Full Length Article

Site-controlled crystalline InN growth from the V-pits of a GaN substrate

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ABSTRACT

A site-controlled crystalline InN growth from the V-pits of a GaN substrate was investigated. The V-pits were fabricated by epitaxial lateral growth of GaN over SiO2 disks patterned on a sapphire substrate. InN crystals were found to preferably grow on the inclined (10–11) crystal planes of the V-pits. A V-pit size of 1 μm or less can provide precise site-controlled InN nucleation at the V-pit bottom, while no InN was grown on the rest of the exposed GaN surfaces. The site-controlled nucleation is attributed to the low surface energy point created by the converging six (10–11) crystal facets at the V-pit bottom. When In source supply is below a certain value, this V-pit bottom is the only location able to aggregate enough active sources to start nucleation, thereby providing site-controlled crystal growth.

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1. Introduction

Recently, InN has attracted intensive studies in terahertz devices and high speed electronics due to its superior electron transport properties [1–3]. Compared to other III-nitride materials (e.g., GaN and AlN), the epitaxial growth of InN still remains challenging [4–6]. The main reasons are the relatively low dissociation temperature of InN, high vapor pressure of In and N2, and the lack of suitable growth templates [7–12]. Conventionally, InN is often grown on a planar template (e.g., sapphire or GaN) [13–19]. The crystal quality is often compromised by the significant lattice mismatch to the template and the reduced growth temperature for avoiding InN dissociation. Defect reduction using selective area growth was reported [20,21]. A metal or AlN mask with small apertures was fabricated on a sapphire substrate. InN was first grown from the aperture then laterally over the mask. While the laterally grown InN had lower defects, the InN grown directly on the apertures still had significant threading dislocation defects. To avoid parasitic InN growth on the mask, a high growth temperature was needed but this could cause InN decomposition [22]. Here, we report the study of a site-controlled crystalline growth of InN from the V-pits of a GaN substrate. The lower surface energy at the V-pit bottom provides precise nucleation location control. Under proper growth conditions, single InN nucleation could selectively grow from the bottom of each V-pit, even though the whole planar GaN surface was exposed to the growth environment. This controlled nucleation can lead to single crystalline InN growth and demonstrates a potential way to grow high quality crystals.

2. Material and methods

We first fabricated a GaN substrate with an array of V-pits by epitaxial lateral growth over a sapphire substrate patterned with SiO2 disks. The substrate was later used for the site-controlled InN crystal growth. Fig. 1(a)–(d) illustrate the fabrication steps of V-pits on a GaN substrate. A low temperature 20 nm GaN buffer layer was first deposited on a c-plane sapphire substrate in a MOCVD chamber (Veeco D180), followed by a 200 nm SiO2 thin film deposition (Fig. 1(a)). A photore sist was spun on the substrate, followed by photolithography patterning to form 5 μm circular disks in a triangular lattice pattern on the sapphire substrate. The spacing between disks was 3 μm. The photore sist pattern was transferred to SiO2 by buffered oxide etching to form an array of SiO2 disks (Fig. 1(b)). The substrate was put into a MOCVD chamber for GaN epitaxial growth.
growth. The chamber pressure was 150 Torr. The TMGa, NH3 and N2 flow rates are respectively 120, 25,000, 25,000 sccm. The substrate was placed on a wafer carrier that could hold up to seven 2” substrates arranged in circle. The wafer carrier had two concentric heating coils underneath, with one located in the center region and the other in the perimeter. The inner coil was set at 1040 °C. The outer one was intentionally set at slightly lower temperature of 1020 °C. This gave the wafer carrier a radial temperature gradient. The GaN epitaxial growth started on the GaN buffer layer not covered by SiO2 disks. It grew first in the vertical direction and then laterally over the SiO2 disks, as shown in Fig. 1(c). The lateral growth resulted in specific tilted crystal planes. The tilted surfaces nominally were the semipolar {10–11} and/or {11–22} crystal planes. The pit size became smaller as growth continued and formed V-pits on the GaN surface (Fig. 1(d)). The SiO2 disks were buried directly under the V-pits. The temperature gradient caused different lateral growth rates to vary from about 2.0 to 2.5 μm/h, which led to a distribution of different V-pit sizes. The vertical growth rate of GaN was 2 μm/h. A GaN layer with a thickness of 3 μm was deposited following 1.5 h of growth.

3. Results and discussion

The GaN substrate was examined by a scanning electron microscope (SEM). An array of inverted pyramidal pits with sizes ranging from less than one to about 6 μm were formed on the surface. The typical SEM images are shown in Fig. 2(a)–(d). The size change was attributed to the growth temperature variations from 1040 to 1020 °C, with the higher growth temperature having a faster lateral growth rate. This allowed GaN to grow over the SiO2 masks more quickly, leading to a smaller pit size. In addition to the size difference, the V-pits also had different geometrical shapes. The V-pits smaller than 2.5 μm size were hexagonal, formed by six inclined crystal planes, as shown in Fig. 2(a) and (b). An enlarged image is shown in the inset in Fig. 2(a). It is known that the as grown GaN m-plane {10–11} crystal orientation lines up with the underlying sapphire a-plane {11–20} [23]. The SiO2 disk array was intentionally aligned with the sapphire a-plane during the lithography process, as depicted by the white dotted line in Fig. 2(b). The hexagon V-pit edges were found to be parallel to the array lines. The inclined crystal facets were therefore identified as the GaN {10–11} semipolar planes. The larger sized V-pits were dodecagonal, as shown in Fig. 2(c) and (d). These V-pits were formed by inclined triangular and rectangular surfaces. From the dodecagon orientations, these triangular and rectangular surfaces are respectively identified as {10–11} and {11–22} crystal planes, as shown in the inset of Fig. 2(d) [24], Fig. 2(a)–(d) demonstrated a controlled pit size growth by different growth temperatures.

The substrate was reloaded into a MOCVD for InN growth study. The growth pressure was 500 Torr. Trimethylindium (TMIn) and ammonia (NH3) were used as precursors for In and N. Previous studies have examined the dependence of InN growth on growth parameters [12–17]. Indium droplets can form at high temperatures due to dissociation of InN (N dissorption). They could also form at low temperatures due to insufficient N from NH3 in the reactor. We found that the proper growth temperature was in the 450–465 °C range. We set the growth temperature at 455 °C. The NH3 flow rate was 2500 sccm. It was set at a relatively high flow rate to maximize the reactive N supply. We varied the TMIn source supply to study its effect on the InN growth. We first used the TMIn flow rate of 105 sccm to grow InN. The growth time was 80 min. The V/III ratio was ∼105. The SEM pictures of InN grown on different V-pit sizes are shown in Fig. 3(a)–(c). The corresponding enlargements are shown in Fig. 3(d)–(f). The pit sizes are respectively 1.5, 3, and 6 μm. In general, the InN crystals aggregated around the V-pit edges as well as on the inclined semipolar pit surfaces while small InN particles were scattered on the top surface. The hexagonal InN growth on the V-pit edges, as shown in Fig. 3(d), indicates that it was a crystalline growth, which is similar for larger pits shown in Fig. 3(e) and (f). The enlargement in the inset of Fig. 3(e) shows the crystalline hexagon structure of the small InN particles grown on the c-plane surface. The crystal orientations of the hexagons of the small InN particles, depicted by the solid lines for visual guidance, are all aligned. These InN particles were thus still crystalline growth. The enlarged SEM Fig. 3(d) and (e) show denser InN crystals grown on the V-pit surface than on the c-plane surface. This is in particularly prominent in Fig. 3(d). These SEM images indicate that InN prefers to grow on the inclined V-pit surface than on the top planar surface. Fig. 3(d)–(e) show that InN growth is slightly greater on the V-pit edges than on the inclined surfaces.

To further study the preferred growth of InN on the inclined surface, we lowered the TMIn flow rate to 70 sccm and repeated the growth on a V-pit substrate. The growth time was extended to 120 min to keep the total amount of TMIn source the same as in the previous 105 sccm case. All other growth parameters were kept the same. The SEM images of the substrate surfaces with different V-pit sizes from 1 μm to 6 μm are shown in Fig. 4(a)–(d) with enlarged images in the insets. There was less InN deposition, as compared with Fig. 3, even though the total supplied amount of TMIn source was the same. The lower TMIn flow rate increased the diffusion length of the active species diffusing on surface, which resulted in an increase of the desorption of In adatoms due to the growth temperature. The total InN deposition was thus reduced. None of the SEM images showed InN growth on the c-plane surface. We did also put in a flat GaN substrate in the same growth run and there was no InN growth at all on the flat surface. This indicated that the growth was below the critical condition needed for InN nucleations to occur on the planar top surface. The InN nucleation however still occurred inside the V-pits. It is worth noting that single InN crystal grows on every V-pit in Fig. 4(a) where V-pit size is ∼1 μm. The lateral size of the InN crystal is about 1.2 μm after 120 min of growth time. The lateral growth rate was about 10 nm/min. It should be noted that the InN crystal also grew vertically to a height was 0.5 μm. The vertical growth rate was ∼4.2 nm/min. For the larger pit sizes in Fig. 4(b)–(d), InN growth appears to start near the V-pit edges and the upper part of the inclined surface. The inset of Fig. 4(d) for the 6 μm V-pit shows the growth details. InN grew on the upper region of the {10–11} surfaces (dotted triangle), extending from V-pit edges to about 0.6 μm down on the inclined {10–11} surfaces as indicated by the red arrows. There were no InN growths on {11–22} surfaces (dotted rectangle). Fig. 4(c) and the inset for the 4 μm V-pit also show InN growth near the {10–11} plane edges, while no growth on the {11–22} edges. Some InN growths occurred halfway down the {10–11} planes, as indicated by the red arrows. The 2.5 μm V-pits in Fig. 4(b) were formed solely by {10–11} planes. InN growth occurred near the {10–11} plane edges and inside the V-pit (red arrow) as well. The converging growth from the large V-pits
(Fig. 2(d)) to the small V-pits (Fig. 2(a)) shows the change from the starting (10–11) and (11–22) planes to the final (10–11) planes. In the converging growth mode, the fast growing facets expand and define the final growth fronts while slow growing facets diminish in size. The result of the final (10–11) planes indicates they grew faster than the (11–22) planes. The faster growth rate on the (10–11) planes results from a preferential decomposition of organometallic species on this surface. This explains the preferential growth of InN on (10–11) as opposed to (11–22), as revealed in Fig. 4(c)–(d). If we look closer at Fig. 4(b) and (c), InN seems to grow more on the V-pit (10–11) edges than on the inclined surfaces. We also see similar growth behavior for the TMIn flow rate of 105 sccm in Fig. 3(d)–(e). This was because the InN nucleations once formed on the edges had a higher chance of capturing In adatoms diffusing on the top c-plane surface than those nucleations further down on inclined surfaces. As a result, InN appeared to grow more on the V-pit edges.

To investigate whether InN crystals in Fig. 4(a) was grown from a single nucleation or the coalescence of multiple nucleations near the V-pit edges, we repeated the growth using a shorter growth time of 40 min under the same TMIn 70 sccm flow rate. SEM pictures of a 1.2 μm size V-pit before and after InN growth are respectively shown in Fig. 5(a) and (b). The symmetric pyramidal crystal growth from the V-pit bottom indicates that a single nucleation started from the V-pit bottom. The transition from multiple to single nucleation as pit size reduces to about one or below μm is explained in the following. From the above study, InN prefers to grow on the (10–11) planes and the growth occurs on the upper region of the (10–11) planes. This region projected on the c-plane is about 0.6 μm from the V-pit edge, as illustrated in Fig. 5(c). Given the 62° inclined angle of the (10–11) surface (Fig. 6(a)) [25], this is about 1.3 μm (0.6 μm/cos 62°) on the {10–11} surface measured from the V-pit edge. This implies that the In adatoms can diffuse ~1.3 μm into the V-pits on the {10–11} surface. If the V-pit side wall length exceeds 1.3 μm, the In adatoms cannot reach...
to the bottom. This finite 1.3 μm diffusion length is illustrated by the dotted circle position in Fig. 5(c). When the V-pit diameter is below 1.2 μm (twice the projected In adatom diffusion length on c-plane), the In adatoms can now diffuse all the way down to the bottom of V-pit, as depicted by the purple solid circle in Fig. 5(c). At the very bottom, the simultaneous presence of six (10–11) planes provide more potential chemical bonds to capture the adsorbed In and N sources. This makes the V-pit bottom the lowest surface energy point for InN nucleation to occur, thereby enabling the site-controlled nucleation.

Besides the low surface energy at the V-pit bottom, the proper choice of source supply is also important. The precise V-pit controlled nucleation occurred at a low TMIn flow rate to prevent multiple nucleations from occurring on the planar surface. When the source supply impinges on a substrate surface, the adatoms diffuse on the surface and may aggregate at local surface potential energy minimums. From nucleation theory, an irreversible nucleation can start when aggregation reaches a critical mass. When the source supply is high, shallow potential energy minimums on the planar surface can aggregate sufficient critical mass to initiate nucleation. This was the case in Fig. 3(a), where nucleation occurred inside V-pits as well as on the planar surface at a TMIn flow rate of 105 sccm. The higher nucleation density inside the V-pits, as shown in Fig. 3(d), indicates that the V-pits have much lower potential energy minimums. Using this difference, when the source supply falls below a certain value, the shallow energy minimums on the planar surface cannot aggregate sufficient adatoms to start nucleation, though the deeper energy minimums in the V-pits can. This was what happened at a TMIn flow rate of 70 sccm, as shown in Fig. 4, where nucleation occurred only inside the V-pits but not on the top planar surface. When the pit size is small, the lowest surface energy of V-pit bottom can effectively aggregate adatoms and start single nucleation. This leads to the site-controlled nucleation for InN single crystal growth. Under proper growth conditions, this site-controlled nucleation can be highly repeatable on every V-pit with a nearly 100% yield, as shown in Fig. 4(a).

We used TEM, X-ray diffraction (XRD), and photoluminescence (PL) to characterize the InN crystal quality. A cross-sectional TEM through the center of an InN crystal sample, as depicted by the dotted line in Fig. 5(b), is shown in Fig. 6. Fig. 6(a) is an over view of the InN nano-structure growing from a V-pit of GaN. Three square regions at the top of InN crystal, the bottom of the V-pit, and the InN/GaN interface are further magnified for detail inspection. The enlarged TEM of the top area shows good crystalline structure at the atomic scale (Fig. 6(b)), as illustrated by the 4.5x enlarged inset and confirmed by the sharp diffraction spots in Fig. 6(c). The entire InN area, from top to nearly the V-pit bottom, all shows a well aligned crystalline structure. Fig. 6(d) shows the enlarged area near the V-pit bottom. The InN crystal quality becomes worse judging from the blurred picture of Fig. 6(d), and the blurred diffraction pattern in Fig. 6(e). The further enlarged area close to the very V-pit bottom (Fig. 6(f)) shows degraded atomic order. This was the starting point of nucleation where active species were in the process of forming a crystalline structure. As they grew upward (Fig. 6(d)), adatoms were gradually organized into perfect crystal structure. An enlarged square area across the InN/GaN boundary is shown in Fig. 6(g), with the diffraction of each area shown in Fig. 6(h) and (i). They all show good crystalline quality with limited boundary defects. This TEM inspection confirms that the crystal quality of InN nano-pyramid is relatively good and the nucleation site is at the bottom of the V-pit where major defects are confined in that area only.

The X-ray diffraction (XRD) 2-theta scan of the InN crystal sample (Fig. 4(a)) is shown in Fig. 7(a). Several characteristic peaks including InN (0002) peak at 31.26° and GaN (0002) peak at 34.52° with additional peaks around 35.67° can be observed. The weaker intensity of the InN peak is due to much less coverage of the InN.
material on the GaN substrate. To clarify the additional 35.67 Å peaks, a 2-theta scan of a V-pit GaN substrate without InN growth was measured. It also shows the 35.67 Å peaks, which indicates that they are due to the V-pit substrates. The rocking curve is shown in Fig. 7(b). The FWHM linewidth is 1300 arcsecs, demonstrating good crystal quality as compared with other reported values from MOCVD growth (~3000 arcsecs) [26,27]. Finally, Fig. 7(c) shows the PL spectra excited by a 632 nm He-Ne laser at various temperatures. It shows a major peak at 0.78 eV with a long tail down to 0.65 eV at 10 K. At 220 K, the maximum shifts to 0.75 eV with more symmetric roll off on both sides. The major PL emission is consistent with previous reports in the 0.7–0.8 eV range [26,28,29]. There are several possible transition paths. The free carrier concentration in InN is usually high, leading to a Fermi level located above the conduction band minimum. Transitions can occur from the conduction band edge or the Fermi level to the valence band edge or some acceptor level in the bandgap. As temperature increases, the band gap shrinks following Varshini’s law, while Fermi level increases above band edge minimum. The Fermi level transition can therefore red or blue shift depending on the relative magnitude of these two effects. Previous studies have reported the dependence of red or blue shift on carrier density with increasing temperature [26,30,31]. At moderate high carrier density, the PL peak can slightly blue shift at lower temperature region due to the increase of thermal energy, then red shift at higher temperature region due to bandgap shrinkage [31]. In our case, the major 0.78 eV PL peak slightly blue shifts from 10 K to
50° K, then red shifts from 70° K to 300° K. We attribute this PL peak shift to the Fermi level transition. The long tail in the lower energy transition is probably attributable to band edge to band edge and band edge to acceptor transitions in the bandgap or surface states.

4. Conclusion

In summary, we have studied a site-controlled crystalline InN growth from the V-pits of a GaN substrate. The V-pits were formed by epitaxial lateral growth of GaN over SiO2 disks patterned on a sapphire substrate. InN prefers to grow on the inclined V-pit {10–11} planes. The V-pit bottom, where six {10–11} surfaces converge, provides more potential chemical bonds to capture the adsorbed In adatoms diffusing on the surface. This makes the V-pit bottom the lowest surface energy point for InN nucleation. When the flow rate of the InN source supply falls below a critical value, the V-pit bottom becomes the only location that can aggregate enough adatoms to start nucleation and enables the site-controlled nucleation and crystal growth. The as grown InN shows good crystalline quality from TEM, XRD, and PL measurements.

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