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Hydride vapor phase epitaxy of strain-reduced GaN film on nano-island template produced using self-assembled CsCl nanospheres

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ABSTRACT

Thick GaN films were overgrown by HVPE on nano-island templates, which was fabricated by inductively coupled plasma etching using self-assembled CsCl islands as etch masks. The truncated cone-shape nano-islands exhibited significant effects on improvement of crystalline quality and reduction of crack density for subsequent GaN growth. Photoluminescence and micro-Raman measurements showed improved optical properties and partial strain relaxation in the overgrown GaN when compared to that grown on as-grown template, originated from the initial selective growth. Compared to conventional epitaxial lateral overgrown GaN, the economic and rapid method would put forward new promising pathway to fabricate high quality GaN.

1. Introduction

GaN and its related alloys have attracted much interest in recent decades because of their wide bandgaps, excellent physical properties and chemical stability. Nitride-based devices such as light emitting diodes (LEDs) and field effect transistors (FETs), have became commercial realities relying on heteroepitaxial approaches by employing a variety of foreign substrates including sapphire, silicon carbide and silicon. However, their performance is significantly limited by the structural quality of these materials as a result of well-known disadvantages of the heteroepitaxy. To solve these problems, special approaches have been developed such as epitaxial lateral overgrowth (ELO) and pendeoepitaxy techniques [1–3]. Nevertheless, in these conventional methods with micrometer masks, *ex situ* SiO_x or SiN_x deposition and multi-step photolighography are required, which increase the process's complexity and cost.

Recently, a new nonlithographic nanoheteroepitaxy technique, taking advantage of three-dimensional stress relief mechanisms, is expected to exhibit a further improvement of GaN epilayer quality [4–5]. Furthermore, in view of uniformity in a large area for the overgrown GaN films, nanometer-scale feature sizes and spacings play important roles in uniform distribution of threading dislocations (TDs) in the epilayers compared with the conventional ELO. For example, Fu et al. [6] reported the reduction of TDs in GaN layer on nanoporous TiN networks. Chen et al. [7–8] prepared crack-free GaN grown on AlGaN/(111)Si micropillar array by polystyrene microsphere. Likewise, Wang et al. [9–10] also presented the similar results using anodized aluminum oxide (AAO) film as membrane. In this letter, we describe a novel technique to obtain uniform GaN nano-island arrays by inductively coupled plasma (ICP) etching of GaN film through self-assembled CsCl nanoislands as etch masks. The method is economic, controlled and rapid, and may be extensively applied in the fabrication of semiconductor nanostructures in the future. Subsequent overgrowth of thick GaN film is carried out on highly ordered template by hydride vapor phase epitaxy (HVPE) method. GaN epilayer grown on nano-island template shows improved crystalline quality and effective stress relaxation via nanoepitaxial lateral overgrowth (NELO) process.

2. Experiments

A 3.0 μm thick GaN was first grown on *c*-plane sapphire substrate using metal organic chemical vapor deposition (MOCVD) in a Veeco P125 system. A schematic of the fabrication process of nano-pattern template was shown in Fig. 1(a–c). Firstly, a CsCl thin layer with a thickness of 80–350 nm was deposited on GaN surface at room temperature by thermal evaporation in vacuum 0.01 Pa using a homemade vacuum equipment. Then, on exposure to water vapor, nanosize hemispherical islands were formed, driven by the size-dependent solubility of CsCl. [11–12] Here, CsCl nano-islands with the average size ranging from 150 to 650 nm were obtained at relative humidity of 40–50% within 20–50 min, following a coverage ratio of 30%. Subsequently, these samples were transported to an ICP chamber and etched for 160–220 s with 450 W power, 75 bias power, and 4 mTorr chamber pressure and then dipped into deionized water for 5 min to remove remaining CsCl

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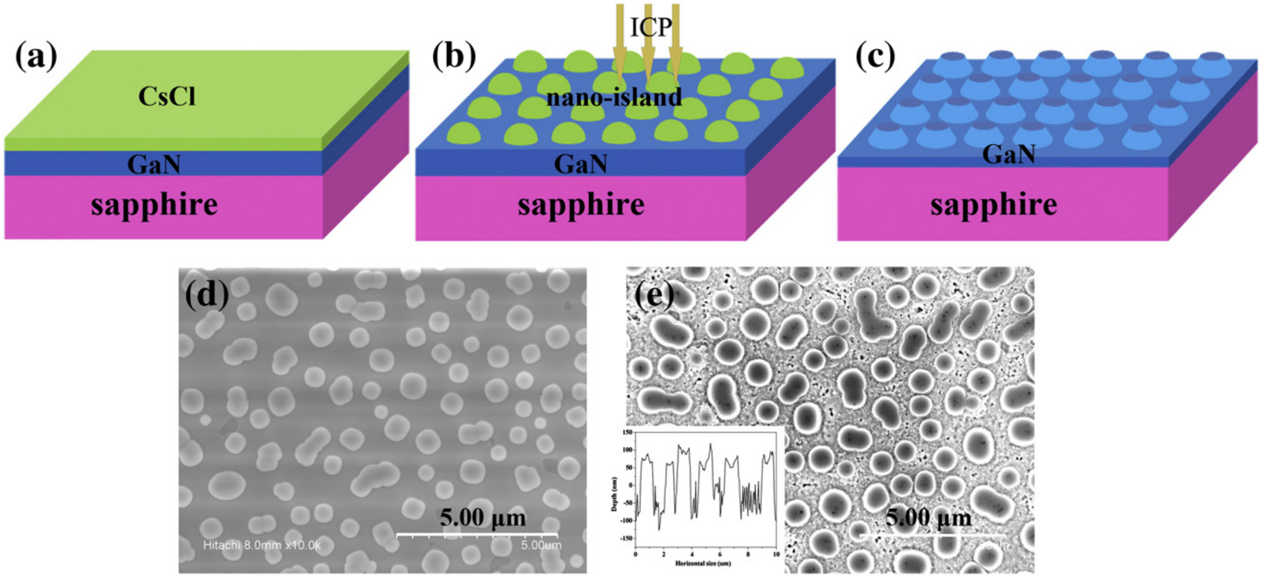

Fig. 1. (a–c) Fabrication flowchart of nano-island template using CsCl hemispheres as an etch mask. SEM top views of the morphology of (d) CsCl nano-islands and (e) nano-island template with an average size of about 650 nm.

islands. Thus, the nanostructures were transferred by ICP dry etching and separate island-shaped GaN surface structure was formed. Fig. 1(d) presents the top-view SEM morphology of the representative self-assembled CsCl islands with an average diameter of about 650 nm. After the ICP etching process, the truncated cone-shape nano-islands have been formed on the GaN template surface. As shown in Fig. 1(e), the height of truncated cone-shape nano-islands is approximately 180–200 nm, determined by the time of ICP etching.

Afterwards, the nano-island templates were immediately loaded into the home-designed vertical HVPE reactor. In the subsequent growth process, HCl diluted by N_2 reacted with liquid Ga at 850°C to form GaCl gas and was then transported into the growth zone where it directly reacted with NH_3 at temperature of 1050°C at atmospheric pressure. The NH_3 flow rate was held in the range of 3000 sccm, while the HCl flow rate was typically 80–100 sccm. The total flow rate of the NH_3/N_2 mixture passing the NH_3 inlet was fixed to 4 L/min. Total flow rates of $GaCl/N_2$ via the showerheads were 5.5 L/min. In addition, 4 L/min main N_2 flow to drive reactants and purge the complete reactor was used from the reactor bottom. Finally, an approximate 50 µm thick GaN film was obtained at a typical growth rate of 50–60 µm/h. The morphology of thick GaN films was analyzed by scanning electronic microscopy (SEM), Nanoscope III atomic force microscopy (AFM) and optical microscopy. Crystalline and optical properties of films were evaluated by high-resolution X-ray diffraction (HRXRD), photoluminescence (PL), and micro-Raman scattering.

3. Results and discussion

As shown in Fig. 2, the full-width at half maximum (FWHM) values of (0002) peak for GaN epilayers grown on the nano-island template exhibit a significant reduction compared that on as-grown template. Similar to previous reports [13], the partial bending of vertical TDs causes the dislocation reduction in the subsequent HVPE growth, following the different growth rate on the truncated cone-shape islands and flat area before full coalescence. Furthermore, a further improvement of GaN epilayers in the efficacy of the nano-epitaxy is observed as the nano-island diameter is increased, only 134 arcsec for GaN grown on 650 nm nano-template. It is also noted that the density of nano-islands varies from 9.1×10^8 to 7.8×10^7 cm^{-2} as the average size of nano-islands increases from 150 to 650 nm. Here, FWHM values of GaN epilayers scale inversely proportional to the size of nano-islands because dislocations are easily regenerated upon the GaN coalescence between the nano-islands [14]. More nano-islands lead to more coalescence events, which lead to dislocation formation.

Fig. 3(a–c) illustrates the typical optical micrographs of GaN films grown on different templates. For the GaN layer grown on as-grown template, lots of cracks are formed as network and comprised of three sets of parallel arrays at 120° to one another [15]. Unlike the GaN layer on Si, such a crack phenomenon is arisen not by excessive biaxial tensile strain, but large compressive stresses in the GaN induced thermal mismatch. By using the nano-island template, crack density is greatly reduced in the GaN epilayer and even absent over the entire area for 650 nm template as shown in Fig. 3(c). Taking these results into account, it would be expected that nano-islands help to reduce the compressive stress in the GaN epilayer. In addition, it is also worth noting that in SEM images, the GaN surface of all samples is featureless and there is no indication of the presence of the cracks seen in optical micrographs. Thus, it can be concluded that the cracks lie within the film and rarely extend to the top surface.

Further insight into nature of the cracks is revealed in cross-section of GaN film in Fig. 3(d–e). These cracks originate from the interface between HVPE GaN and template, propagate along c-axis and do not extend to the top of film. Here, the cracks are slightly enlarged by etching of H_2SO_4 due to stable prismatic $(11\bar{2}0)$ facets. After etching, hexagonal pyramids with $\{11\bar{2}2\}$ family planes are produced at the interface near to sapphire, which has been observed in etching of N-polar

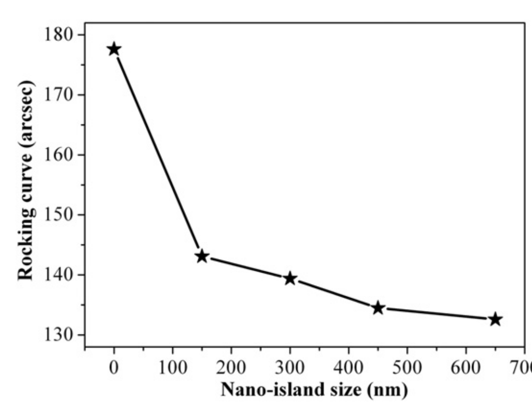

Fig. 2. FWHM values of (002) reflection peaks of thick GaN epilayers on the nano-island templates vary with different island diameters and as-grown template.