In situ investigation of self-induced GaN nanowire nucleation on Si

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The nucleation of GaN nanowires grown by molecular beam epitaxy on bare Si(111) and Si(001) has been investigated *in situ* by reflection high-energy electron diffraction (RHEED) and line-of-sight quadrupole mass spectrometry. On either substrate, the incorporation rate of Ga increases in two steps to steady-state conditions, and the RHEED transmission pattern of GaN appears only in the second stage. *Ex situ* transmission electron microscopy on samples from both stages grown on Si(001) revealed that the nanowire nucleation is strongly affected by the simultaneous nitridation of the Si substrate.
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Over the past decade, the great potential of group III-nitride nanowires (III-N NWs) for photonic applications has been demonstrated by the fabrication of promising nanoscale devices (light emitting diodes, laser diodes, and solar-cells).[1–3] A particularly attractive aspect of the NW approach is that it represents an alternative way for the monolithic integration of high-quality optoelectronic material with Si-based technology.[4,5] Although NWs are frequently grown by the vapor-liquid-solid mechanism that involves catalyst seeds,[6] external metals used to promote NW growth may contaminate the NW material and degrade its optoelectronic and structural properties.[7] Hence, self-induced NW growth appears to be more suitable, as it has been demonstrated for GaN NW growth on bare Si in plasma-assisted molecular beam epitaxy (MBE).[8] In this case the underlying mechanisms of NW nucleation are much less clear, and there are only very few studies on this topic.[9–13] Besides, an important experimental issue for nucleation studies is the alteration of the grown structures upon cooling and exposure to the ambient. In this letter, we present an *in situ* investigation of the self-induced GaN NW formation on bare Si substrates by reflection high-energy electron diffraction (RHEED) and line-of-sight quadrupole mass spectrometry (QMS).

GaN NWs were grown by plasma-assisted MBE on bare Si(001) and Si(111). The substrates were prepared by the standard Radio Corporation of America (RCA)[14] laboratories procedure. Immediately after deoxidation at 950 °C, the substrate temperature was lowered to 730 °C and the (2×1) and (7×7) reconstructions of Si(001) and Si(111), respectively, showed up in RHEED. On Si(111), although the higher order streaks appeared, they were not all well resolved. The bare Si surface was then simultaneously exposed to the Ga and N fluxes, unless otherwise specified. The V/III ratio determined from the N and Ga equivalent growth rates of thick planar reference layers grown either in the Ga- or N-limited regimes[15] was set to five. During nucleation, the incorporated amount of Ga was monitored *in situ* by QMS mounted in direct line-of-sight to the substrate[16,17] and the sample surface was probed by RHEED at the same time. For the need of RHEED acquisition, the sample was not rotated but held in the $\langle 110\rangle$ and $[1\bar{1}0]$ azimuths of Si(001) and Si(111), respectively. Reference experiments showed that the sample rotation did not introduce any major difference in the Ga desorption behavior and the temporal evolution of the QMS profiles varied at most by 15 s. In addition, the crystal structure of samples for which the growth was interrupted during nucleation was investigated by transmission electron microscopy (TEM).

Figure 1 shows the Ga desorption signal and the intensity of the $(0002)_{GaN}$ RHEED spot during the nucleation on Si(001) and on Si(111). On both surfaces, two different stages in the nucleation were identified and the time dependence was similar in both cases. During stage 1, the opening of the shutters immediately induced an increase in the Ga desorption signal to nearly the full amount of supplied Ga. In other words, initially no Ga was incorporated, as has also been observed for heteroepitaxial nucleation of GaN on SiC.[17] On both Si(001) and Si(111), the (1×1) pattern appeared briefly in RHEED, indicating that the original reconstructions of higher periodicity were destroyed (see insets). However, the pattern obtained on Si(111) was very diffuse and additional faint reflections were observed. These reflections may result from experimental artifacts or from another reconstruction related to the formation of Si_xN_y.[18] Subsequently, the Ga desorption signal decreased to about half the impinging rate and the RHEED pattern became weaker and blurry. In the case of Si(001) the drop in Ga desorption was

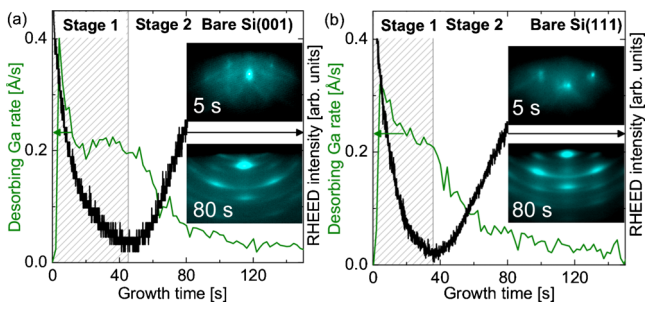

FIG. 1. (Color online) Calibrated QMS profile of Ga desorption in correlation with the $(0002)_{GaN}$ RHEED spot intensity during the self-induced nucleation of GaN NWs on (a) Si(001) and (b) Si(111). Both the Ga and N shutter were opened at $t=0$ *s*. The insets show for each surface orientation Si(001) and Si(111) two characteristic RHEED images acquired in the $\langle 110\rangle_{Si}$ and $[1\bar{1}0]_{Si}$ azimuths, respectively. Nucleation can be divided into two stages as indicated by the shading.

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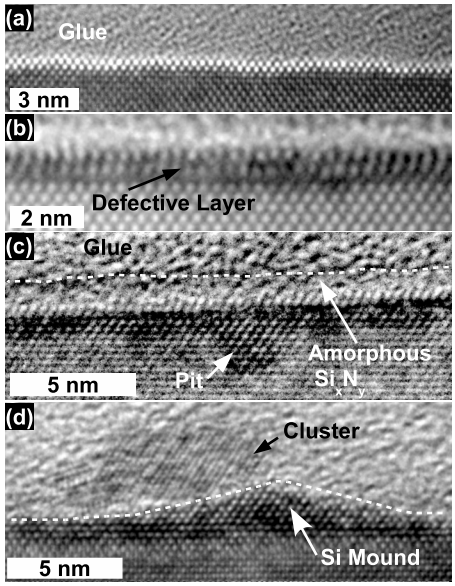

FIG. 2. HRTEM images of different areas of a sample from stage 1 grown on Si(001) [(a)–(d)] cross-sections along $[110]_{Si}$ revealing an atomically flat Si area, the formation of a thin crystalline layer, and Si mounds and pits, respectively. The layer in (b) is possibly disordered Si or Si_xN_y, and the clusters in (d) are attributed to GaN.

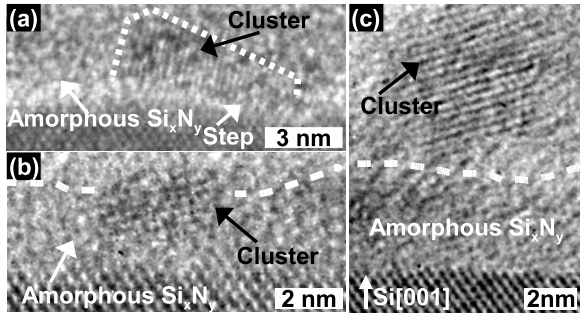

FIG. 3. Cross-sectional HRTEM images of a sample from stage 2 grown on Si(001). The sample is covered by GaN clusters (a) in contact with the underlying Si substrate at a step, (b) embedded in the amorphous Si_xN_y layer, and (c) on top of the amorphous Si_xN_y layer. There is no indication of the defective layer observed in Fig. 2(b).

more abrupt than on Si(111), and the diffraction pattern finally vanished completely, whereas on Si(111) very faint reflections were still observable. The nucleation stage 2 started with a second drop in the Ga desorption, i.e., a rapid increase in Ga incorporation. After this drop, the steady state was established, in which the supplied Ga was completely incorporated. Simultaneously, the RHEED spot intensity increased and broken rings caused by the transmission diffraction through misoriented GaN islands appeared (see insets).[19] Thus, the beginning of stage 2 indicated the start of the massive growth of three-dimensional GaN crystals. Remarkably, the substrate orientation does not seem to have a significant influence on nucleation.

The two steps in the decay of Ga desorption suggest two different regimes for Ga incorporation. During the nucleation stage 1, Ga incorporation is impeded but not completely suppressed, whereas the decay occurring during stage 2 corresponds to the prevailing formation of three-dimensional GaN nuclei. It is worth noting that this temporal evolution of the Ga desorption is markedly different from the heteroepitaxial nucleation of GaN films on SiC under Ga-rich conditions where there is a continuous decay.[17] To clarify the origin of the two step decay, samples from both stages grown on Si(001) were investigated by TEM.[20]

The morphology of the sample representative of stage 1 is depicted in Fig. 2 displaying cross-sectional high-resolution TEM (HRTEM) images of four different surface areas. The surface structure of this sample was inhomogeneous. A large area without any obvious change in the atomically flat Si surface was observed [Fig. 2(a)]. Another more irregular area seemed to be partially covered by an inhomogeneous and crystalline but highly defective layer [Fig. 2(b)], which may be either disordered Si or crystalline Si_xN_y according to the measured lattice parameter (3.8 ± 0.3 Å). In addition to these smooth areas, the surface roughened and a few pits and Si mounds formed as seen in Figs. 2(c) and 2(d). These features demonstrate the high mobility of Si atoms which may have outdiffused to react with N at the free surface during the initial nitridation processes.[21,22] Also, an amorphous layer overgrowing this last-named area was clearly observed [Fig. 2(c)]. In agreement with the Ga incorporation revealed by QMS, very few GaN clusters were also found [Fig. 2(d)]. Although the cluster observed in Fig. 2(d) grew epitaxially to the underlying Si, no statistical information on the exact epitaxial orientation of these clusters can be given due to their low number density. Moreover, as GaN diffraction was not observed by RHEED at that time, these disordered clusters may also have formed during the cooling procedure following the growth. Furthermore, the irregular layer and the amorphous one could be intermixed with Ga.

In contrast, the Si surface of the sample representative of stage 2 was continuously covered by a homogeneous amorphous Si_xN_y layer of 3–4 nm in thickness. Such a layer has often been found between self-induced GaN NWs and the Si substrate.[12,13,19] Numerous GaN clusters were observed in cross-section TEM either in contact with the underlying Si substrate [Fig. 3(a)], embedded in, or lying on the amorphous layer [Figs. 3(b) and 3(c)]. Hence, the major change between the two stages is the disappearance of the defective crystalline layer and the formation of GaN clusters on the amorphous Si_xN_y. Even if the defective crystalline layer observed during stage 1 is Si_xN_y, its amorphization could be induced by the low N adatom mobility and surface roughening[23] or a change in composition[24] through the diffusion processes involved in the nitridation.

Consequently, during the nucleation stage 1 there is a competition between the nucleation processes of Si_xN_y and GaN on Si whereas stage 2 is associated to the formation of GaN islands on top of the amorphous Si_xN_y. Presumably, the transition from stage 1 to stage 2 is induced by the formation of amorphous Si_xN_y layer. However, on the basis of the available data, no direct correlation between the start of the massive GaN island nucleation and the completion of the amorphous Si_xN_y formation can be drawn. Indeed, GaN NW nucleation at 790 °C is strongly delayed even when the Si substrates are nitrided for 2 min before growth.[25] Nevertheless, the outdiffusion of Si and the simultaneous formation of Si_xN_y certainly affect the nucleation mechanism of GaN NWs. At the very beginning of growth, when the availability of Si is large compared to that of N and Ga, the preferential binding of N with Si may occur in competition with the binding of N with Ga.[13,26] This results in an increase in the desorption of Ga, comparable to some extent with the one

observed during the nucleation of AlGaN revealing the Al for Ga exchange.[27] Moreover, the formation of the amorphous Si_xN_y layer on top of the Si surface leads to the removal of the epitaxial constraint of the substrate. The time-dependent stress field generated through this process influences the formation of the GaN clusters. The ones which form already during stage 1 may yield NWs growing epitaxially to the underlying substrate (Si or thinner crystalline Si_xN_y). However, NW nucleation during stage 2 occurs under the loss of proper epitaxy and the orientation of $(0001)_{GaN}$ parallel to the substrate surface depends on the smoothness of the underlying amorphous Si_xN_y layer.[13,25,28] Subsequent faster growth of the lower energy $(0001)_{GaN}$ facet[9,12,13] and NW coalescence may then lead to the distribution sharpening of the $[0001]_{GaN}$ NW orientation relatively to the substrate normal.[29,30] Also, as the Si_xN_y layer constitutes an efficient way to reduce the diffusion of Si into GaN,[18] clusters nucleating at different time may also exhibit different composition which can further impact on the NW growth. Si indeed acts as an antisurfactant for GaN grown under N-rich conditions[26] and it was recently shown that Si doping is necessary for the complete formation of NWs grown by MOCVD.[31] Lastly, the formation of the amorphous Si_xN_y layer explains why the evolution of the Ga desorption and the GaN diffraction is so similar on Si(001) and Si(111).

In conclusion of this study, the self-induced nucleation of GaN NWs in MBE occurs in two stages that are similar on Si(001) and Si(111). During stage 1, there is a competition between the formation of Si_xN_y and GaN. Stage 2 is marked by the massive nucleation of GaN islands on an amorphous layer of Si_xN_y. Most likely due to the formation of this amorphous layer, nucleation proceeds in a very similar way on Si(001) and Si(111). Therefore, the nitridation of the Si substrate strongly influences the NW nucleation.

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[20]See supplementary material at http://dx.doi.org/10.1063/1.3464956 The growth time for the sample representative of stage 1 was 15 s. The stage 2 sample was exposed prior to GaN growth for 15 min to the Ga flux. During that time, the N plasma burnt behind the closed shutter, resulting in a dramatically smaller but still relevant flux of active N species. QMS monitoring showed for other samples that this preexposure prepones the nucleation processes by about 30 s. The growth time for this sample was 15 s and QMS and RHEED revealed that stage 2 was reached. Also, the TEM investigation of a Si substrate that was treated by the preexposure routine without any further growth confirmed that the preexposure leads to similar changes on the substrate as the initial nucleation during stage 1.
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