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Synthesis and optical properties of sword-like GaN nanorods clusters

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ABSTRACT

Purpose of this work is to synthesize highly pure gallium nitride (GaN) nanomaterials without using any foreign materials as a catalyst to avoid unintentional metal contamination. Therefore, a simple method for synthesizing sword-like GaN nanorods clusters has been proposed through ammoniating a new type of single molecular complex precursor [ammoniumhexafluro gallate, $(NH_4)_3GaF_6$], under a flow of ammonia gas. We investigated that the growth of sword-like GaN nanorods clusters was mainly depending on the decomposition rate of ammonia and the availability of sufficient amount of atomic nitrogen (N) species. Sword-like GaN nanorods clusters consist of outwardly orientated nanorods grown from the central part of source material to all possible direction, but not parallel to the substrate. Average diameters of an individual nanorod were found to be around 700, 350, and 100 nm from the bottom, middle and near top portion, respectively. The characteristic peaks in X-ray diffraction and Raman spectra were substantiated that the nanorods are pure hexagonal GaN with single crystalline wurtzite structure. Morphology and high crystal structure of GaN nanorods clusters were confirmed by the scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM).

1. Introduction

Gallium nitride (GaN) is one of the most effective nitride materials among the semiconducting III–V nitride groups. It offers to be a promising optoelectronic material for such applications as blue and ultraviolet (UV) light emitting diodes (LEDs) and laser diodes (LDs) [1] due to its large direct energy band gap of 3.39 eV at room temperature. Recently, one-dimensional nanostructured GaN materials, such as nanorods, nanowires and nanotubes, have attracted extensive interest owing to their great prospects in the fundamental and applied novel nanotechnology applications [2]. Being nanometer-sized low dimensional GaN is expected to have quantum confinement effects and be free from various defects [2–4], which ultimately improve their device characteristics and to be used as building block for future nano-devices.

One dimensional GaN materials have received much attention after the successful attempt made to synthesis the GaN nanorods through a carbon nanotube-confined reaction of Ga/Ga_2O_3 mixture with ammonia gas, many efforts have been dedicated to developing different techniques for preparing GaN nanorods. Among the successful techniques include carbon nanotubes confined [4] reaction or template-induced growth [5], metal catalyzed growth [6], and direct reaction of metal Ga with NH_3 [7–9]. Even after successful growth of the GaN nanomaterials from template assisted technique or with the help of a catalyst, this would introduce metal contamination unintentionally [10], causing strain [11], non-radiative recombination [12], carrier trapping, or junction leakage [13]. Therefore, direct reaction between the sources of the Ga with NH_3 could be the better alternative for the high quality nanomaterials development for the future electronics. Hence, ammoniumhexafluoro gallate $[(NH_4)_3GaF_6]$, a new type of Ga source material has been prepared from the simple two-step solution technique and allow to react with ammonia gas to synthesis various types of GaN nanomaterials.

In the present work, we report a simple method for the production of highly crystalline sword-like GaN nanorods clusters on Si substrate without assistance of any catalyst using a new type of single molecular precursor, under a flow of ammonia. This article mainly deals with the synthesis and their optical characteristics of GaN microspheres and sword-like GaN nanorods clusters.

2. Experimental

The gallium source complex precursor $[(NH_4)_3GaF_6]$ was prepared by slightly modifying the procedure reported in the literature [14]. In brief, stoichiometric quantity of gallium nitrate $[Ga(NO_3)_3]$ was dissolved in 25% ammonia solution to get gallium hydroxide as a solid. Then, ammoniumhexafluoro gallate complex was isolated from the 1:6 molar ratio solutions of gallium hydroxide and aqueous ammonium fluoride solution. In the typical preparation of GaN materials, crushed precursor powder was dispersed

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in isopropyl alcohol and dropped over the pre-cleaned Si substrate and subsequently dried. Then, the sample was inserted into center part of quartz tube in the tubular furnace. Nitridation process was carried out at 1000 °C for 3 h under the different NH_3 gas flow, GaN microspheres and nanorods clusters were obtained with 20 and 50 sccm of ammonia gas flow, respectively. After the completion of reaction time, NH_3 gas flow was replaced by N_2 gas (200 sccm) and allowed to cool naturally to room temperature.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of GaN microspheres and sword-like GaN nanorods clusters, along with a Ga source complex for comparison. X-ray diffraction peaks of our samples confirm the wurtzite type structure of GaN material, which consistent with those of hexagonal GaN (JCPDS file-76-0703) [15]. However, the peaks corresponding to sword-like GaN nanorods clusters sample are clearly visible when compared to the GaN microsphere sample. This result probably resulted from the imperfect growth of GaN microsphere, which may be due to insufficient N species during GaN growth. The broadened X-ray diffraction peaks resulted from the quantum size effects of GaN materials [15]. In parallel, for a better comparison with GaN samples, X-ray pattern of Ga source complex was displayed in Fig 1c, which has a plenty of sharp and narrow diffraction peaks in the entire 2θ range from 20 to 80. Therefore, based on these observations, none of our GaN samples has detected the crystalline diffraction peaks, belong to any other impurities and also from the source material, which strongly substantiates the total conversion of GaN and also free from unknown impurities.

The surface morphology of as synthesized GaN materials was analyzed from the FESEM photographs, as presented in Fig 2. Two different types of GaN materials were obtained by adjusting the speed of ammonia flow. For example, GaN microspheres and

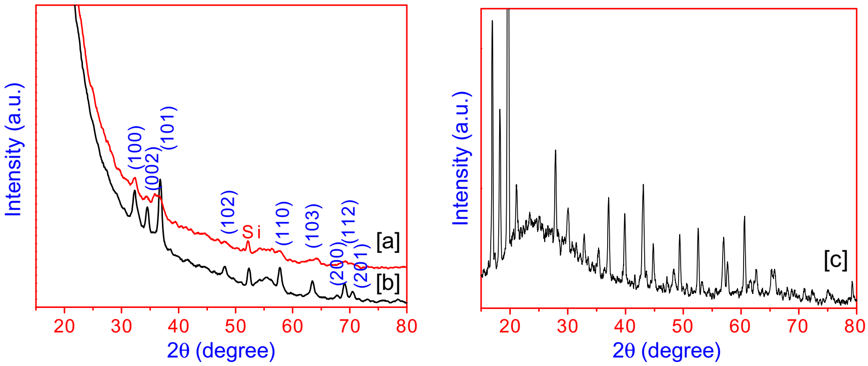

Fig. 1. X-ray diffraction patterns of (a) GaN microsphere (b) sword-like GaN nanorods clusters and (c) Ga source complex.

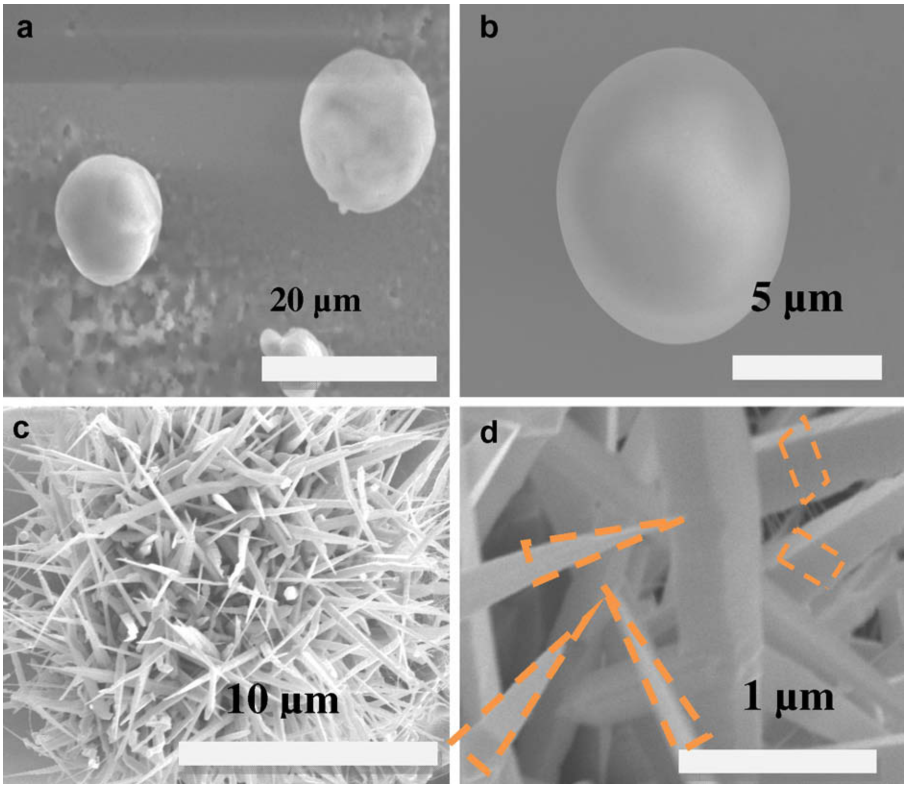

Fig. 2. Low and high magnified FESEM images of (a–b) GaN microspheres and (c–d) sword-like GaN nanorods clusters.