synthesized using a low NH_3 gas flow rate grew via the VLS mechanism. The micro-Raman spectra were investigated that the GaN nanowires synthesized using condition A have less stress than those synthesized using condition B.

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