

Analysis of GaN Grown on Vertically Standing Fractal-Like Si Nanostructures

Qixun Wee¹, Keyan Zang², Chew Beng Soh², Soo Jin Chua^{*1,2} and Carl V. Thompson^{1,3}

¹ Singapore-MIT Alliance, E4-04-10, NUS, 4 Engineering Drive 3, Singapore 117576

² Institute of Materials Research & Engineering, 3 Research Link, Singapore 117602

³ Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139, USA

* Corresponding author: e-mail: elecsj@nus.edu.sg, Phone: +65 6516 4784, Fax: +65 6775 2920

ABSTRACT

We have investigated the microstructure and optical properties of GaN grown on vertically standing Si nanostructures by MOCVD. The array of Si nanostructures was formed by a simple metal-assisted etching of Si(111) substrates. The resulting nanostructures have size features ranging from 20 to 70 nm with fill-factor between 40-45%, and varying heights (200-800 nm) were formed across a single 2 inch Si wafer. It is found that the length of the Si nanostructures has a great effect on the microstructure of GaN grown on them. It is observed that continuous GaN film was formed on shorter Si nanostructures (< 240 nm), while discontinuous GaN was formed on longer Si nanostructures (~ 600 nm). It is found that the GaN film on Si nanostructures has reduced total dislocations density and lower tensile strain, when compared to GaN film on bare Si.

Keywords: electroless etching, gallium nitride, Si nanostructures, strain engineering, metalorganic chemical vapor deposition

1 INTRODUCTION

It is desirable to grow GaN on Si as this material system can lower the cost of manufacturing optoelectronic devices, since Si wafers are cheaper than the conventional substrate, sapphire. Si is also available in large wafer sizes, which leads to cost reduction from large scale manufacturing. However, growth of GaN on Si are associated with high tensile stresses, mainly due to the thermal mismatch. Strain engineering [1] is required for stress reduction. Previously, we have achieved improved GaN film quality by nanopatterning of Si(111) substrate to form nanopores, prior to growth [2]. GaN was observed to grow laterally across the nanopores, forming nano air-bridges. This lateral growth is known as nano-epitaxial lateral overgrowth (NELO). It is shown that the nano air-bridges offer strain relaxation to the GaN film. Since nanoporous Si surface provides strain relaxation, a Si surface with nanopillars will provide an even more effective strain relaxation. Hence, a MOCVD growth of GaN on separated vertically standing Si nanostructures was attempted. To the best of our knowledge, such growth has not been reported before. Although III-nitride growth had been carried out on porous Si [3, 4], growth on

fractal-like Si nanostructures is different as they are separated standing structures

2 EXPERIMENTAL

2.1 Preparation of Silicon Nanostructure Array Substrate

The fabrication of Si nanostructure array (see Figure 1) closely follows that of Peng et al. and Tan et al. [5, 6]. A single-side polished n-type Si (111) (phosphorus-doped, resistivity of 1-10 ohm-cm) was ultrasonically cleaned in acetone then in isopropanol, for 5 minutes each. The substrate was then rinsed with deionized water and dried with nitrogen. Next, to ensure no organic contaminants, the substrate was etched in piranha solution at about 200 °C for 10 minutes. The substrate was then rinsed copiously with deionized water. As piranha solution leaves Si with a layer of silicon dioxide, a short dip in 10% HF was done to remove it. An etching solution containing 5.0 M HF and 0.02 M AgNO₃ was prepared. The cleaned Si wafer was immersed into about 150 ml of the etching solution at 50 °C for 1 minute, with a PTFE coated magnetic stirrer beneath the wafer. After etching, the substrate was covered by a thick layer of silver dendrites which can be removed by immersing in a solution containing HNO₃, HCl and H₂O (1:1:1 volume ratio) at room temperature. The substrate was then rinsed with running deionized water and dried with nitrogen gas.

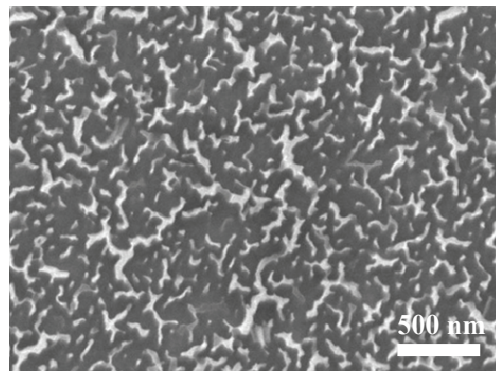


Figure 1: Top view SEM image of the fractal-like Si nanostructures. Feature size is 20-70 nm.

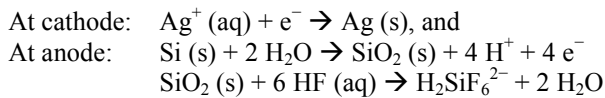
2.2 MOCVD Growth of GaN

GaN were subsequently grown on the substrate using the Emcore D-180 MOCVD system. A bare Si (111) wafer of the same grade was also placed in the same growth run for reference.

3 DISCUSSION AND RESULTS

3.1 Fractal-Like Silicon Nanostructures

Due to the aggressive reaction between Si and the HF/AgNO₃ solution [7], uniformity of the nanostructure height was a problem. This resulted in height variation between 200 to 800 nm. The chemical reaction can be described as an electrochemical reaction [7], where:



Hence, for every Si atom etched away, 4 Ag⁺ ions will be consumed. Assuming that nanostructures of about 800 nm in height were formed and they have a fill factor of about 40% (i.e. 60% of Si is etched away),

$$\begin{aligned} \text{Total volume of Si etched away} \\ &= \pi (2.54 \text{ cm})^2 \times 800 \times 10^{-7} \text{ cm} \times 60\% \\ &= 9.73 \times 10^{-4} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Total mass of Si etched away} \\ &= \text{Volume etched} * \rho_{\text{silicon}} \\ &= 9.73 \times 10^{-4} \text{ cm}^3 \times 2.3290 \text{ g/cm}^3 \\ &= 2.27 \times 10^{-3} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Total moles of Si etched away} \\ &= 2.27 \times 10^{-3} \text{ g} / 28.0855 \text{ g/mol} \\ &= 8.07 \times 10^{-5} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Moles of silver ions consumed} \\ &= 8.07 \times 10^{-5} \text{ mol} \times 4 \\ &= 3.23 \times 10^{-4} \text{ mol} \end{aligned}$$

Since 150 ml of the etching solution contains only 0.150 × 0.02 = 3 × 10⁻³ mol of Ag⁺ ions, 1 minute of etching (the etching time used) will consume about 10% of the Ag⁺ ions. Such high consumption rates of Ag⁺ ions affects the overall uniformity of the nanostructure. Since silver dendrites are formed when the ions are reduced [8], any region where the reaction takes place will encourage even more Ag⁺ ions to react, due to the presence of silver and high surface area of the dendrites. This positive feedback reaction contribute to the non-uniformity in height (200-800 nm). The resulting nanostructure has feature size ranging from 20 to 70 nm, and a fill factor of 40-45%. After GaN growth, 3 different regions are observed: specular, diffused and patchy (see Figure 2).

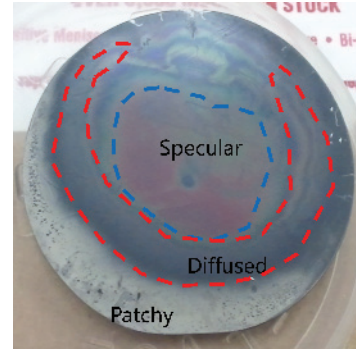


Figure 2: Photograph showing the different regions on the wafer.

3.2 Relation between GaN Morphologies and Height of Silicon Nanostructures

Figure 3 shows the SEM images of the three different regions on the wafer where GaN is grown on the fractal-like Si nanostructures. It can be seen that GaN on the specular region has fully coalesced to form a continuous film. GaN on the diffused region has not yet fully coalesced. For the patchy region, the GaN only manages to form isolated islands of various sizes, ranging from 1 to 7 μm. Another obvious difference between the cross-sectional SEM images, is that the Si nanostructures are buried by III-nitride in both the specular and diffused regions, whereas GaN grows only partially into the nanostructures for the patchy region. For nanostructures with height less than 300 nm, GaN can grow on the base of the nanostructures and bury the Si nanostructures altogether. However, if the height of the nanostructures is increased (to 600 nm, for example), GaN would not be able to bury the structures.

As such non-uniformity is not observed at all on the reference wafer, the non-uniformity must be derived from the height variation of the nanostructures. It can be inferred that to form a continuous GaN on Si nanostructures, the height should be 240 nm or less, if the size features are about 50 nm. It is also postulated that the gaseous precursors would have significantly reduced mobility when diffusing down the nano-sized gaps along the Si nanostructures for more than 300 nm.

3.3 Crystal Quality of GaN

TEM shows the alignment of the GaN crystal to the Si substrate. Inset of Figure 4 shows a selected area electron diffraction (SAED) pattern obtained in the specular region. It can be seen, from the diffraction patterns, that GaN crystal is aligned to the Si crystal (GaN(0002) // Si(111) and GaN(11 $\bar{2}$ 0) // Si(220)). The GaN crystal is also aligned for the diffused region. The SAED of GaN in the patchy region shows that GaN diffraction pattern forms circular arcs (see inset of Figure 5), indicating that the GaN is polycrystalline.

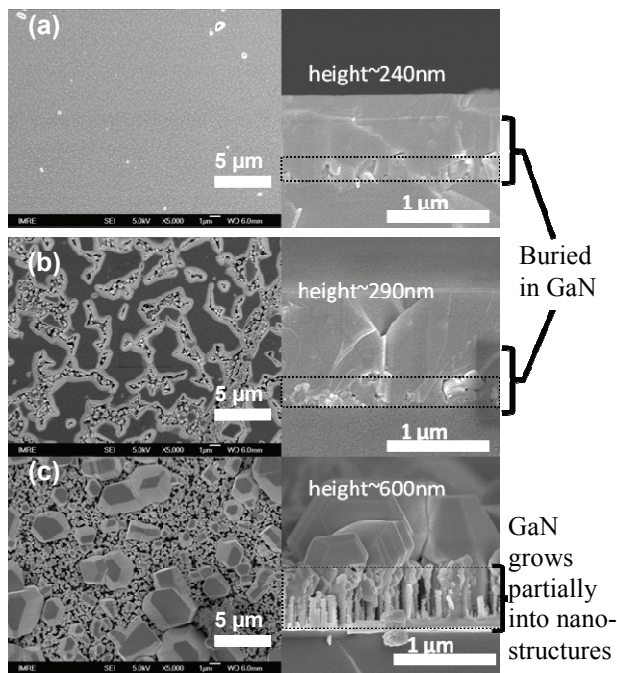


Figure 3: SEM images of (a) specular region GaN film, (b) diffused region GaN film and (c) patchy region GaN. Plan view is on the left and cross-sectional view is on the right.

The boxes in the cross-sectional view provide a visual guide to the average height of the nanostructures.

A six-fold symmetry in a phi-scan is seen in XRD measurement of GaN film in specular region, indicating that it is a single crystal. In the diffused region, a six-fold symmetry is also observed in a phi-scan, hence there is alignment of GaN crystal orientation (not single crystal because it is still discontinuous). Table 1 showed a compilation of the FWHM of rocking curves of GaN(0002) for the three different regions and for the reference bare Si. It can be seen that the reference bare Si has the narrowest GaN(0002) omega scan peak, hence lower screw and mixed dislocations [9, 10]. A note about the GaN in the patchy region: although TEM shows that the GaN is polycrystalline, we can still obtain a GaN(0002) peak signal because there is still alignment of the isolated GaN crystals' c-plane, collectively, to the Si(111) plane. However, it should be emphasized that the alignment is poor, as its GaN(0002) rocking curve is fairly broad.

Although GaN in the specular region has a larger FWHM rocking curve for GaN(0002) than GaN on reference Si, it has a lower dislocation density. Figure 6 shows the top view SEM images of both GaN in specular region and GaN on reference Si. The pits are threading dislocations which showed on the GaN surface. Estimated dislocation density for GaN in specular region and on bare Si are $5 \times 10^8 \text{ cm}^{-2}$ and $1.5 \times 10^9 \text{ cm}^{-2}$, respectively. This confirms that GaN on specular regions has less pure edge dislocations than GaN on bare Si.

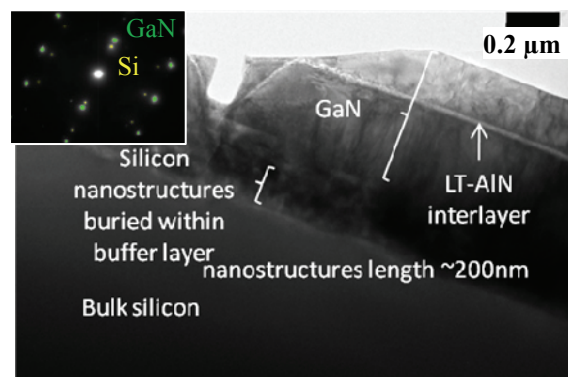


Figure 4: Cross-sectional TEM image of GaN in the specular region, and (inset) SAED pattern of the TEM. SAED shows that the single crystal GaN is aligned to the Si substrate, where GaN(0002) // Si(111) and GaN(11 $\bar{2}$ 0) // Si(220).

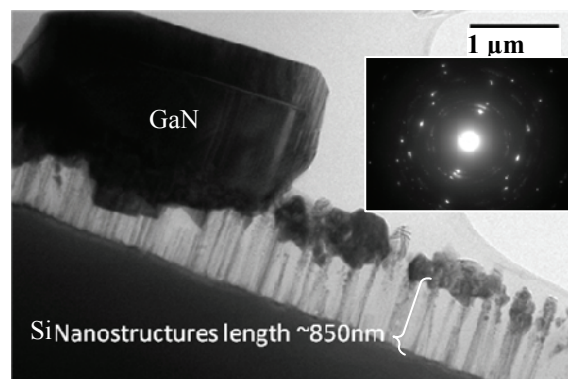


Figure 5: Cross-sectional TEM image of GaN in the patchy region, and (inset) SAED pattern of the TEM.

3.4 Biaxial Stresses in GaN

According to Tripathy et al. [11], Raman shift of $E_2(\text{TO})$ phonons of GaN can be used to determine the biaxial stress, where the shift $\Delta\omega = 4.3 \sigma_{xx} \text{ cm}^{-1} \text{ GPa}^{-1}$, and a red shift is related to tensile stress. Taking the $E_2(\text{TO})$ value of 567.5 cm^{-1} as stress-free (taken from $400 \mu\text{m}$ thick free standing GaN [11]), the biaxial stresses of GaN in specular, diffused and patchy regions are 0.47 GPa, 0.35 GPa and 0.12 GPa, respectively. The biaxial stresses of GaN on reference bare Si wafer is 0.58 GPa. All are in tensile biaxial stresses.

From the results, stress can be alleviated by inclusion of Si nanostructures in between the GaN film. Some of the thermal stresses created from the high temperature growth can be relieved by composite of Si nanostructures within GaN layer.

Samples	FWHM of XRD rocking curve of GaN(0002)	Dislocation density	E ₂ (TO) phonon peak	Stress in GaN*
Specular	49.9 arc-min	$5 \times 10^8 \text{ cm}^{-2}$	565.5 cm^{-1}	0.47 GPa (tensile)
Diffused	41.3 arc-min	N.A.	566 cm^{-1}	0.35 GPa (tensile)
Patchy	93.4 arc-min	N.A.	567 cm^{-1}	0.12 GPa (tensile)
Bare (reference)	28.1 arc-min	$1.5 \times 10^9 \text{ cm}^{-2}$	565 cm^{-1}	0.58 GPa (tensile)

Table 1: FWHM of the symmetrical rocking curve of GaN(0002) peak, dislocation density, E₂(TO) phonon peak and calculated GaN stress of the three regions and reference sample. *Taking E₂(TO) = 567.5 cm⁻¹ as stress-free.

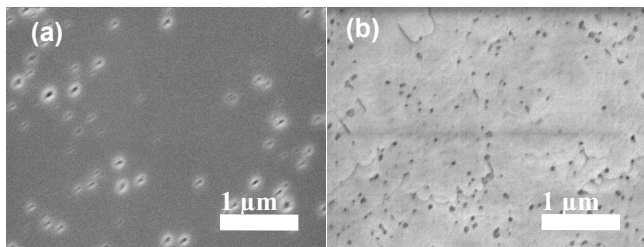


Figure 6: SEM image of top view of GaN on (a) specular region after hot phosphoric etch to reveal threading dislocations, and on (b) bare reference Si. Dislocation density of GaN on specular region and bare Si are estimated to be $5 \times 10^8 \text{ cm}^{-2}$ and $1.5 \times 10^9 \text{ cm}^{-2}$, respectively.

4 CONCLUSION

We have investigated the microstructure and optical properties of GaN grown on vertically standing Si nanostructures by MOCVD. The Si nanostructures array is formed by a simple metal-assisted etching of Si(111) substrates, where both metal deposition and Si etching occur simultaneously in one step, using HF and AgNO₃. The resulted nanostructures have size features ranging from 20 to 70 nm, and the fill-factor is between 40-45%. As the process has a tendency of non-uniform etching, nanostructures of varying heights were formed across a single Si wafer. It is found that continuous GaN film was formed on shorter Si nanostructures (< 240 nm), while discontinuous GaN was formed on longer Si nanostructures (~ 600 nm). It should be noted that III-nitride material completely filled in between the gaps of Si nanostructures for continuous film (specular region), while air gaps are still present for discontinuous film (patchy region). GaN in the specular region has a lower dislocation density, yet a larger FWHM GaN(0002) omega scan than GaN on flat Si. This suggests that the nanostructures induced more screw and mixed dislocations in the GaN grown on it, but reduced the overall total dislocations density and specifically much lower pure edge dislocations. Raman spectroscopy indicate that GaN grown on nanostructures are more relaxed than GaN on flat Si. Our research concluded that tensile strain and total dislocation in GaN is reduced by the fractal-like Si nanostructures.

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