Polarity selective etching: A self-assisted route for fabricating high density of c-axis oriented tapered GaN nanopillars

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(Received 8 March 2011; accepted 30 June 2011; published online 10 August 2011)

High density of c-axis oriented tapered GaN nanopillars are fabricated simply by exposing GaN epitaxial layers in argon–chlorine plasma without any prior lithographic processing. The nature and the formation process of the pillars are investigated by different optical and structural characterization techniques. Our study reveals that the pillars are columnar inversion domains with distinctly different optical properties as compared to the bulk. These are formed as a result of a polarity selective etching process. © 2011 American Institute of Physics. [doi:10.1063/1.3622142]

I. INTRODUCTION

GaN and its alloys with Al and In have been the focus of intense research for their application in various optoelectronic and electronic devices that operate at high temperatures, high powers, and high frequencies. Currently, GaN nanowires and nanopillars have attracted a lot of attention for their potential in the future nanoscale integrated electronic and optoelectronic devices. For instance, devices based on individual GaN 1D nanostructures, such as single nanowire light emitting diodes (LEDs), single nanowire high electron mobility transistors, photodetectors, and field emission transistors, to name a few, have already been demonstrated.1 However, in order to develop 1D nanostructure based full scale integrated electronics and optoelectronics, it is necessary to fabricate them with a narrow distribution of orientation, size, and length on top of a substrate. Different bottom-up techniques have been employed to achieve 1D nanostructures of GaN.2–5 However, they often show a broad distribution of size, length, and orientation. Alternatively, GaN nanopillars (or nanocolumns) are also prepared by top-down nanolithography routes.6,7 Periodic arrangements of nanopillars with narrow distribution of size and vertical orientation are reported using these approaches. However, these techniques involve several processing steps that in turn take a long time. There are reports of formation of c-axis oriented fine tip GaN nanopillars just by exposing the surface of a GaN epitaxial layer to argon/chlorine plasma in an inductively coupled plasma reactive ion etching (ICP-RIE) chamber without any prior lithography process.8–10 High density of c-axis oriented nanopillars (∼1010 cm−2) with tip diameter as small as 10 nm and height 700 nm has been reported using this process. It has been shown that the diameter of the tip as well as the density of the pillars can be controlled by adjusting the pressure inside the ICP-RIE chamber.10 However, the root cause for such a self-assisted fabrication process is yet to be understood.

Here, we have carried out a systematic investigation on the nature and formation process of the pillars fabricated by the above-mentioned (ICP-RIE) technique. The structural and the optical properties of the pillars obtained from GaN epitaxial layers grown by different epitaxial routes on different substrates are comparatively studied. Our study reveals that these pillars are the inversion domains (IDs) formed as a result of a polarity selective etching of the GaN layer by the reactive ion etching (RIE) process. Most interestingly, the optical properties of the pillars are found to be distinctly different from rest of the GaN layer.

II. EXPERIMENTAL

A commercial grade c-plane GaN layer of thickness 3 μm grown on a c-plane sapphire substrate by hydride vapor phase epitaxy (HVPE) was procured from Technologies and Devices International, Inc. Details about the growth can be found elsewhere.11,12 Another 600 nm thick c-plane GaN layer was grown on a c-plane 6H-SiC substrate using NH3 molecular beam epitaxy (MBE). Details about the growth can be found in Ref. 13. ICP-RIE equipment from SEMTECH Instruments GmbH Germany was used to carry out the RIE process, where chlorine and argon were used as etchant gases. During etching, the flow rates of chlorine and argon were maintained at 25 and 5 sccm, respectively. Unless otherwise stated, the chamber pressure, ICP power, and RF power were maintained at 2 mTorr, 350 W, and 325 W, respectively, for the samples studied here. Etching time was adjusted to 2 min for the HVPE sample and 1 min for the MBE sample. Under these conditions, the density of the pillars is found to be the maximum. Photoluminescence (PL) spectra were recorded with two different excitation sources—a continuous wave (cw) He–Cd laser source (wavelength: 325 nm) and a nanosecond pulsed dye laser (wavelength: 280 nm) pumped by a Q-switched nanosecond pulsed Nd:YAG laser. Photoluminescence microscopy was performed in an epifluorescence configuration using an inverted microscope where the 365 nm line of a mercury lamp (150 W) was used to excite the samples. The luminescence emerging from the sample was passed through a bandpass (425–475 nm) filter and subsequently imaged using a
CCD detector. In order to perform experiments on the isolated pillars, the RIE-etched sample was dipped in methanol and then kept in an ultrasonic bath for 5 min. The pillars were then separated from the base and a nanopillar suspension in methanol was formed. This colloidal suspension was drop-cast on a suitable substrate for further studies.

III. RESULTS AND DISCUSSIONS

A. Structural properties

Figure 1(a) shows the SEM image of the surface of the HVPE grown GaN sample taken after the reactive ion etching process, where a large density of $c$-axis (growth direction) oriented pillars is observed on the surface. The high level of orientation of the pillars is visible in Fig. 1(b) where the cross-sectional SEM image of the sample is shown. It is interesting to note that the pillars are quite homogeneous in their shape and size. More notably, these are almost of the same height, which suggests that these are formed as a result of a selective etching process: certain parts of the GaN layer are not affected by the RIE process while other parts of the layer are etched. Figure 1(c) shows the SEM top-view image taken with the sample kept at a slightly tilted position. This image is collected from a portion of the sample where the density of the pillars is relatively low. A hexagonal symmetry and a tapered columnar structure of the pillars are clearly visible in this image. The average tip diameter and the density of the pillars obtained by analyzing the top-view SEM images taken at different parts of the sample are found to be 22 nm and $3 \times 10^{10}$ cm$^{-2}$, respectively. The full width at half maximum of the tip diameter distribution (not shown here) is found to be only $\approx 5$ nm. Figure 1(d) shows the SEM scan taken for the MBE sample after the RIE process, where $c$-axis oriented tapered nanopillars are clearly visible.

Unlike in the HVPE sample, the pillars are narrower, have less density, and occur mostly in clusters. The diameter of the tip part of these pillars is too narrow to be measured by SEM. The diameter is thus estimated from the AFM scans taken on these pillars after drop-casting them on top of a freshly prepared mica surface, which reveals the tip diameter for this sample to be as small as $\approx 4$ nm.

Figure 2 shows the SEM surface images of different parts of the same HVPE sample after the RIE treatment with various ICP powers. The rest of the etching parameters are maintained at values stated earlier. Clearly, the density of nanopillars decreases as the ICP power increases. Note that at a power of 350 W, the base diameter of most of the nanopillars is found to be less than 100 nm. A few of the pillars are found to be even thinner with a base diameter as small as $\approx 50$ nm. One such pillar is encircled by a dotted line in Fig. 2(a). At higher ICP powers, the density of thinner pillars gradually decreases. Note that at an ICP power of 450 W (Fig. 2(b)) or 500 W - Fig. 2(c)], only those pillars are found to survive which have base diameter more than 100 nm. In Fig. 2(c), remains of a few thinner pillars are marked by arrows. These pillars are mostly etched and their base parts only exist. Finally, at an ICP power of 650 W most of the nanopillars are completely etched (Fig. 2(d)]. Only a few with a base diameter of more than 150 nm can survive. Note that the scale size in this panel (Fig. 2(d)) is 1 $\mu$m as compared to 300 nm for rest of the panels of this figure. The dependence of the density and the average diameter of the nanopillars on the etching conditions is further discussed in Sec. IV.

Figure 3 compares the SEM images of the surface of a RIE treated HVPE sample before (Fig. 3(a)) and after dipping it in 4 M aqueous solution of KOH for 4 min (Fig. 3(b)) and 10 min (Fig. 3(c)). It is observed that the average height of the pillars is reduced from 600 to 200 nm after 4 min of etching in KOH solution. After 10 min of etching, all the
pillars have disappeared from the surface. Additionally, the surface is found to contain a large density of hexagonal holes. These findings lead us to believe that the holes are generated as a result of an over-etching of the pillars below their bases. This highlights two important points: (1) while the pillars are etched by KOH solution, the rest of the layer is not etched and (2) the pillars extend even below their bases. Similar results are obtained in the case of pillars fabricated from the MBE grown sample (data not shown). It is well known that aqueous solution of KOH etches selectively the N-polar GaN while Ga-polar GaN is not etched by this solution, which has made this test an established technique to determine the polarity of GaN layers. The results of Fig. 3 thus strongly suggest that the pillars are the domains of N polarity, i.e., IDs, while the rest of the layer is Ga polar.

B. Optical properties

Figure 4(a) compares the normalized PL spectra obtained via cw laser excitation at 300 K for a reference HVPE sample (without RIE treatment) and the nanopillars obtained from the same sample after the RIE treatment. In the case of the reference sample, three distinct features in the

FIG. 3. (Color online) SEM scans with 45° surface orientation for a HVPE sample after the RIE process: (a) prior to the KOH etching, (b) after the KOH etching for 4 min, and (c) after the KOH etching for 10 min.

FIG. 4. Normalized PL spectra taken at 300 K on the HVPE sample before the RIE process (thick line) and on the nanopillars after casting them on top of a cleaned Si substrate (thin line) with (a) the cw laser excitation (λ = 325 nm) and (b) the nanosecond pulsed laser excitation (λ = 280 nm). (c), (d) PL images taken using a 425–475 nm bandpass filter for two HVPE samples (after the RIE process) where the pillar density is estimated from SEM analysis to be (c) \(10^8\) cm\(^{-2}\) and (d) \(10^{10}\) cm\(^{-2}\).
emission spectra are clearly visible; a near band edge UV band (peak: $\approx 3.33$ eV), a broad blue luminescence (BL) band (peak: $\approx 2.9$ eV), and a broad yellow luminescence (YL) band (peak: $\approx 2$ eV). Note that the intensity oscillation observed in the spectrum is a result of the interference of the luminescent light by the GaN/Air surface and the GaN/sapphire interface. It is noteworthy that the UV band shows a high energy shoulder at $3.4$ eV, which matches with the bandgap of $3.42$ eV of bulk GaN at $300$ K. The luminescence spectrum for the nanopillars is featured by the intense and broad BL band while the near band edge emission is relatively weak. Interestingly, no YL emission can be observed for the nanopillars. Figure 4(b) compares the normalized PL spectra obtained using a nanosecond pulsed laser excitation at $300$ K for the reference sample (before RIE) and the nanopillars. The near band edge UV luminescence that peaks at $3.4$ eV is clearly visible for both samples. Again, a strong BL band (peaking at $2.9$ eV) is only present in the spectrum for the nanopillars in contrast to the reference sample while the YL band is found to be absent for both. It should be pointed out that the shape of the PL spectrum obtained for the nanosecond pulsed laser excitation may be different from that for the cw excitation because the emission dynamics associated with the two excitations could be entirely different. Figures 4(c) and 4(d) show the PL microscopy images recorded for two RIE treated HVPE samples having different densities of pillars. Note that these images are obtained by collecting the PL between $425$ and $475$ nm. This range falls well inside the BL band observed for the pillars in our cw-PL study. Both the images are featured by a large density of bright spots scattered over a darker background. The density of the bright spots is more in the sample (Fig. 4(d)) where the density of the pillars is found to be higher (through SEM), suggesting that the BL indeed stems from the pillars. This clearly demonstrates that the pillars are the stronger centers for the BL emission as compared to the rest of the GaN layer.

The observations of Fig. 1 clearly suggest that the RIE process selectively does not etch certain columnar domains. These observations further suggest that these domains have a hexagonal in-plane symmetry and their density is $\approx 10^{10}$ cm$^{-2}$ in the epitaxial layer. A large density ($10^8$–$10^{10}$ cm$^{-2}$) of threading dislocations is commonly found in GaN epitaxy. On the other hand, the results of the chemical etching of the nanopillars by an aqueous solution of KOH (Fig. 3) suggest that the pillars are the N-polar domains, while the rest of the layer is Ga-polar GaN. This implies that the pillars are IDs. A large density ($\approx 10^{10}$ cm$^{-2}$) of columnar IDs extending from the interface to the film surface have been often observed in GaN layers grown by HVPE and MBE on sapphire substrates. The width of these domains is found to range from 3 to 20 nm in MBE films and from 20 to 100 nm in HVPE films, in agreement with our observation that the average width of the nanopillars is much less for the MBE grown samples ($\approx 10$ nm) as compared to the HVPE grown sample ($\approx 70$ nm). It is noteworthy that the MBE sample is grown on a 6H-SiC substrate, where the density of IDs is expected to be much less as compared to that reported for films grown on sapphire substrates. Indeed, the density of the pillars for our MBE sample is found to be much less than that for the HVPE grown layer on a sapphire substrate. Much higher density of pillars with narrow tip diameter ($<5$ nm) is thus expected for the GaN layer grown on a sapphire substrate by MBE.

**C. Mechanism**

GaN has a strong spontaneous polarization ($P = 0.29$ C/cm$^2$) along the c axis. Since $P$ is negative for the Ga-polar and positive for the N-polar GaN, a certain amount of negative and positive charges is expected to be spontaneously generated on the Ga-polar and the N-polar surfaces, respectively. If one considers an average width of 10 nm for the IDs, the amount of positive charges building up on the surface of an ID is $\approx 2 \times 10^{-15}$ C, which creates a potential barrier of $\approx 150$ keV for a Cl$^-$ or Ar$^+$ ion to approach within 1 nm from the surface. Since the kinetic energy per ion is few hundred eV, it is plausible that the positively charged reactive ions (Cl$^-$ and Ar$^+$) are repelled by the positively charged surfaces of the IDs and attracted toward the negatively charged surfaces of the Ga-polar regions. This could lead to a faster etching of the Ga-polar regions as compared to that of the IDs and result in the formation of the pillars (schematically shown in Fig. 5). Additionally, the tapered columnar structure of the pillars is likely to be a result of lateral etching of the pillars (also depicted in Fig. 5). Since the top part of the pillar is exposed to the plasma for a relatively longer period of time than the bottom part, the former is laterally etched more than the latter (Fig. 5). Figure 2 shows that the parts of the same sample, when treated with different ICP powers, result in entirely different densities of nanopillars. The density of the nanopillars is found to decrease with the increase of the ICP power. It is even found that at an ICP power of 650 W, hardly any pillar is formed. The average diameter of the pillars, on the other hand, is found to increase with the ICP power. Other RIE parameters, such as the chamber pressure, RF power, flow rates of chlorine and argon, as well as the time of etching, are also found to influence strongly the formation process of the nanopillars. We believe that the dependence of the density and the average...
diameter of the pillars on the RIE conditions results from a competition between the two etching rates; the lateral etching of the nanopillars and the vertical etching of the Ga-polar regions. The ratio between the two rates governs the density and the average diameter of the nanopillars. This ratio could be different at different RIE conditions. For example, if the lateral etching rate of the nanopillars is much larger than the vertical etching rate of the Ga-polar regions of GaN layer for a given set of RIE parameters, no pillars are formed.

PL study reveals a stronger BL emission from the pillars as compared to that of the bulk. On the other hand, the YL is strongly present in the bulk sample, while it is absent in the pillars. It is well known that both the BL and the YL result from certain types of defects. These findings thus suggest that the defects responsible for the BL are present in a large concentration in the domains. This conclusion is also consistent with the PL images shown in Figs. 4(c) and 4(d). It should be mentioned that the shape of the emission envelope for the BL band obtained by cw excitation is distinctly different for the pillars and the reference sample (before RIE). Moreover, in case of the pulsed laser excitation, the BL band is completely absent for the reference sample in contrast to the nanopillars (Fig. 4(b)). These findings suggest that the origin of the BL band observed for the nanopillars is likely to be different from that of the GaN layer. This is currently under further investigation.

FIG. 5. Schematic description of the etching process. The inset schematically represents the arrangements of the atoms in the Ga and N-polar (inversion domains) regions. Positions of the atoms are projected onto the (1-210) plane.

IV. CONCLUSION

A large density of highly c-axis oriented fine tip GaN nanopillars with a narrow distribution of size and height has been fabricated by simply exposing the surface of GaN epitaxial layers to argon/chlorine plasma in ICP-RIE without any prior lithographic processing. The tip diameter of the pillars is found to be as small as 4 nm in case of the sample grown by MBE on a 6H-SiC substrate, compared to \( \approx 22 \) nm for the sample grown by HVPE on a sapphire substrate. These pillars, for both cases, are identified as inversion domains and formed as a result of a polarity selective etching of the GaN layer by the RIE process. Optical studies reveal that the pillars are stronger centers for the BL as compared to the bulk. On the contrary, the intense YL band, which is strongly present in the GaN layers (before RIE), is absent in the pillars. The study therefore offers a way to separate the IDs from the bulk in order to understand their roles in governing the transport and optical properties of GaN.

ACKNOWLEDGMENTS

The authors acknowledge the partial funding received from the Department of Information Technology, Government of India, through the Center of Excellence in Nanoelectronic and the Department of Science and Technology, Government of India. The authors also thank U. Jahn and Oliver Brandt of Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany for providing the SEM support and the MBE grown GaN samples.

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