Heteroepitaxial growth of GaN on vertical Si{110} sidewalls formed on trench-etched Si(001) substrates

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Abstract

A maskless Si trench structure was developed to integrate **crystallographically non-polar GaN microstructures with semi-polar facets** on Si(001). GaN “fins” were preferentially grown by MOCVD on Si{110} trench sidewalls formed by deep reactive ion etching (DRIE) of Si(001) such that GaN(0001)//Si{110} and GaN(10-10)//Si(001), resulting in a non-polar crystal structure with respect to the Si(001) substrate surface. No masking layer was required to prevent GaN growth on the Si(001) top surface of the trenches, instead, it was found that GaN nucleated preferentially on the Si{110} trench sidewalls. GaN was also observed to nucleate at the top corner of the trenches due to Si etching and exposure of high-index Si facets during the pre-growth H₂ anneal. This undesired GaN nucleation was successfully suppressed by reducing the H₂ anneal time and/or increasing the growth temperature and decreasing the precursor V/III to enhance Ga-adatom diffusion. Cross-sectional TEM studies confirmed that the GaN fins were crystallographically non-polar with respect to the Si(001) substrate surface and were bounded by semi-polar and non-polar facets. The reported Si fabrication and GaN growth process shows promise for the integration of non-polar and semi-polar GaN microstructures on industry standard Si(001) substrates.

Keywords: A3. Metalorganic chemical vapor deposition; B2. Semiconducting III-V materials; B1. Nitrides; A1. Microstructures; A3. Selective epitaxy; A1. Non-polar crystal structure

Introduction:

GaN heteroepitaxy on Si substrates is desirable due to the large area, low cost, and highly developed Si wafer fabrication technology. Polar c-axis oriented GaN films are commonly grown on Si(111) due to the crystal symmetry match between Si(111) and GaN(0001). Si(001) is the more commonly used orientation in the Si microelectronics industry, however, leading to an interest in the growth of GaN on Si(001) to allow for on-chip integration of GaN-based and Si-based devices. The Si(001) orientation, however, lacks the appropriate atomic symmetry for the growth of GaN leading to two preferential rotational alignments of GaN(0001) on Si(001)[1]. Additionally, growth of non-polar and semi-polar GaN is of interest due to spontaneous and piezoelectric polarization fields oriented along the c-axis in polar GaN-based heterostructures[2]. These polarization fields separate electrons and holes in multiple quantum well (MQW) layers, which reduces the likelihood of radiative recombination of carriers and thereby reduces the emission efficiency of light emitting diodes (LEDs) and laser diodes (LDs)[2] [3]. The detrimental effects of internal polarization fields can be negated by utilizing non-polar GaN films.

The research presented here aims to address these issues by using vertically etched trenches to obtain crystallographically non-polar GaN microstructures on Si(001) substrates. Prior work reported growth of semi-polar GaN on Si(001) substrates using anisotropic etchants with lithographic masks to form trench structures with exposed Si(111) planes which make an angle of 54.7° with Si(001)[4] [5]. GaN was then grown off of the exposed Si{111} while SiO₂ or SiN_x masks were used to prevent growth on other exposed surfaces. The resulting GaN had semi-polar {10 $\bar{1}$ 1} facets that were tilted with respect to Si(001). To fabricate non-polar GaN on Si substrates, however, the GaN(0001) plane must be perpendicular to the substrate surface.

Tanikawa demonstrated growth of non-polar $(11\bar{2}0)$ GaN on Si(110) substrates by growing off of vertical etch-exposed Si(111) facets[6]. Kuryatkov used a similar approach to obtain submicron GaN growth on Si fins for the fabrication of nitride-based fin field effect transistor (FinFET) structures[7]. This prior work had in common the use of exposed Si(111) facets and the use of masking layers to prevent GaN growth on non (111) facets.

Studies by Won *et al.* presented growth of GaN on vertical Si pillar arrays that were etched into Si (111), (110) and (001) substrates[8]. It was found that the AlN buffer layer conformally coated the Si pillars regardless of orientation. In contrast, GaN grew preferentially on the AlN buffer layer on the sidewalls of vertical pillar arrays on Si(001) substrates such that GaN(0001)//Si{110}. Negligible GaN growth was observed on the Si(001) surface despite the lack of a masking layer. The results of Won *et al.* motivated the present study which investigated the use of vertical trench structures etched into Si(001) substrates for the fabrication of non-polar GaN on Si(001) substrates. The effects of processing conditions on growth selectivity were investigated to identify conditions that would result in GaN growth off vertical Si{110} trench sidewalls such that GaN(0001)//Si{110} with negligible GaN deposition on the top Si(001) surface. The results of this study show the viability of this approach for the incorporation of semi-polar faceted GaN microstructures with the microelectronics standard Si(001) orientation. Furthermore, fabrication of GaN microstructures is presented without masking of non-preferential planes, which reduces the fabrication complexity.

Experimental Methods:

Si trenches were fabricated on 4" diameter Si(001) wafers using a Bosch deep reactive ion etching (DRIE) process and optical lithography to define the trench arrays with a SiO₂ hard mask. The arrays were arranged in rectangular cells that were orientated with respect to the

wafer flats such that the trench sidewalls were of the {110} family of planes. A schematic cross-sectional diagram of the Si trenches including trench dimensions and the resulting GaN faceting is given in Figure 1. Substrates were ultrasonicated in acetone and isopropanol then rinsed in deionized water to remove organics on the surface followed by a 10 minute dip in hydrofluoric acid to remove the SiO₂ hard mask. The trenches were annealed in H₂ at the growth temperature prior to growth of AlN in a vertical, cold-walled metalorganic chemical vapor deposition (MOCVD) reactor. The H₂ annealing process was shown to reduce the Si{110} sidewall roughness caused by DRIE and remove any residual oxide left on the substrate after HF cleaning[8]. A 90 nm AlN buffer layer was then grown at 1100°C using trimethylaluminum and NH₃ precursors with flow rates of 10 µmol/min and 62 mmol/min, respectively. AlN buffer conditions were constant throughout all growths and AlN conformally coated the upper region of the trench structures where GaN growth occurred. GaN growth was performed between 1100-1170°C. The reactor pressure was held at 50 Torr for all growth segments. The trimethylgallium (TMG) flow rate was 7.8 µmol/min and the NH₃ flow rate was varied between 17.9 and 62.5 mmol/min to vary the precursor V/III between 2300 and 8000. GaN growth was performed for 90 minutes unless otherwise noted. A Hitachi S3000H scanning electron microscope (SEM) was used to study the faceting of GaN grown on Si(001) trenches post-growth. A JEOL 2010F transmission electron microscope (TEM) was used to study the crystal orientation and microstructure of GaN using bright-field imaging and selected area diffraction (SAD) patterns. TEM samples were prepared by mechanical polishing followed by focused ion milling.

Results and Discussion:

The effects of precursor V/III, growth temperature, and pre-growth anneal time on GaN nucleation and growth were examined as discussed below. Initial GaN growths were performed with a V/III of 8000, a growth temperature of 1100°C, and a 10 minute pre-growth H₂ anneal in order to mimic growth conditions used on pillar structures in previous work[8]. Figure 2a shows cross-sectional SEM of initial short duration (~17 min) GaN growth on Si(001) trenches. GaN was observed to grow preferentially on the Si{110} trench sidewalls while no growth was observed on the top Si(001) surface. The GaN faceting will be discussed further later. A top down image of the trenches (Figure 2b), showed the presence of additional GaN islands that appeared to form at the top corner of the Si trench as indicated by arrows in the figure. **These islands were not continuous along the length of the trenches, which may explain why they were not observed in the cross-sectional SEM image reported in Figure 2a.** The GaN grown on the Si{110} sidewalls did not extend vertically above the Si(001) plane. This was possibly due to the short GaN growth time or the presence of GaN islands at the trench corners which may have blocked the vertical propagation of sidewall nucleated GaN.

A longer growth (90 minutes) was performed with identical growth conditions to study the evolution of GaN nucleated at the trench sidewalls and GaN islands at the trench corners. Cross-sectional and top-down SEM images of the 90 min GaN growth are shown in Figure 2c and 2d, respectively. GaN was observed to have grown vertically above the Si(001) trench as well as laterally over the Si(001) trench forming a “fin” structure. The overgrown GaN appeared to have different faceting than the sidewall nucleated GaN which suggested a difference in crystallographic orientation between the two regions. TEM was performed on a cross-section of the GaN fins as shown in Figure 3 in order to study the crystallographic orientation of GaN

relative to the Si surfaces. Bright-field TEM and selected area diffraction (SAD) patterns showed three regions (labelled (a), (b), and (c)) with different crystallographic orientations of GaN present in the overgrown fins. Region (a) near the Si{110} sidewall was oriented such that GaN(0002)//Si{110} as was predicted based on the work by Won *et al*[8]. Regions (b) and (c) were crystallographically distinct and were observed in the overgrown GaN. The arrows in Figure 3 correspond to the orientation of the GaN[0001] direction in each region. In region (b), GaN was observed to grow in the [0001] direction off of the rounded top corner of the Si trench. In region (c), GaN grows with the [0001] direction at an angle relative to the Si(001) plane and the surfaces of this facet are terminated with primarily non-polar {10 $\bar{1}$ 0} (m-plane) and semi-polar {10 $\bar{1}$ 2} (r-plane) facets.

As shown in Figure 3, the Si trench corners were found to be rounded after growth which was possibly due to etching of the Si during the high-temperature pre-growth H₂ anneal. The pre-growth anneal, which was utilized to reduce sidewall roughness, was suspected to also have etched the corners of Si trenches exposing Si{111} facets resulting in GaN nucleation and growth of regions (b) and (c). A determination of the orientation of the exposed Si facet was attempted based on the relative angles of the c-axis of GaN in regions a, b, and c, however no matching Si facet could be determined. We believe this may have been due to a tilting of the exposed Si corner facets out of the plane of the TEM image which led to an erroneous angle as measured from the image. The exposed facet may be Si{111}, which is a well-known growth facet for c-plane GaN and which would be expected to lie out of plane of the given cross-sectional TEM image.

Two methods were developed to test the hypothesis of Si facet exposure at trench corners. One method was to reduce the length of the pre-growth H₂ anneal. Tilted cross-

sectional SEM images of growths carried out with 10 and 5 minute pre-growth anneal times are shown in Figure 4a and 4b, respectively. Rough faceting was observed on the top surface of the GaN fins after a 10 minute anneal due to the presence of multiple GaN regions at the trench corners, similar to the sample shown in Figure 3. Reducing the pre-growth anneal to 5 minutes resulted in GaN with a smooth inclined top facet and a cross-section similar to the sidewall growth shown in Figure 2a which suggested that the GaN nucleation originating at the trench corners had been suppressed. Small GaN nuclei were still observed at the corners of Si trenches in higher magnification top-down SEM images (not shown here). These corner nuclei did not block the vertical overgrowth of sidewall GaN, however, and reducing the pre-anneal time to 2 minutes further reduced the corner nuclei density.

It was also speculated that GaN nucleation and growth at the trench corners and on the top Si(001) surface could be suppressed by increasing the surface diffusion length of Ga adatoms, resulting in increased Ga diffusion across exposed corner facets to existing sidewall-nucleated GaN. Samples were grown using decreasing V/III ratios to increase the lateral diffusion length of metal adatoms on the Si(001) surface to test this hypothesis. It is understood that lowering the V/III ratio allows for longer lateral atomic diffusion lengths due to the increased residence time of Ga adatoms on the surface before reacting with NH_3 [9] [10]. A 10 minute pre-growth anneal was used for comparison to the initial growths shown in Figure 3. The V/III was varied from 5600 to 2300. At a V/III of 5600 (Figure 4(c)), the cross-sectional GaN fin structure was similar to that of previous samples grown with a V/III of 8000 (Figure 4(a)) and the top of the GaN fins were rough, indicating that multiple orientations were present along the trenches. The GaN fins grown at a V/III ratio of 3400 (Figure 4(d)) had smooth inclined facets and a cross-sectional shape similar to initially grown sidewall nuclei (Figure 2(a)) which

suggested that GaN fins originated solely from the Si{110} sidewalls. The GaN fins grown at a V/III of 3400 had rough faceting in the near-sidewall region. Decreasing the V/III further to 2300 resulted in smooth GaN fins that coalesced between the trench gaps (Figure 4(e)). Due to the width of the Si(001) trench facet ($\sim 7\mu\text{m}$), some GaN nucleation was still observed along the top Si(001) trench facet at a V/III of 2300 as can be observed in Figure 4e and Figure 5. The increased lateral diffusion of Ga adatoms, however, was still sufficient to prevent the formation of GaN islands at the corners of the Si ridge.

The smooth inclined facets and cross-sectional shape of the GaN fins grown at low V/IIIs and short H_2 anneal times suggested that they consisted of a single crystallographic orientation which originated at the Si{110} trench sidewalls. Cross-sectional bright-field TEM was therefore performed on the sample grown with a V/III of 2300 to accurately determine the crystallographic orientation of the overgrown GaN fins. TEM results are presented in Figure 5. No grain boundaries were observed in the GaN fin cross-section which indicated that the fin was a single orientation of GaN. SAD patterns were obtained in the vertically overgrown region of the fin (marked (a)) and near the Si{110} sidewall (marked (b)). These diffraction patterns showed that regions (a) and (b) have the same crystallographic orientation and the GaN fin was oriented such that GaN(0002)//Si{110}. Additionally, a small non-polar facet is present at the top of the fin such that GaN ($10\bar{1}0$)//Si(001). Separate studies (not shown here) demonstrated that with a V/III of 8000 and a pre-growth anneal of 10 minutes, the presence of semi-polar GaN at trench corners could also be suppressed by increasing the growth temperature from 1100°C to 1170°C which would have also increased the lateral diffusion length of Ga adatoms.

Under conditions of low precursor V/III, the GaN nucleating on the Si{110} trench sidewalls formed a triangular structure bounded primarily by the semi-polar ($10\bar{1}1$) top facet.

These facets grew vertically above the top Si(001) surface as opposing GaN fins coalesced over the Si trench. The GaN fin was then bounded by the $(10\bar{1}1)$ facet and the non-polar $(10\bar{1}0)$ facet over the trench and the $(000\bar{2})$ facet, which is a slow growth facet, over the top Si(001) surface as indicated in Figure 5. Similar faceting has been observed in previous epitaxial lateral overgrowth studies[11] [12]. The origin of the $(10\bar{1}0)$ facet in our work as opposed to the previously observed $(11\bar{2}2)$ observed in the work by Kuryatkov[7] can be explained by the difference in crystallographic match between wurtzite GaN/Si(111) and GaN/Si(110). Prior work[1] has shown that GaN on Si(111) grows such that GaN($11\bar{2}0$)//Si(110) which results in the formation of GaN($11\bar{2}2$) semipolar facets as observed by Kuryatkov[7]. GaN grown on planar Si(110), however, shows GaN($10\bar{1}0$)//Si(001) which is the same orientation observed in the current study. The inclined facet observed inside the trench did not match the angle for any commonly observed GaN facets reported in literature. We propose that the “buried” region of the GaN microstructure experienced decreased flux of precursor gases as the GaN microstructures closed over the trench region with opposing GaN(0002) growth. This pinching off of the precursor gases would have lead to depletion of the source in the trench and a non-standard angle to the inclined facet of the GaN microstructure.

It is worth noting that threading dislocations were observed to propagate perpendicular to the Si{110} sidewall in additional TEM studies of the sample grown with V/III = 2300. The propagation of the threading dislocations can be seen in Figure 6. Short basal plane defects were also observed in the overgrown GaN region, as indicated by arrows in Figure 6, but did not propagate to the inclined $(10\bar{1}1)$ surface. These defects were determined to be short edge dislocation segments by scanning TEM (not included). The origin of these defects is, as of yet, unknown but will be studied further in future work. Previous studies of non-polar and semi-

polar GaN growth have shown a high density of stacking faults in regions grown from the GaN(000 $\bar{2}$) facet[13] [14]. No such stacking faults were observed in the overgrown GaN region using this method.

Conclusions:

The preferential growth of GaN microstructures on the sidewalls of trench-etched Si(001) has been demonstrated. The growth of GaN was observed to originate from Si{110} trench sidewalls resulting in a non-polar crystallographic structure with respect to the Si(001) substrate surface. GaN was preferentially grown on Si{110} sidewalls of trench structures without a masking layer to prevent growth on the Si(001) surface. GaN was shown to nucleate at exposed Si facets at the trench corners caused by H₂ etching of the Si at elevated temperatures prior to growth. This detrimental GaN nucleation at trench corners was suppressed by increasing the lateral diffusion length of Ga adatoms (via a reduction in the precursor V/III or an increase in growth temperature) and decreasing the pre-growth H₂ anneal. Vertical overgrowth of single orientation GaN fins was achieved through these methods. The results presented here have shown the viability of this method to control the crystal orientation of GaN grown on patterned Si(001). GaN fins may be utilized in microstructured device architectures using the semi-polar and non-polar facets to fabricate light emitting devices. Additionally, it may be possible to modify the dimensions of the trench structure and tailor the growth conditions after obtaining single-orientation GaN fins to promote growth of the observed (10 $\bar{1}$ 0) facet, resulting in a continuous, non-polar GaN film for planar device fabrication.

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Figure 1. Schematic of Si trench cross-section and the resulting GaN growth structure.

Figure 2. SEM images of 17 minute GaN growth (a and b) and 90 minute GaN growth (c and d) on Si trenches. (a) and (b) show cross-sections of the trench structure while (c) and (d) show a top-down view.

Figure 3. Cross-sectional TEM of GaN grown on Si trenches. SAD patterns are given for three distinct crystallographic regions indicated by arrows.

Figure 4: Tilted cross-sectional SEM of GaN on Si trenches. (a) and (b) had precursor V/III=8000 and H_2 anneals of (a) 10min and (b) 5min. (c)-(e) had a 10min H_2 anneal and varying V/III as listed.

Figure 5. Cross-sectional TEM of GaN grown on Si trenches with V/III=2300. SAD patterns are given for (a) near sidewall and (b) overgrown GaN regions.

Figure 6. Cross-sectional TEM of GaN grown on Si trenches with V/III=2300. Arrows indicate (1) threading dislocations propagating from the Si{110} sidewall and (2) short edge-type dislocation segments in the overgrown GaN region.