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Self-organized formation and optical study of GaN micropyramids

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ABSTRACT

In this paper, we report the formation of GaN micropyramids via a self-organized process by ammoniating Ga_2O_3 powders at high temperature. The obtained GaN micropyramids are typically in wurtzite hexagonal structure, exhibiting six-fold symmetrical morphology and single crystalline characteristic. Cathodoluminescence (CL) studies demonstrated that a weak near-band-edge emission centered at ~385 nm and a broad yellow-band in the range of 500–800 nm were observed in the GaN micropyramids, and the related light emission mechanism was discussed based on the microstructure analysis.

1. Introduction

Semiconductor nanostructures with diverse shapes and morphologies have received extensive research interest in the past years due to their intriguing properties and technologically important applications in electronic fields [1–3]. Gallium nitride (GaN), with a wide direct band gap of 3.4 eV at room temperature, is an important III–V group semiconductor material and is of special interest and importance for its promising applications in high power laser, light-emitting diodes (LED) and detectors due to its excellent physical and chemical properties [4,5]. In particular, the nanostructured GaN materials with smaller size and huge surface area are ideal candidates for establishing building blocks for a variety of functional nanodevices such as nano-LED, nano-laser, nano-electron emitters and so on [6–8]. Because of its technological importance, extensive efforts have been devoted to the growth of various GaN nanostructures with controllable size, morphology and crystallinity. Among all GaN nanostructures, highly symmetrical pyramid-like GaN nanostructures are of great importance and have attracted special research interest due to their potential applications in geometry-dependent lasers, as well as their enhanced quantum efficiency [9–11]. Generally, the synthesis of GaN pyramids mainly relies on a complex growth process named selected area epitaxy (SAE) [12], which was carried out via metal-organic chemical vapor deposition (MOCVD) method. The GaN pyramids fabricated from this method are usually lateral epitaxial overgrown on sapphire substrate with SiO_2 mask. The dislocation existing in sapphire substrate can easily penetrate into the as-grown GaN crystal due to lattice and thermal mismatch even though it can be artificially controlled to spread horizontally [13]. In addition, the strain distribution along the axial direction of GaN pyramids is quite non-uniform and thus leads to the different optical emissions within the crystal, which strongly affects the performance stability of GaN-based optoelectronic devices [14]. Therefore, it is definitely required to search for an effective routine to synthesize GaN pyramids with improved crystal quality for the consideration of high-performance GaN nanodevices. Compared with the high cost and complex operability of MOCVD, self-organized CVD process provides a low-cost, effective and feasible approach for the realization of GaN pyramids with enhanced crystal quality and uniformity of light emission.

In this paper, we report the self-organized fabrication of GaN micropyramids with large yield and good crystal quality via a simple and low-cost chemical vapor deposition process. The GaN micropyramids exhibit typical 6-fold or multi-fold symmetrical morphology with a central axis along the *c*-axis of wurtzite hexagonal GaN. Cathodoluminescence (CL) measurement indicated that the GaN pyramid film possessed two broad emissions, a near-band-edge (NBE) emission centered at ~385 nm and another yellow band in the range of 400–900 nm.

2. Experimental

The GaN micropyramids were synthesized via a simple evaporation process of mixed Ga_2O_3 and GaN powders (1:1 in molar ratio) in NH_3 gas at high temperature, as reported elsewhere [8].

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In a typical experiment, well-mixed Ga_2O_3 and GaN powders were first loaded into a boat-like high-purity Al_2O_3 crucible, which was inserted into the center of a quartz tube (140 cm long, 40 mm in diameter). In the next step, a well-cleaned [1 0 0]-oriented Si wafer ($10 \times 10\,mm^2$) was placed on the graphite bulk, which is employed to improve the temperature homogeneity and thus depress the effect of the temperature difference within the substrate. The graphite bulk was set downstream of the quartz tube with a distance of ~10 cm from the central reaction source. The quartz tube connected with gas supplying system was then inserted into a resistance furnace and heated to 800 °C under the protection of Ar flowing with a rate of 200 standard cubic centimeters per minute (sccm). Pure NH_3 gas (300 sccm) was introduced to substitute Ar gas until the temperature reached 1150 °C. After reacting at 1150 °C for 1.5 h, yellow layers of GaN were found to deposit on the Si wafer and the product was collected for subsequent analysis. Morphology observation and structure analysis for the as-synthesized GaN micropyramids were carried out using scanning electron microscopy (SEM, JEOL, JSM-5600LV), X-ray diffraction (XRD RINT 2200) and high-resolution field emission transmission electron microscopy (TEM, FEI, Tecnai-G220) with an accelerating voltage of 200 kV. Compositional analysis was done with an energy-dispersive X-ray spectroscope (EDS) attached to the TEM. The cathodoluminescence (CL) spectrum was recorded at room temperature in a rebuilt CL chamber connected with a Hitachi S-4700 SEM.

3. Results and discussion

The structure and phase purity of the as-synthesized GaN micropyramid film were first examined by XRD measurement, as shown in Fig. 1. The majority of the diffraction peaks besides the one with $2\theta = 69.1$, which comes from the Si substrate, can be indexed into a wurtzite GaN with a hexagonal structure (space group $P63mc$, lattice constants: $a = 0.318$ nm, $c = 0.517$ nm), implying the high phase purity of as-synthesized GaN film. No obvious peak shift compared with that of standard GaN crystal was observed, and

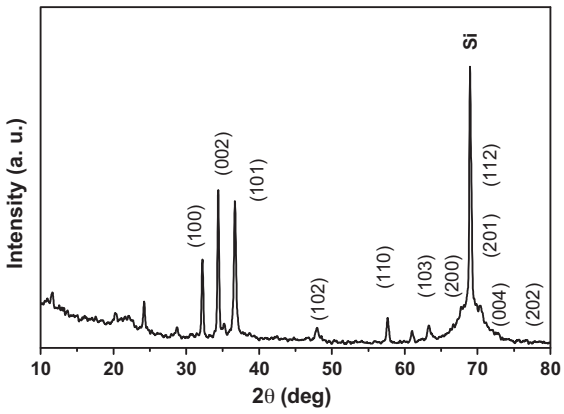

Fig. 1. XRD pattern of as-grown GaN micropyramids on Si substrate.

the lattice constants calculated from the XRD pattern are also in good agreement with the values of bulk GaN powders (see JCPDS NO: 65-3410), suggesting the bulk characteristic of as-synthesized GaN film. Different from previous epitaxial GaN pyramids grown on sapphire [15], in which the (0 0 0 2) peak showed strong diffraction intensity, the as-synthesized GaN micropyramid film exhibited a polycrystalline characteristic in XRD pattern, reflecting a random nucleation on the Si substrate, even though the individual GaN micropyramid is [0 0 1]-oriented along the *c*-axis.

Unlike the selected area growth of GaN pyramid arrays [9–12], which were formed through the epitaxial MOCVD method, the nucleation of GaN micropyramids synthesized in this work were obtained via a self-organized process. Fig. 2a shows the SEM image of a GaN micropyramid film after 30-min growth. It could be seen that all the Si substrate was covered with a high density of GaN pyramids. Typically, the GaN micropyramids are 6-fold symmetrical in shape and with an average size of ~2 μm. Different from the patterned growth of GaN pyramid arrays, which exhibit a preferential growth orientation perpendicular to the substrate, the

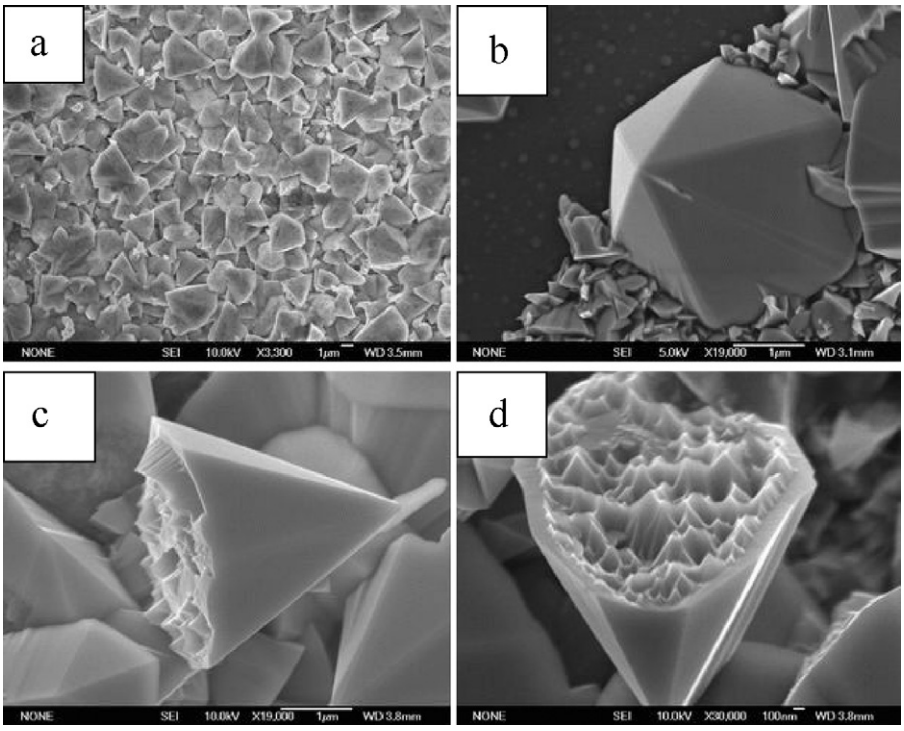

Fig. 2. (a) Low-magnification SEM image of GaN micropyramids; (b–d) representative SEM images of GaN micropyramids randomly grown on Si substrate.