APPLIED PHYSICS LETTERS **100**, 061602 (2012)

Spontaneous formation of quantum height manganese gallium islands and atomic chains on N-polar gallium nitride(000$\bar{1}$)

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(Received 2 November 2011; accepted 18 January 2012; published online 9 February 2012)

Deposition of manganese onto the gallium-rich, nitrogen-polar GaN(000$\bar{1}$) surface results in the formation of quantum-height island structures. Two unique island heights differing by one atomic layer are observed, including 0.93 nm high islands which are unstable against the formation of 1.13 nm high islands. A row structure at the islands' surface suggests a mixture of Mn and Ga, while growth of one-dimensional atomic chains at the surface of the stable 1.13 nm high islands indicates a strongly anisotropic diffusion. The observed behavior is consistent with a quantum size effect driven growth mechanism. © *2012 American Institute of Physics*. [doi:10.1063/1.3682487]

Controlled growth of metallic layers at the surface of semiconductors is a field of on-going interest due to many widespread applications. Of great interest is the spontaneous (self-organized) formation of well-defined metallic nanostructures on various Group III-V and Group IV semiconductors. For example, Ag was shown to form a flat, two-dimensional island structure with a specific critical thickness on GaAs(110),[1] and Pb has been shown to form islands of quantized thicknesses on Si(111).[2] Much effort has been applied to investigate such interesting systems in which the layer growth and stability are driven at least in part by the quantum size effect (QSE), also referred to as "electronic" growth.[3]

It would therefore be very important if such physical phenomena—namely the spontaneous formation of quantized thick metallic islands—were found in the case of GaN. Already, there is great interest in the deposition and growth of transition metal and rare earth metal layers on GaN for the purpose of creating ferromagnet/wide-gap semiconductor interfaces.[4–10] In particular, the Heusler MnGa alloy is currently of high interest as a ferromagnetic contact to GaN, and as well GaAs.[5,7,11] In this letter, we report the formation of quantum-thick metallic islands on the surface of N-polar GaN(000$\bar{1}$) induced by the deposition of manganese. The islands are formed spontaneously and are consistent with an alloy of Mn and Ga.

The sample preparation consists of first depositing by molecular beam epitaxy a ~0.2 μm-thick layer of N-polar GaN(000$\bar{1}$) onto an *ex situ* solvent-cleaned sapphire(0001) substrate. Gallium nitride growth is carried out by means of a radio frequency (rf) N-plasma source with N_2 as source gas and a Ga effusion cell, while the substrate is held at a temperature of ~650 °C. The GaN growth is carried out under Ga-rich conditions, resulting in a final surface with excess Ga accumulation of ~0.1-0.4 monolayer (ML) (not including Ga droplets). The substrate temperature is then lowered to ~250 °C and manganese is evaporated, also using an effusion cell, resulting in the development of segmented 2× streaks as seen in reflection high energy electron diffraction along both [11$\bar{2}$0] and [10$\bar{1}$0]. The amount of Mn deposited is ~0.4 ML, a quantity sufficient to induce the quantum island formation and similar to the amount of excess (non-droplet) Ga. After this, the sample is transferred into the adjoining surface analysis chamber for scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES) investigations.

Presented in Fig. 1(a) is a 3D perspective view (3D perspective view image rendered using WSxM software described in Ref. 12) STM image with area 80 nm × 87 nm of the island structures formed on the N-polar GaN(000$\bar{1}$) surface. These islands stand out clearly from the reconstructed GaN surface and display absolutely flat tops and steep sides all around. The edges of the islands are typically oriented along GaN high symmetry [11$\bar{2}$0] directions. The GaN surface between the islands is reconstructed into a type of adatom wetting layer. Two distinct island heights can be determined, one being 0.93 ± 0.01 nm high (islands labeled B, A, F) and the other 1.13 ± 0.01 nm high (island labeled E) relative to the GaN surface (specifically, the Ga adlayer).[13]

As can be seen from the zoom-in STM images in Figs. 1(b) and 1(c), distinct surface structures are observed for both the islands' faces as well as for the GaN surface wetting layer. In Fig. 1(b) is the zoom-in view of the 0.93 nm high island revealing a row-like structure with rows running along [11$\bar{2}$0]. A rectangular unit cell is discerned with a size of 11.4 ± 0.6 Å × 6.3 ± 0.3 Å. At certain points within the image, an additional protrusion appears near the center of the rectangular unit cell (as marked in the image). At the bias voltage shown ($V_S = -0.67$ V), there are nearly alternating variations of the row height (brightness) from row to row, with brightness variations as well along the rows (as marked by arrows). A consistently dark valley is also seen with a 22.8 Å superperiodicity. The brightness variations may be related to structure alone, but they may also indicate different atomic constituents (Mn vs. Ga).

The zoom-in view of the GaN surface wetting layer as shown in Fig. 1(c) reveals a structure consisting of a network

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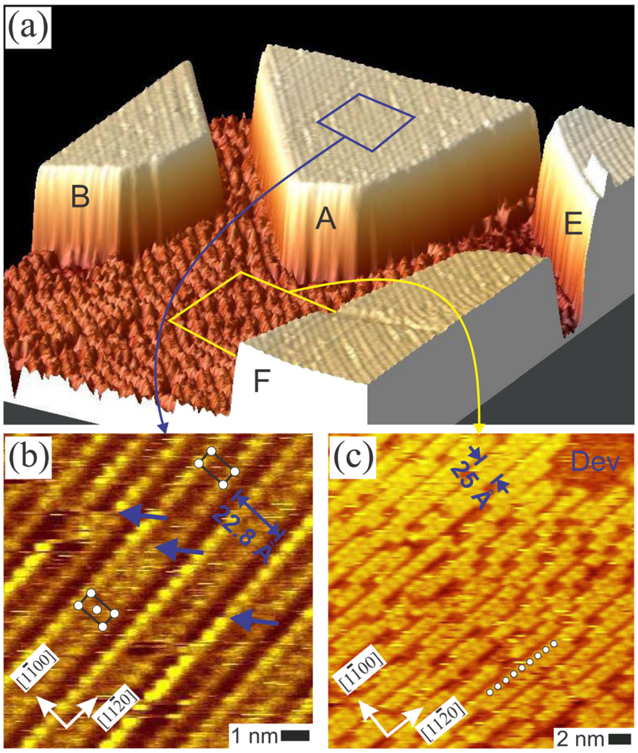

FIG. 1. (Color online) (a) Large-scale (80 nm × 87 nm) STM image in 3D perspective view[12] of MnGa islands on N-polar GaN surface ($V_S = -0.87$ V; $I_T = 156$ pA); (b) zoom-in STM image of island A surface ($V_S = -0.67$ V; $I_T = 154$ pA); (c) similar zoom-in of adatom wetting layer ($V_S = -0.87$ V; $I_T = 156$ pA); region devoid of adatom stripes is labeled "Dev"; adatom protrusions are marked with white circles.

of meandering stripes with typical spacing of ∼25 Å running mainly along [11$\bar{2}$0]. The stripes themselves consist of lines of protrusions (as marked in the image) ordered also along [11$\bar{2}$0]. At upper right in the image is a patch devoid of the stripes, which we interpret as the Ga adlayer with the stripes therefore corresponding to adatoms (Ga and/or Mn), similar to the well-known Ga 3×3 reconstruction on N-polar GaN(000$\bar{1}$).[13]

In order to estimate the chemical composition of the surface, AES measurements were performed on the same island-covered sample. The strong Mn peak measured indicates the prevalence of Mn within the surface and yields an average Mn/Ga ratio of 0.20 ± 0.02. Considering the high surface sensitivity of AES, this number is large given that Mn may not necessarily be in the first (top-most) layer. As such, the islands could contain a significant quantity of Mn, in the range from 20% to 50%.

Shown in Fig. 2(a) is a large scale STM image of the island-covered GaN surface. Fig. 2(b), covering the central region of Fig. 2(a), corresponds to the perspective view image seen in Fig. 1(a). While in some cases the island shapes conform to curving GaN step edges [as marked in Fig. 2(a)], the triangular/hexagonal-like shapes of the step-edge-free islands with 120° angles having side-walls oriented along ⟨11$\bar{2}$0⟩ indicate a (111) [or (0001)] type island orientation.

Determination of the island heights is obtained by line profile analysis, carefully taking into account the existence of substrate (GaN) steps and dislocations found at the substrate surface. Line section L1 seen in Fig. 2(c) is a cut across the islands labeled C-A-B-D, taken from the image of Fig. 2(a). Islands A and B, residing on the same GaN terrace, have clearly different heights with a height difference measured of ∼2.0 Å. Islands C and D appear to be of even lower height compared to island B, as seen especially in line section L1. However, a GaN bilayer step of height 2.59 Å runs along the right-most edge of island C and along the left-most edge of island D; so islands C and D are coming from a lower GaN terrace and have the same height as island B.

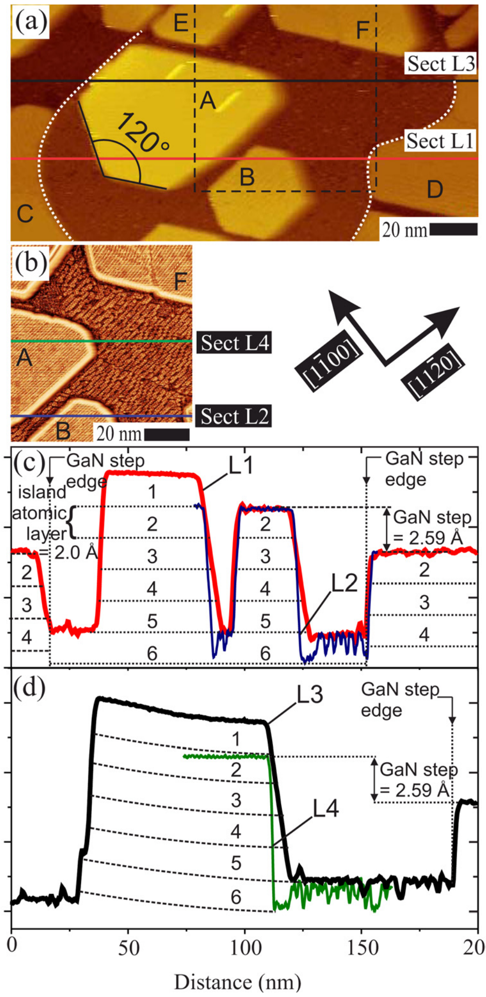

FIG. 2. (Color online) (a) Rectangle view (190 nm × 97 nm) STM image showing numerous MnGa islands covering the N-polar GaN surface ($V_S = -2.44$ V; $I_T = 103$ pA); curving dotted lines correspond to GaN step edges; (b) 80 nm × 87 nm STM image corresponding to the dashed outline region shown in (a) and also the image of Fig. 1(a) but acquired ∼2 h earlier ($V_S = -0.87$ V; $I_T = 156$ pA); (c) line cross-sections L1 and L2 as indicated in (a) and (b); (d) line cross-sections L3 and L4. Island layer numbers in (c) and (d) are indicated. A local background subtraction was applied to the image in (b).

Given the measured height difference between islands A and B as well as their individual heights relative to the top of the wetting layer, we can deduce the average atomic layer spacing and the number of atomic layers within the islands. We use the following two equations: $ns = h_1 + h_0$, $(n-1)s = h_2 + h_0$, where n is the number of layers in island A, $n-1$ is the number of layers in island B, s is the average atomic layer spacing, h_1 and h_2 are the measured heights of islands A and B relative to the adatom wetting layer, respectively, and h_0 is the thickness of the wetting layer relative to the GaN top layer (Ga adlayer).

Given that h_0, h_1, and h_2 are measured quantities (1.87 ± 0.1 Å, 9.47 ± 0.1 Å, 7.43 ± 0.1 Å, respectively), the two equations may be solved for n and s. The result is found that $n = 5.6 \pm 0.6$ and $s = 2.04 \pm 0.2$ Å. However, if $n = 6$, then $s = 1.89$ Å, in good agreement with the STM line profile measurements, as seen in Figs. 2(c) and 2(d). Slightly less good agreement would exist if $n = 5$, in which case $s = 2.27$ Å; therefore, since n must be an integer, in the following we select $n = 6$.

Although islands A and B as seen in cross-section L1 have different height, as seen in Fig. 2(c) we find by looking at line section L2 taken across the same two islands at an earlier point in time (~2 h) [image of Fig. 2(b)] that these islands were originally of the exact same height—namely 5 atomic layers. Line section L2, acquired under sharper tip conditions, also reveals the corrugation (adatom height) of the wetting layer.

The change in height of island A is further confirmed by comparing line sections L3 and L4, which were taken across the same island A, one later (section L3) and one earlier (section L4). A clear single atomic layer height difference is found. We conclude that an additional (and final) atomic layer has developed on top of island A during the STM experiment. We find in fact that this change occurred abruptly between two successive image frames separated by ~1 min. No partial completion of the 6th layer was observed. This shows us two things: (1) the surface at room temperature is dynamic and (2) the 5-layer islands are unstable with respect to 6-layer islands (note: the upward curvature to the left seen for island A in line section L3, commonly seen on clean GaN surfaces as well, is due to the existence of an underlying GaN growth spiral caused by a screw dislocation; this leads to a local warping of the surface but does not affect our conclusions).

Since there was no apparent change in the footprint of island A, the additional Ga and/or Mn atoms are presumed to have come from the adatom wetting layer, possibly induced by scanning. A tip-triggering mechanism leading to mass transport and growth of an additional Pb ML was reported for the case of Pb/Si(111).[14] In the case here, however, the conversion process was unintentional.

The relative stability of the 6-layer islands and their clear structural difference with the incomplete 5-layer islands is seen clearly in the close-up STM image of Fig. 3(a). The 6-layer island (island E, at upper left) shows a uniform parallel-row structure, weak corrugation along the $[11\bar{2}0]$ row direction, and the existence of long atomic chains which also run along the row direction. The existence of these 1-dimensional chains on top of the 6-layer islands proves directly that a 7th atomic (2D) layer is not stable. At the same time, the 5-layer island (island F at lower right) shows a complex and unstable structure with non-uniform rows and several domain boundary regions. Although the 5-layer island is atomically flat, it does not exhibit the structural perfection of the 6-layer islands, and the atomic chains seen on the 6-layer islands are never observed on the 5-layer islands.

With further regard to the atomic chains, they extend arbitrary distances (up to several 10's of nanometers) along $[11\bar{2}0]$ with an observed width as measured by the line cross-section [Fig. 3(b)] of ~1.5 nm. The chains are centered exactly halfway between the atomic rows of the island. Accounting for the shape of the probe tip, the real chain width is most likely just a single atom and at most a few atoms (convolution with the probe tip results in single adatoms appearing up to 10× their actual size). The spacing of the atoms along $[11\bar{2}0]$ is measured to be 6.3 ± 0.3 Å. Although the inter-chain spacing, as seen in Fig. 3, is typically 4× the island row spacing, other spacings (such as 3×) are also observed. Based on the highly anisotropic 1D shape of the chains, it is clear that adatoms diffuse along $[11\bar{2}0]$ with a higher barrier to diffusion along the orthogonal $[10\bar{1}0]$ direction.

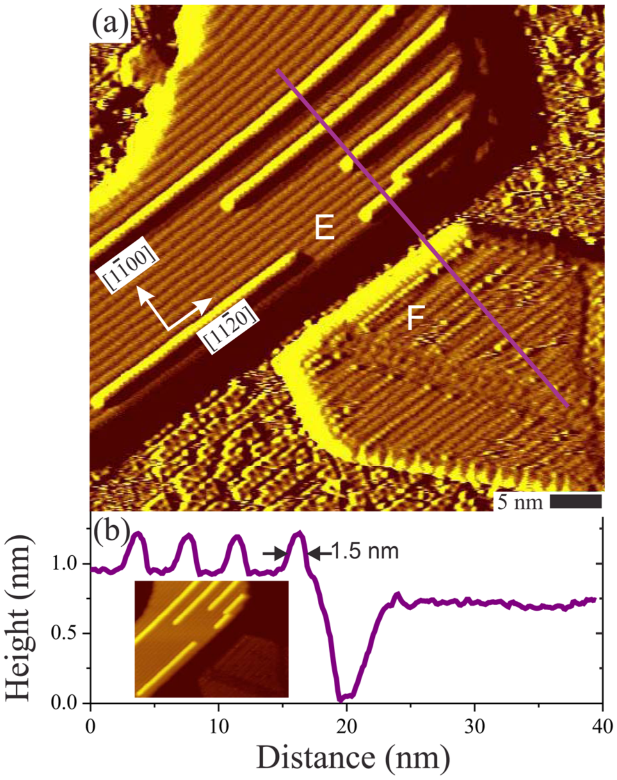

FIG. 3. (Color online) (a) 50 nm × 49 nm STM image showing 6-layer island (E) with uniform row-structure covered with several atomic chains and 5-layer island (F) with several domain boundaries ($V_S = -2.45$ V; $I_T = 74$ pA); (b) line cross-section corresponding to the line shown in (a). Image in (a) is shown in derivative mode; inset in (b) shows the normal image.

A large difference in diffusion barrier (up to 40 meV) between odd- and even-layered islands (bilayer oscillation) was reported for the Pb/Si(111) system which was attributed to the QSE, based on theoretical calculations.[2] If this principle can be extended to other systems, the very clear morphological difference between 5-layer and 6-layer islands seen here, as well as the presence of atomic chains only appearing on 6-layer islands, also indicates a large difference in diffusion barriers thus implying QSE-driven growth.

In conclusion, we have shown the formation of quantum height islands induced by the deposition of Mn onto the Ga-rich, N-polar GaN$(000\bar{1})$ surface. The relative stability of the 6-layer islands, as evidenced by (1) the completion of the 6th atomic layer at room temperature; (2) the formation of atomic chains on the 6-layer islands; and (3) the fact that no stable islands of different thicknesses have been observed, suggests that these MnGa islands form via a QSE-enabled growth mechanism, similar to what has been observed in *elemental* systems such as Pb/Si or Ag/GaAs. In this case, the formation of quantum-height MnGa *alloy* islands may have spintronic applications. The island stoichiometry along with detailed structural and magnetic properties will be interesting topics for further investigations.

Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317 (STM studies of magnetic nitride systems) and by the National Science Foundation under Award No. 0730257 (development of SP-STM expertise through international collaboration).

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