Silicon-Induced Strain Relaxation and Enhanced Gallium Surfactant Effects on Gallium Nitride Island Shaping

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The self-organization of large-scale uniform aligned three-dimensional GaN nanoislands with triangular (0001) and distinct sidewall faceting has been realized by metal organic vapor-phase epitaxy on in situ Si-rich SiN nanoislands patterned c-sapphire substrates. We find that the GaN island shaping is closely related to the SiN pretreatment chemistry. It is suggested that enhanced surface Ga surfactant effects and compressive strain relaxation caused by site exchanges between excess Si and subsurface Ga atoms are responsible for the distinct triangular island shaping with large lateral size, smooth sidewall facets, and sharp triangle corners. Photoluminescence studies also show Si-doping-induced compressive strain relaxation and improved crystalline qualities for triangular GaN islands grown with the Si-rich SiN pretreatment.

I. Introduction

Self-organization of semiconductor nanostructures,1–3 especially for GaN-based materials,3–11 has attracted intense research interest due to the potential applications in nanoscale short-wavelength optoelectronic devices.12–16 Syntheses of various GaN nanostructures have been realized by use of Stranski–Krastanov growth,4 metal catalysts,5–9 metalorganic chemical vapor deposition system. The c-plane sapphire substrates were thermally cleaned at 1060 °C and 100 Torr for 15 min under H2 ambient followed by flowing 5000 sccm NH3 at 545 °C for 4 min. After nitridation the SiNx patterning was performed by introducing SiH4 (100 ppm, 40 sccm) and NH3 (2000 sccm) into the reactor simultaneously with H2 as the carrier gas (5500 sccm).18 Low-temperature growth with low NH3/SiH4 ratio and H2 ambient was employed for patterning Si-rich SiNx nanoislands on the substrate surface. On the in situ patterned substrate surface 25 nm GaN layers were grown at 535 °C and 500 Torr under Ga-rich growth conditions with trimethylgallium/NH3/H2 flow rates of 15/1700/7500 sccm.21 During the annealing process,26 the temperature was first ramped to 1035 °C in 400 s without changes of pressure and flow rates of NH3/H2. After the temperature reached 1035 °C, the reactor temperature was decreased to 300 Torr in 120 s with a H2 flow rate of 6000 sccm. The surface morphologies of SiNx layers and GaN layers were investigated by an atomic force microscope (AFM, PicoSPM and PSI XE-100) and a scanning electron microscope (SEM, LEO1530) equipped with an energy-dispersive X-ray spectrometer (EDX). The surface elemental information was characterized by X-ray photoelectron spectroscopy (XPS, PHI Quantum2000) and SEM—EDX. The photoluminescence (PL) excited by a 325 nm He–Cd laser was measured at low temperature (77 K) and room temperature (RT) for the GaN nucleation layers (NLs) prepared on sapphire substrates of different treatment methods.

II. Experimental Methods

The experiments were performed in a Thomas Swan metal organic chemical vapor deposition system. The c-plane sapphire substrates were thermally cleaned at 1060 °C and 100 Torr for 15 min under H2 ambient followed by flowing 5000 sccm NH3 at 545 °C for 4 min. After nitridation the SiNx patterning was performed by introducing SiH4 (100 ppm, 40 sccm) and NH3 (2000 sccm) into the reactor simultaneously with H2 as the carrier gas (5500 sccm).24 Low-temperature growth with low NH3/SiH4 ratio and H2 ambient was employed for patterning Si-rich SiNx nanoislands on the substrate surface. On the in situ patterned substrate surface 25 nm GaN layers were grown at 535 °C and 500 Torr under Ga-rich growth conditions with trimethylgallium/NH3/H2 flow rates of 15/1700/7500 sccm.25 During the annealing process,26 the temperature was first ramped to 1035 °C in 400 s without changes of pressure and flow rates of NH3/H2. After the temperature reached 1035 °C, the reactor pressure was decreased to 300 Torr in 120 s with a H2 flow rate of 6000 sccm. The surface morphologies of SiNx layers and GaN layers were investigated by an atomic force microscope (AFM, PicoSPM and PSI XE-100) and a scanning electron microscope (SEM, LEO1530) equipped with an energy-dispersive X-ray spectrometer (EDX). The surface elemental information was characterized by X-ray photoelectron spectroscopy (XPS, PHI Quantum2000) and SEM—EDX. The photoluminescence (PL) excited by a 325 nm He–Cd laser was measured at low temperature (77 K) and room temperature (RT) for the GaN nucleation layers (NLs) prepared on sapphire substrates of different treatment methods.

III. Results and Discussion

Figure 1a shows a typical AFM image (5 μm × 5 μm) of “200 s LT SiN,” pretreated substrate surface. In the figure the average island lateral size, island height, and island density are about 100 nm, 2 nm, and 1.4 × 109 cm−2, respectively. Figure 1b shows that at the island sites Si was detectable, whereas at

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the nonisland sites Si was not detected. This implies that the sapphire surface was not fully covered by the SiN\(_x\) layer. Furthermore, the XPS spectrum of the Si2p photoelectron peak in Figure 1c confirms that the SiN\(_x\) layer was Si-rich with a Si/N ratio of about 3.2. The peak broadening of the X-ray photoelectron peaks was due to weak signals from the as-investigated nonstoichiometric SiN\(_x\) nanoislands not fully covering the sapphire substrates.

In Figure 2a we show a 10 \(\mu\)m \(\times\) 10 \(\mu\)m AFM image for the surface morphology of annealed GaN layers grown on Si-rich SiN\(_x\) patterned substrate. A striking phenomenon of large-scale uniform aligned 3D islands of distinct triangular (0001) facets was observed. The line profile also shows that the islands are of island height of about 25 nm and have oblique sidewalls. The in-plane crystallographic alignment of the triangular base is in accordance with the (0001) sapphire substrate surface. The formation of triangular islands is due to the enhanced diffusion anisotropy.\(^{27-29}\) By performing SEM-EDX measurements we found that Si was detected at the GaN island sites, whereas it was not detectable at the nonisland sites. Without SiN\(_x\) patterning, i.e., GaN was grown on bare sapphire substrates. For sample A there was no SiN\(_x\) patterning, and for samples B and C the SiN\(_x\) patterning was prepared at low temperature (545 °C) for 200 and 400 s, respectively. For sample D the SiN\(_x\) patterning was performed at high temperature (HT, 1035 °C) for 400 s. The SiN\(_x\) deposition at high temperature is expected to have more efficient dissociation of NH\(_3\) and thus the SiN\(_x\) layers are expected to be less Si-rich. Typical AFM images for the surface morphologies of the four samples are shown in Figure 3. Islands of triangular base were observed for samples A-C. Without SiN\(_x\) treatment the triangular islands were nonuniform with rounded triangle corners (Figure 3a). With increase of the SiN\(_x\) treatment time to 200 s (Figure 3b) and 400 s (Figure 3c), the triangular GaN islands coarsened with a small reduction of island density from \(2.4 \times 10^{9}\) to \(1.3 \times 10^{9}\) and \(7 \times 10^{8}\) cm\(^{-2}\). The average side length of the triangles (estimated by one-third of the perimeter) is about 180, 240, and 330 nm, respectively. The change of island lateral size is consistent with that of island density for the same GaN deposition “thickness”. As an example we show a typical line profile crossing the triangular islands (inset in Figure 3b) from which the angles of the oblique sidewall facets can be measured. When “LT SiN\(_x\)” treatment time increased from 0 to 400 s, the GaN islands became even sharper at the triangle corners. Corresponding to Figure 3 we show in Figure 4 the typical 3D
AFM images (1 μm × 1 μm) of the surface morphologies. Obviously, without SiNₓ treatment the islands are domelike without distinct sidewall faceting (Figure 4a). With Si-rich SiNₓ treatment the islands in Figure 4b are pyramid-like with triangular bases and sidewall faceting, and the triangular pyramids in Figure 4c have flat and wide top facets and very distinct sidewall faceting.

Considering the atomic radius of Ga, N, and Si (1.26, 0.75, and 1.10 Å), incorporation of Si at Ga substitutional sites (Si Ga) is energetically favorable, whereas a large strain would be caused if Si is incorporated at the N sites (SiN) or interstitial sites. Under Ga-rich growth conditions, Si prefers subsurface sites rather than surface sites, and thus the “kicked out” Ga atoms may form Ga bilayers on the surface, which is expected to reduce the Ehrlich–Schwoebel (ES) diffusion barrier. 29,30 Therefore, considering the critical island size proportional to the limited adatom diffusion length, the islands coarsened with the increase of SiNₓ treatment time from 0 to 200 and 400 s; moreover, the reduction of the ES diffusion barrier has actually explained the reduction of island density because the formation of large islands by annihilation of very small islands becomes possible. Furthermore, the incorporation of Si into GaN relieves the compressive strain of GaN islands on sapphire and thus causes the variation of island shapes.23,31 By measuring the oblique angle α of the sidewall facets referring to the (0001) plane (see the line profile in Figure 3b), we found that without SiNₓ treatment the islands have steeper sidewalls of α_A ≈ 24°, whereas islands of samples B and C have α_B ≈ 16° and α_C ≈ 12°, respectively. The increase of the critical lateral island size and the decrease of the oblique angle of the island sidewall facets for the triangular islands with the Si-rich “LT SiNₓ” pretreatment have become an evidence for the Si-doping-induced strain relief and the enhanced surface Ga surfactant effect (in the following sections we will demonstrate the increase of “surface Ga” coverage when the Si-rich “LT SiNₓ” pretreatment was employed).

To further study the chemistry of the SiNₓ treatment process and the impact on island shaping, we prepared sample D grown under the same conditions as sample C except the deposition of SiNₓ layers was at high temperature. The surface morphologies of sample D are shown in Figures 3d and 4d. It is interesting that hollow islands instead of triangular compact islands were observed. To understand the drastic changes of GaN island shapes, we investigated the chemistry of the SiNₓ layers and GaN layers on substrates with different treatment methods.

Figure 5a shows the XPS spectrum of the Ga 3p photoelectron peak for GaN on sapphire substrates without SiNₓ patterning and under Ga-rich growth conditions. According to the XPS data book,32 the spectrum can be fitted into six peaks, P1 (109.2 eV), P2 (108.2 eV), P3 (107.2 eV), P4 (106.0 eV), P5 (105.0 eV), and P6 (104.0 eV), corresponding to Ga3p1/2 (Ga 2 O 3 ), Ga3p1/2 (GaN), Ga3p1/2 (Ga), Ga3p3/2 (Ga 2 O 3 ), Ga3p3/2 (GaN), and Ga3p3/2 (Ga), respectively. The fitted peak areas of Ga3p3/2 were kept as twice that of Ga3p1/2. After annealing, Ga droplets are generally accumulated on bare substrates due to the high decomposition rate of GaN at high temperature and Ga-rich growth conditions. After exposure to air, surfaces of Ga are partially oxidized to form Ga2O3. We define $X^{Ga}_{Gal2} = (S^{\alpha}_{p1} + S^{\alpha}_{p2})/(S^{\alpha}_{p1} + S^{\alpha}_{p2} + S^{\alpha}_{p3})$ and $X^{Ga}_{Gal3/2} = (S^{\alpha}_{p4} + S^{\alpha}_{p6})/
Here as a rough estimation for the coverage rate of “surface Ga” (including Ga droplets, adlayers, and oxidized Ga after exposure to air) in total Ga (including “surface Ga” and GaN) for the outermost surface layers of sample A, where $S$ denotes the fitted peak area. We get $X_{Ga_{1/2}}^A = X_{Ga_{3/2}}^A = 47\%$. For comparison, in Figure 5b we show the XPS spectrum of the Ga3p photoelectron peak for a GaN sample prepared under much less Ga-rich growth conditions on sapphire substrates without SiN patterning. We find a decrease of the “surface Ga” coverage rate to $X_{Ga_{1/2}}^S = X_{Ga_{3/2}}^S = 40\%$. Therefore, employment of Ga-rich growth conditions could increase the “surface Ga” coverage rate.

Figure 5c shows the XPS spectra (Ga3p and Si2p) of GaN grown on substrates with SiN pretreatment for 400 s at low temperature. In comparison with Figure 5, parts a and b, a small and broad new peak P7 (102.0 eV) corresponding to Si2p (SiN$_x$)
appears because of the Si-rich SiN$_x$ pretreatment. The “surface Ga” coverage rate increased to $X_{Ga1/2} > X_{Ga3/2}$ = 57%. This has become an experimental evidence that the presence of excess Si in Si-rich SiN$_x$ islands would induce the Si–Ga exchange process and thus further increase the “surface Ga” coverage rate, i.e., $X_{Ga} > X_{A} > X_{u}$. The increase of surface Ga coverage reduces the ES diffusion barrier and thus increases the critical diffusion length and critical island size (Ga surfactant effect).

Furthermore, the island edge adatoms would have higher probability to migrate and reach the triangle corners; hence, sharp triangle corners were formed (Figure 3c).

Figure 5d shows the XPS spectra (Ga3p and Si2p) of GaN grown on substrates with SiN$_x$ pretreatment for 400 s at high temperature. For HT SiN$_x$ treatment the intensity of P7 became very strong. This is consistent with the XPS spectrum of the Si2p photoelectron peak of SiN$_x$ layers deposited at high temperature (Figure 6). The formation of thick SiN$_x$ layers is due to the high dissociation efficiency of NH$_3$ and deposition rate of SiN$_x$ at high temperature. Meanwhile, in Figure 6 peaks P8 (99.3 eV) and P9 (96.5 eV) corresponding to Ga3p1/2 (Ga$_2$O$_3$), Ga3p1/2 (GaN), Ga3p1/2 (Ga), Ga3p3/2 (Ga$_2$O$_3$), Ga3p3/2 (GaN), Ga3p3/2 (Ga), and Si2p (SiN$_x$), respectively.

The RT PL of samples A, C, and D have also been measured and are shown in Figure 7. At RT the near band edge emissions are broad with a long tail of UV luminescence (UVL) possibly arisen from the surface structural defects and interface states. In comparison with samples A (without SiN$_x$ treatment) and D (with non-Si-rich “400 s HT SiN$_x$” treatment), a red shift of the GaN near band edge emissions was observed for sample C (with Si-rich “400 s HT SiN$_x$” treatment), which suggested Si-induced compressive strain relaxation of GaN on sapphire and luminescence from the distinct sidewall facets.

For further comparisons we also measured the LT PL of samples A, C, and D at 77 K. Clearly, as shown in Figure 8, the intensity peak of the band edge emission (hexagonal GaN) of the triangular GaN islands on Si-rich “400 s HT SiN$_x$” treated...
distinct sidewall faceting by means of in situ thin Si-rich “LT SiN,” nanoislands patterned on the c-sapphire substrates and growth of GaN under Ga-rich conditions. We find that the in situ pretreatment chemistry of SiNₓ on substrate has significant influences on the GaN island formation. The increase of “surface Ga” coverage rate caused by the Si–Ga site exchange and thus enhanced surface Ga surfactant effect resulted in the formation of GaN nanoislands with larger lateral size, smoother sidewall facets, and sharper triangle corners when the “LT SiN,” treatment time increased from 0 to 200 and 400 s. In addition to the surface Ga surfactant effect, intentional Si-doping via patterning of Si-rich SiNₓ nanoislands also relieved the compressive strain of GaN on sapphire and caused the variation of island shapes. Strain relaxation and enhanced surface Ga surfactant effects are responsible for the remarkable uniformity and distinct shaping of the strained islands. Photoluminescence studies showed Si-doping-induced compressive strain relaxation of GaN on sapphire and improved crystalline qualities for distinct triangular GaN islands on Si-rich “LT SiN,” treated sapphire. Further studies on optimization of the growth conditions of SiNₓ and GaN nanoislands for better regularity and crystalline qualities, the optical properties, and applications will be continued.

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Supporting Information Available: SEM and PL data of larger GaN islands of quasi-hexagonal and hexagonal base. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


IV. Conclusion

In summary, we have realized the self-organization of large-scale uniform aligned 3D GaN islands of triangular (0001) and


(33) See the Supporting Information.
