Applied Surface Science 255 (2009) 3843–3847

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Synthesis of N-deficient GaN nanoparticles and its enhanced dielectric response

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ARTICLE INFO

*Article history:*
Received 30 August 2008
Received in revised form 14 October 2008
Accepted 16 October 2008
Available online 1 November 2008

*Keywords:*
N-deficient GaN
Nanoparticles
Raman scattering spectrum
Dielectric response

ABSTRACT

In this paper, GaN nanoparticles were firstly synthesized through a facile solid-state reaction using an organic reagent cyanamide ($CN_2H_2$) and $Ga_2O_3$ as precursors. The structural properties were investigated in detail. It is found that these nanoparticles having average size of 40 nm were N-deficient with the N vacancies reaching as high as 12%. The Raman scattering spectrum of these nanoparticles presented some interesting features. The room-temperature frequency spectrum of the relative dielectric constant $\varepsilon_r$ was measured and indicated that these nanoparticles exhibited sharp enhancement at low frequency range comparing with GaN nanomaterials and N-deficient microparticles. It is thought both the rotation direction polarization (RDP) and the space charge polarization (SCP) process should be responsible for the enhancement of $\varepsilon_r$ in these N-deficient GaN nanoparticles.



## 1. Introduction

GaN, a direct wide band-gap semiconductor ($E_g$ = 3.4 eV), has attracted extensive attention because of its great potentials for UV opoelectronic applications and high temperature/high power electronic devices [1–5]. Due to these unique applications, the microstructures, electrical, and optical properties of GaN, which are critical for the performance of the fabricated devices, have been investigated in detail [6–11]. Compared with these properties that have received much experimental and theoretical attention, the dielectric behavior of GaN bulk and nanostructures are poorly known. Up to date, there are only a few works investigating the dielectric properties of wurtzite GaN nanomaterials [12–16]. It is found that nanostructured GaN materials possess enhanced dielectric behavior mainly due to the great space charge polarization (SCP) process [17,18]. As for the dielectric property of N-deficient GaN materials, it has received less attention and was poorly investigated up to now [19]. It is found that the rotation direction polarization (RDP) process should be responsible for the enhancing dielectric property. However, the dielectric property of N-deficient GaN nanoparticles has not been investigated up to now. In this paper, by a simple route, we synthesized N-deficient GaN nanoparticles with average size of 40 nm using an organic reagent cyanamide ($CN_2H_2$) as precursor. The Raman scattering and dielectric property of the N-deficient GaN nanoparticles were investigated. Raman scattering spectrum of these nanoparticles presented some new features, and dielectric property measurements of these N-deficient nanoparticles show the sharp enhancement of $\varepsilon_r$ over those GaN nanomaterials and N-deficient microparticles at the low frequency.

## 2. Experimental procedure

All starting materials are of analytical pure grade and are purchased from commercial sources. In the typical synthesis, firstly, 5 mmol cyanamide ($CN_2H_2$) and 1 mmol $Ga_2O_3$ were mixed together and then pressed to a pellet. The pellet was put into a silica ampoule (out diameter, 15 mm; inner diameter, 12 mm). Secondly, the ampoule with the pellet was evacuated to $1 \times 10^{-6}$ Pa and sealed at length of 10 cm. In succession, the ampoule was heated to 750 °C at the rate of 5 °C $min^{-1}$. Then the whole system was kept at 750 °C for an hour. At last, the ampoule was cooled naturally to room temperature and gray powder was found after cooling.

The as-prepared powder was collected from the ampoule, and then was characterized by Hitach (Tokyo, Japan) S-4200 field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The X-ray diffraction (XRD) patterns obtained on rotating-anode Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer with Cu Kα radiation were used to determine the identity of crystalline phase. The particle size and high-resolution lattice fringe of samples were examined by

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doi:10.1016/j.apsusc.2008.10.057

transmission electron microscopy (TEM, JEOL 2010). The X-ray photoelectron spectra (XPS) are recorded on a VGESCALAB MKII X-ray Photoelectron Spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source. Raman measurement is performed on a JY-HR800 laser Raman spectrometer using a 532 nm solid-state laser as excitation source. Then the as-prepared powder was pressed to be a disk-shape sample ($D$ = 1 cm, $d$ = 1 mm) under a uniaxial pressure of 50 MPa with a relative density of 98%. The dielectric properties of the as-prepared sample were measured on a HP-4274A and HP-4275A LCR meters with a signal voltage of 0.5 V rms in the range of $10^2$–$10^5$ and $10^5$–$10^7$ Hz, respectively.

## 3. Results and discussion

The EDX data (Fig. 1a) indicate that the sample only consists of Ga and N element. The average Ga/N ratio is 1:0.88, indicating nitrogen-deficient condition in the sample. The composition of the sample can be also determined by XPS spectra. The binding energies, centered at 397.6, 1117.8, 1144.7 eV for N1s (Fig. 1b), Ga2p$_{3/2}$ and Ga2p$_{1/2}$ (Fig. 1c), respectively, are in agreement with the values of bulk GaN from the literature [20]. Quantification of the Ga2p and N1s peaks gives an average Ga/N atomic ratio of 1:0.873, further confirming that the sample is the formation of N-deficient GaN. The powder XRD pattern indicates that the sample can be indexed as hexagonal GaN and no other peaks from impurities is detected under the X-ray diffractometer's resolution (Fig. 2). The lattice parameters of the sample are calculated to be $a$ = 3.183 Å, $b$ = 5.175 Å, which is less than the calculated diffraction pattern (ICDD-PDF No. 50-0792; $a$ = 3.189 Å, $b$ = 5.185 Å), which is maybe due to the N-deficient condition in the sample. The widening diffraction peaks are maybe due to the nano-size effect of the sample. The SEM and TEM images shown in Fig. 3a and b clearly indicate the sample is composed of well-crystallized nanoparticles with average size of 40 nm. The corresponding HRTEM micrograph (Fig. 3c) displays that the interplanar spacing of the lattice planes is 0.235 nm, less than the known value of GaN (ICDD-PDF No. 50-0792, $d_{101}$ = 0.243 nm), probably due to the great N vacancies in the lattice. The EDX analysis of single nanoparticle (Fig. 3d) shows that the chemical composition mainly consists of Ga and N element and the detected C and Cu elements come from the carbon-coated copper grid. The ratio of the Ga/N is 1:0.878, which further confirmed the nitrogen-deficient condition of the sample.

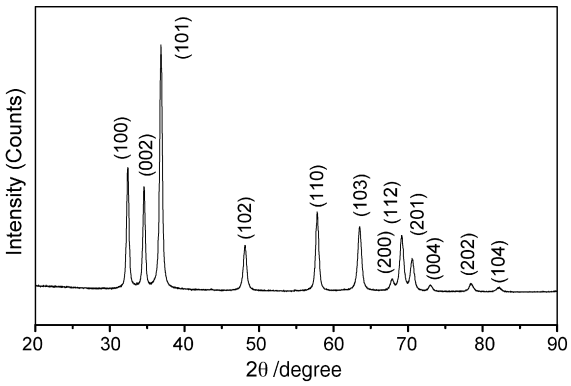


**Fig. 2.** XRD pattern of the sample.

Raman properties of GaN nanomaterials have been extensively investigated [21–23,13]. The space group of wurtzite GaN is $C_4^{6v}$ ($P6_3mc$) with all atoms occupying the $C_{3V}$ sites. Considering the Raman selection rules, six Raman-active modes may be present, i.e. $A_1$ (TO), $A_1$ (LO), $E_1$ (TO), $E_1$ (low), $E_2$ (high) and $E_2$ (low) can be observed in the hexagonal GaN. In this work, however, the Raman scattering spectrum of the N-deficient GaN nanoparticles shows some interesting features compared with previous reports. Considering the Raman selection rules, four peaks of the N-deficient GaN nanoparticles at 129.3, 530.2, 565.1 and 726.2 cm$^{-1}$ can be corresponding to $E_2$ (low), $E_2$ (high), $A_1$ (TO) and $A_1$ (LO) modes of GaN (Fig. 4). The peaks are asymmetric and more broadening, and large red-shift of the four modes can be found compared with the known data of GaN bulk and film. An interesting phenomenon is that five additional modes are also observed at 251.5, 414.6, 673.9, 802.5 and 1009.4 cm$^{-1}$, respectively, all of which are not allowed by the

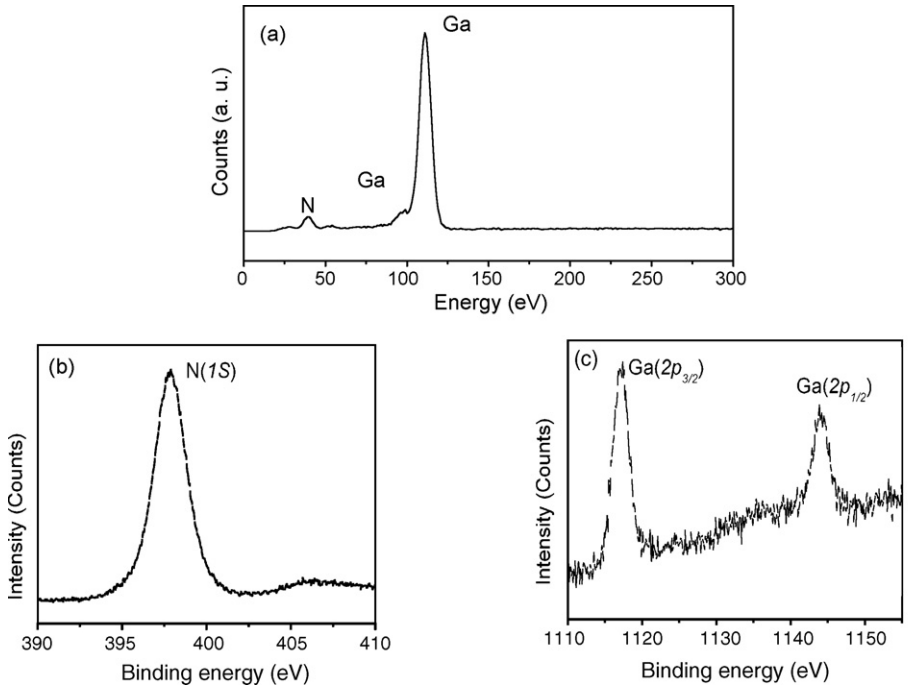


**Fig. 1.** (a) EDX analysis of the sample; (b) XPS spectrum of N1s region of the sample; (c) XPS spectrum of Ga2p region of the sample.