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GaN on Si-rich SiN_x-coated sapphire at different growth stages: The surface morphologies and optical properties

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Abstract

Distinct GaN islands of triangular base were formed during the annealing processes of GaN nucleation layers grown on Si-rich SiN_x nanoislands patterned sapphire substrates due to enhanced diffusion and regrowth anisotropy. Subsequent high temperature growth of GaN epilayers on the nucleation layers resulted in island coarsening and shape variations from triangular to hexagonal due to the dominating gas phase transport growth mechanism and limited diffusion length. Further growth with high V/III ratios resulted in layer-growth of atomic flatness. The atomic force microscopy, X-ray diffraction, and photoluminescence studies showed a significant improvement of the crystalline qualities and enhancement of the optical properties.

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1. Introduction

The epitaxial growth of III-nitrides usually induces high density of threading dislocations typically on the order of 10^9–10^{11} cm^{-2}, which have deleterious effects on the optical properties, reliability, and lifetime of the fabricated optoelectronic devices. Several methods, e.g. low-temperature (LT) GaN, AlN, InN, or multiple buffers [1–4], facet controlled epitaxial lateral overgrowth [5,6], selective area growth [7,8], pendeoepitaxy [9], epitaxial lateral overgrowth (ELO) [10,11], have been employed to reduce the dislocation density. Conventional methods by means of LT AlN or GaN buffers are relatively technically simple [1,2]. While the topic of LT buffers for better crystalline qualities (e.g. reduction of initial nuclei density and increase of grain size, improvement of crystallite alignment, grain structure, etc.) has been widely and intensively studied [12–15], it is still difficult to grow GaN films of very low dislocation density (e.g. 10^7 cm^{-2}) by use the of the conventional method. As one of the most effective techniques, ELO can reduce dislocation density to mid 10^6 cm^{-2}. However, traditional ELO requires complicated *ex situ* lithography process (e.g. deposition of dielectric masks followed by partial etching) with risk of contamination. Furthermore, thick GaN layers on the order of 10 μm have to be grown for full coalescence and surface smoothing, and thus ELO is generally time-consuming and expensive though the quality of ELO-grown GaN is highly attractive. Recently, nanoscale ELO was proposed and demonstrated by means of patterning nanoporous dielectric masks on GaN templates or directly forming nanoporous GaN templates followed by lateral overgrowth [16–18]. In view of the nanoscale windows, nanoscale ELO is expected to have faster and more uniform coalescence of neighboring nanoislands and possible reduction of strain and misorientation between these nanoislands. However, in most of the nanoscale ELO *ex situ* lithography has to be employed for nanopatterning. Further studies are needed for understanding, well control, and facilitation of the nanoscale ELO.

Recently, *in situ* SiH_4 treatment after or prior to the growth of LT GaN buffer has been used to improve the crystalline qualities and optical properties of GaN films [19–27]. The *in*

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situ patterning of nanoporous SiN_x layer has been proposed to be a promising *in situ* nanoscale ELO method with advantages of no *ex situ* processing and fast coalescence. However, as far as we know, detailed studies about the relationship between the SiN_x treatment chemistry and the growth mechanism, surface morphologies, and optical properties of GaN films have not been presented. In this study, we performed epitaxial growth of GaN films on Si-rich SiN_x nanoislands patterned c-sapphire substrates and investigated the SiN_x treatment chemistry, the surface morphologies and optical properties of GaN epilayers at different growth stages.

2. Experimental details

The sapphire substrates were prepared by thermal cleaning at 1060 °C and 1.33×10^4 Pa for 8 min under H_2 ambient (8000 sccm) followed by nitridation at 550 °C for 4 min in a close coupled showerhead planetary reactor of the Thomas Swan metalorganic chemical vapor deposition (MOCVD) system. Before the GaN growth an incomplete SiN_x layer was *in situ* predeposited by introducing 20–40 sccm SiH_4 (100 ppm) and 2000 sccm NH_3 into the reactor simultaneously with 5500 sccm H_2 as the carrier gas. Growth at low temperature with low NH_3/SiH_4 ratio and H_2 ambient was used for patterning Si-rich SiN_x nanoislands on the substrate surface. On the SiN_x-coated sapphire a conventional 25 nm LT GaN nucleation layer (NL) was grown at 535 °C and 6.66×10^4 Pa followed by a high temperature (HT) annealing process. The subsequent growth of HT GaN epilayers was carried out at 1035 °C and 1.33×10^4 Pa using trimethylgallium and high-purity ammonia as the source precursors and hydrogen as the carrier gas. Low V/III ratio was used in the initial growth stages of HT GaN for enhancement of island growth and improvement of the crystalline quality. To study the growth processes of GaN on the Si-rich SiN_x patterned sapphire substrates, different growth stages of GaN films were prepared by varying the growth time and other growth conditions. An interferometer was used to *in situ* and *real time* monitor the growth stages by directly measuring the time-dependent reflectivity from epilayers. The surface morphologies of SiN_x layers, LT GaN NLs, and HT GaN films at different growth stages were investigated by atomic force microscope (AFM, PicoSPM and PSI XE-100) and scanning electron microscope (SEM, LEO1530) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford Instrument). The SEM-EDX operating voltage is 20 kV and the collection time is 50 s. Different spot areas have been measured for consistency. The EDX hardware gives high quality, stable output for accurate, automatic peak identification, and standardless, quantitative analysis. The surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantum2000) and also SEM-EDX. The crystal structure was characterized by X-ray diffraction (XRD, PHILIPS X'Pert PRO and Bede QC200) rocking curve measurements with Cu Ka line as the X-ray source. The photoluminescence (PL) excited by a 325 nm He–Cd laser was measured at low temperature (77 K) and room temperature (RT) for GaN islands and films prepared on sapphire substrates.

3. Results and discussion

3.1. In situ Si-rich SiN_x patterning

The surface morphology of SiN_x layers greatly depends on the growth conditions such as growth temperature, pressure, NH_3/SiH_4 ratio, and growth ambient. In previous studies where porous structure was observed, either a mixture of N_2 (surfactant effect) and H_2 or high NH_3/SiH_4 ratio or HT growth with high NH_3 dissociation rate were used [19,23,27]. In this study, very low NH_3/SiH_4 ratio with high flow rate of H_2 as the carrier gas was applied during the growth of SiN_x layers at low temperature. In Fig. 1(a) we show the surface morphology of the SiN_x layers. The average size, height, and density of the SiN_x islands are ~100 nm, ~2 nm, and $\sim1.6\times10^9$ cm^{-2}, respectively. The application of low NH_3/SiH_4 ratio, low-temperature growth, and use of high flow rates of H_2 as the carrier gas (antisurfactant effect) are likely responsible for the formation of island-like Si-rich SiN_x layers.

Fig. 1(b) shows the XPS spectrum of the N1 s photoelectron peak. The peak can be fitted into three peaks: "surface N" (NO, AlNO, etc.), "SiN_x", and "AlN". The emergence of "SiN_x" has indicated the formation of SiN_x layer due to the Si-rich SiN_x patterning. By doing SEM-EDX measurements we found that at the island sites Si was detectable whereas at the other sites Si was not detected. Therefore we conclude that the substrate surface was partly covered by the SiN_x islands. In Fig. 1(c) we show the XPS spectrum of the Si2p photoelectron peak. The peak can be fitted into three peaks corresponding to "SiN_x", "Si", and "SiAl", respectively. Apparently by comparing the fitted peak areas of "SiN_x" and "Si", the SiN_x layers were found to be Si-rich with a Si/N ratio of ~3.2. The existence of excess Si is expected to be incorporated into GaN at the subsurface Ga substitutional sites. More Ga-rich surface would be formed and thus the diffusion barrier would be reduced [28–32]. Furthermore, Si-doping would play roles in the compressive strain relaxation for GaN on sapphire [33,34]. As a result, the generation of misfit dislocations would be suppressed by the Si-doping induced strain relaxation and enhanced diffusion.

3.2. MOCVD of GaN at different growth stages on Si-rich SiN_x-coated sapphire

Fig. 2 shows the *in situ* reflectance data during the growth of GaN films on sapphire substrates without and with Si-rich SiN_x treatment. In the figure, "S1" and "S2" denote the reflectance curves for GaN growth on sapphire substrates with SiN_x treatment time of 0 s and 400 s, respectively. The SiN_x deposition conditions have been described above. Obviously after SiN_x treatment the recovery time (the time for the reflectance intensity to reach the plateau of maximum oscillation amplitude) increases for ~1600 s. This indicated the increase of surface roughness at the initial growth stages when Si-rich SiN_x treatment was applied. The nucleated GaN island size increased accompanied by a reduction of island density. During the subsequent HT growth of GaN films these larger islands are expected to coalesce with lower defect density. The increase of