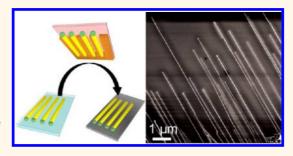
Guided Growth of Horizontal GaN Nanowires on Quartz and Their Transfer to Other Substrates

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ABSTRACT The guided growth of horizontal nanowires has so far been demonstrated on a limited number of substrates. In most cases, the nanowires are covalently bonded to the substrate where they grow and cannot be transferred to other substrates. Here we demonstrate the guided growth of well-aligned horizontal GaN nanowires on quartz and their subsequent transfer to silicon wafers by selective etching of the quartz while maintaining their alignment. The guided growth was observed on different planes of quartz with varying degrees of alignment. We characterized the crystallographic orientations of the nanowires



and proposed a new mechanism of "dynamic graphoepitaxy" for their guided growth on quartz. The transfer of the guided nanowires enabled the fabrication of back-gated field-effect transistors from aligned nanowire arrays on oxidized silicon wafers and the production of crossbar arrays. The guided growth of transferrable nanowires opens up the possibility of massively parallel integration of nanowires into functional systems on virtually any desired substrate.

KEYWORDS: nanowires · gallium nitride · quartz · self-assembly · transfer · epitaxy · bottom-up

uccessful integration of nanowires into practical devices is strongly dependent on how and on which substrate the nanowires are assembled. The most common approach today for planar assembly of nanowires is to manipulate and organize vertically grown nanowires after their synthesis. Vertical nanowires are usually grown off the surface by the vapor-liquid-solid (VLS) method and then harvested and deposited onto a target substrate in a controlled manner.¹⁻⁵ The alignment obtained by these techniques is usually not perfect due to thermal and dynamic fluctuations, and most of them offer limited control over the position and directionality (e.g., polarity, p-n heterojunctions, etc.) of each nanowire. Recent advances in postgrowth assembly by a combing method have significantly improved the degree of alignment and the lateral positioning of the nanowires.⁶ However, there is still no deterministic control over the positions of the two ends of each assembled nanowire, requiring further trimming to control the nanowire lengths. The guided growth method is an alternative approach for

nanowire assembly that can produce unprecedented control over the position, orientation, and length of nanowires already at the stage of their synthesis, ^{7–10} including the exact positioning of the two ends of each nanowire. ¹¹ Hence, the guided growth eliminates the need for complex and inaccurate postgrowth manipulations and enables massively parallel "self-integration" of the nanowires into circuits and other functional systems.

The guided growth approach has significant advantages over postgrowth methods but also some limitations with regards to its applicability to different substrates. In contrast to vertical nanowires that are used for postgrowth assembly, guided nanowires are grown horizontally on the surface of a substrate (also in the VLS mechanism). The growth direction is dictated by well-defined epitaxial interactions of the nanowires with the substrate or by relief features on the surface in the case of graphoepitaxial growth. This ensures a high degree of alignment and long-range order. A significant limitation of the guided growth so far is that it has only been demonstrated on a limited

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number of substrates, including sapphire⁸ (Al₂O₃), SiC,⁹ GaN,¹² and GaAs.¹³ These substrates are not optimal for many applications and not compatible with present and future technologies, such as Si-based integrated circuits and flexible electronics. The incorporation of guided nanowires onto substrates with different functional properties, such as transparency, flexibility, thermal and electrical conductivity, should pave the way to the fabrication of many unique devices. 14,15 Therefore, finding a substrate that enables the guided growth of horizontal nanowires and their subsequent transfer to any other substrate is currently a key objective.

In this work, we demonstrate the guided growth of horizontal GaN nanowires on quartz and their subsequent transfer to silicon wafers. The nanowires maintain their original orientation and relative position during the transfer process, thus no alignment steps are required after their growth. Guided growth of horizontal GaN nanowires on sapphire⁸ and SiC⁹ was previously reported by our group. Here we present for the first time the guided growth of aligned GaN nanowires on quartz substrates. Horizontal guided growth on quartz was extensively studied for carbon nanotubes, 16-18 as this is the most common way to produce highly aligned arrays of nanotubes, but to our knowledge, the guided growth of horizontal nanowires on quartz has not yet been reported. In this article, we demonstrate the guided growth of horizontal GaN nanowires by the VLS mechanism (Figure 1A) on different planes of quartz (Figure 1B), showing a different degree of alignment on each plane. The best alignment was obtained on X-cut ($11\overline{2}0$) and Y-cut ($10\overline{1}0$) quartz, and the horizontal nanowires grown on these planes were characterized to determine their crystallographic orientation. We recognized different

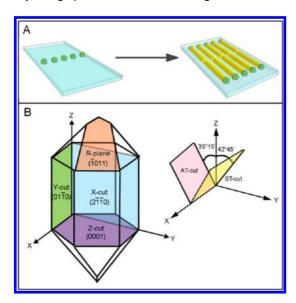


Figure 1. (A) Schematic representation of the guided growth of horizontal nanowires selectively from a catalyst pattern in specific directions. (B) Different planes of quartz on which GaN nanowires were horizontally grown in this work.

crystallographic orientations of the nanowires grown on the same substrate. This suggests a complex mode of guided growth, which is not typically epitaxial but could involve a chemically induced surface restructuration accompanied by graphoepitaxy. On the basis of our observations, we suggest a new guided growth mode for the growth of GaN nanowires on guartz that we tentatively term "dynamic graphoepitaxy". In this mode, the nanowires grow partially embedded into nanogrooves that are formed in situ within the quartz substrate in a preferred lattice direction. Following the characterization of the guided growth of GaN nanowires on quartz, we demonstrate the transfer of these nanowires from the quartz to other functional substrates, on which the aligned nanowire array did not grow directly. The transfer of aligned arrays of horizontally grown 1D nanostructures was previously demonstrated only for carbon nanotubes on sapphire 19 and quartz^{20,21} and for horizontally grown GaAs nanowires on GaAs,¹³ but not for other inorganic nanowires grown on other substrates. We demonstrate this methodology by transferring nanowires from X-cut quartz to silicon (Si/SiO₂) wafers and show that the nanowires maintain their alignment and relative position during the transfer. The transfer process is relatively straightforward, and we believe that it can be equally performed with other target substrates, paving the way to many applications that were not enabled so far by either postgrowth assembly or guided growth.

RESULTS AND DISCUSSION

Horizontal GaN nanowires were grown on quartz substrates by the VLS method in a chemical vapor deposition (CVD) system, consisting of a quartz tube that was placed inside a three-zone tube furnace. The nitrogen source was NH₃ gas; H₂ was used as a carrier gas, and the pressure in the fused silica tube was held at 400 mbar during the synthesis. Gallium was supplied from Ga₂O₃ powder held at 1000 °C inside the tube, and the samples were held downstream at temperatures ranging from 950 to 980 °C on a fused silica carrier plate. The Ni catalyst was patterned on the quartz substrates by photolithography and electronbeam evaporation as a nominal 5-10 Å layer. At the end of each synthesis, the sample was sonicated in isopropyl alcohol for a few seconds to remove GaN nanowires that grew vertically from the bulk of the patterned catalyst islands, while the horizontal nanowires that grew from the pattern edges onto the quartz surface remained in place.

The growth of horizontal GaN nanowires was carried out on six different planes of quartz (Figure 1B): X-cut $\{11\overline{2}0\}$, Y-cut $\{10\overline{1}0\}$, Z-cut $\{0001\}$, R-plane $\{10\overline{1}1\}$, ST-cut (42°45′ Y-cut), and AT-cut (35°15′ Y-cut). Out of these six planes, guided growth of well-aligned nanowires was achieved on X-cut and Y-cut quartz (Figure 2A-C). Weaker alignment was observed on

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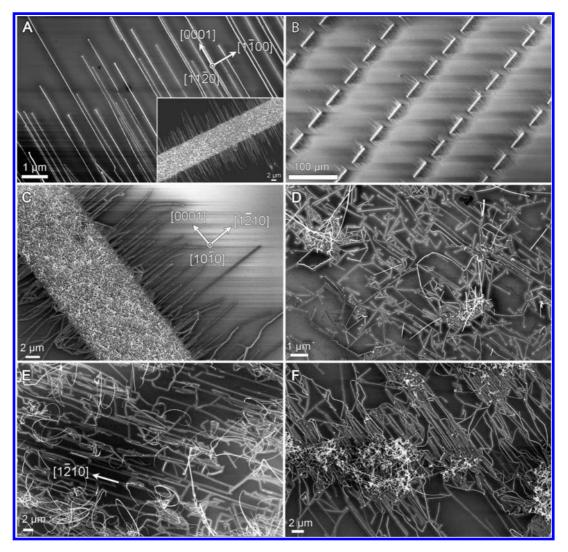


Figure 2. SEM images of horizontal GaN nanowires grown on different planes of quartz: (A,B) X-cut $(11\overline{2}0)$, (C) Y-cut $(10\overline{1}0)$, (D) R-plane $(10\overline{1}1)$, (E) ST-cut $(42^{\circ}45'$ Y-cut), and (F) AT-cut $(35^{\circ}15'$ Y-cut). The inset in A displays a lower-magnification image showing the patterned catalyst and the guided nanowires horizontally protruding from it. The catalyst nanoparticles can be observed at the opposite ends of many of the nanowires, consistent with a VLS tip-growth mechanism. The images show different degrees of alignment for each substrate. The best alignment was obtained on X-cut and Y-cut quartz, while nanowires grown on R-plane, ST-cut, and AT-cut quartz showed weaker alignment.

R-plane, ST-cut, and AT-cut quartz (Figure 2D-F). Horizontal nanowires that grew on Z-cut showed no alignment at all (see Supporting Information Figure S1). It should be noted that the synthetic conditions were often found to affect the alignment of the nanowires; hence we believe that, by further optimizing the growth parameters, better alignment could be achieved also on R-plane, ST-cut, and AT-cut quartz, which already demonstrated horizontal growth with some degree of alignment along certain favorable directions. For X-cut quartz $\{11\overline{2}0\}$, the effect of substrate annealing (13 h at 900 °C) prior to synthesis was examined. Horizontal GaN nanowires grew with a similar degree of alignment on both annealed and non-annealed X-cut quartz (see Supporting Information Figure S2). However, additional improvement of the alignment might be attained by surface pretreatment such as reactive ion etching (RIE), wet etching, or annealing of other quartz substrates. These treatments were proved in the past to improve the alignment of carbon nanotubes that were horizontally grown on different quartz planes.²²

In the next section, we characterize in-depth the guided growth of GaN nanowires on X-cut and Y-cut quartz, as the guided growth on these two planes was the most successful in terms of alignment among all the examined quartz planes.

Guided Growth of GaN Nanowires on X-cut and Y-cut Quartz. On X-cut $(11\overline{2}0)$ quartz, horizontal GaN nanowires grow along the $\pm [0001]$ directions of the quartz, while on Y-cut $(10\overline{1}0)$ quartz, horizontal GaN nanowires grow along the $\pm [1\overline{2}10]$ directions of the quartz. Under our experimental conditions, the horizontal nanowires grown on X-cut show a higher degree of alignment compared to the Y-cut. It is not yet clear whether this is an inherent comparison or further optimization of the

synthetic conditions would result in better alignment on the Y-cut, as well. The guided nanowires on X-cut and Y-cut were grown to lengths of up to 45 μ m, with a typical diameter of 15-40 nm. To understand the crystallographic structure and orientation of the guided nanowires, thin (50–100 nm) slices of the samples were cut across the nanowires using a focused ion beam (FIB) and observed under a high-resolution transmission electron microscope (HRTEM). The epitaxial relations between the nanowires and the substrates could not be directly observed in the crosssectional HRTEM images because the quartz becomes amorphous at the interface between the substrate and the C/Pt protecting layer during the lamella preparation with the FIB (based on the available data, a certain extent of amorphization during growth unrelated to the FIB cannot be completely ruled out). The crystallographic orientation of the quartz was determined from HRTEM images further away from the surface and was found to be consistent with the wafer flat provided by the manufacturer. Surprisingly, a variety of crystallographic orientations were observed among the guided nanowires on the same substrate, indicating that no specific epitaxial relations dictate the directionality of the horizontal growth.

Table 1 summarizes the crystallographic orientations of 32 nanowires grown on X-cut and Y-cut quartz. Overall, nine types of nanowires were observed in the cross-sectional TEM images of X-cut quartz, each type with a different crystallographic orientation of the GaN along the nanowire axis. Most axial orientations were observed only once, except three more common orientations: $[1\overline{2}10]$, $[0\overline{2}21]$, and $[14\overline{5}3]$ (Figure 3A–C). In each group of nanowires that shared the same axial orientation, the nanowires were rotated in different

TABLE 1. Crystallographic Orientations of Guided Nanowires on X-cut and Y-cut Quartz

substrate orientation	# of NWs	axial orientation $GaN \parallel SiO_2$
X-cut (11 <u>2</u> 0)	7 ^a	[1210] [0001]
	5 ^a	[0001] ال[0001]
	3 ^a	[1453] [0001]
	1	[1123] [0001]
	1	[7253] [0001]
	1	[1100] [0001]
	1	[4223] [0001]
	1	[7273] [0001]
	1	[10283] [0001]
Y-cut (1010)	4 ^a	[1210] [1210]
	3 ^a	[1100] [1210]
	1	[2423] [1210]
	1	[0332] [1210]
	1	[0112] [1210]
	1	[1783] [1210]

^a All of these nanowires have the same crystallographic axial orientation but are rotated with different angles with respect to their axis, presenting different horizontal planes to the substrate.

angles around their axis, presenting different horizontal planes of the GaN lattice to the quartz substrate. Cross-sectional TEM images of Y-cut quartz revealed six types of nanowires with different crystallographic orientations. The $[1\bar{2}10]$ and $[1\bar{1}00]$ orientations of the GaN were observed more frequently, while each of the other four orientations was observed only once (Figure 3D,E). As described for the X-cut case, the most common crystallographic orientations of the nanowires on Y-cut also exhibited different rotation angles around the nanowire axis and hence different horizontal planes with respect to the substrate.

In our previous work on the guided growth of GaN nanowires on sapphire, we also observed different crystallographic orientations of the nanowires on certain substrate planes, but never more than three different orientations for each plane.8 We explained this degree of variability by the existence of a few epitaxial relations with small energetic differences, which dictate the guided growth in the same direction. However, in the case of GaN nanowires grown on quartz, the variability of the orientations is significantly higher. This implies that all the orientations have similar interfacial energies with the substrate within the range of the thermal energy. This lack of specificity in the epitaxial relations between the nanowires and the substrate for both X-cut and Y-cut suggests that a stronger effect, such as graphoepitaxy⁸ rather than epitaxy, guides the nanowire growth in a specific direction along the substrate. This might seem surprising, considering that both X-cut and Y-cut quartz are singular and atomically flat.

Another interesting feature that was observed from the cross-sectional TEM images of the nanowires is that the nanowires are usually embedded in the substrate with a depth of 4–7 nm, for both X and Y-cut quartz (Figure 4). The nanowire cross section appears round at the interface with the substrate and faceted at the areas that were not in direct contact with the quartz substrate. This distinctive shape might be explained by a unique growth mechanism in which the nanowires grow slightly into the quartz.

Guided Growth Mechanism on Quartz. Several modes have been suggested in the past for the guided growth of horizontal nanowires: (1) epitaxial growth, based on a specific lattice match between the nanowire and the substrate that minimizes the interfacial energy and strain; (2) graphoepitaxial growth along nanosteps or nanogrooves, which are usually formed upon substrate annealing, driven by maximization of the interface area between the substrate and the nanowire or the catalyst; (3) endotaxial growth, involving epitaxial growth of the nanowires by a chemical reaction with the substrate to form with it a new compound;²³ and (4) a confinement guided growth method that enables control over nanowires' geometry and position by restricting their growth within artificial channels.^{24,25}

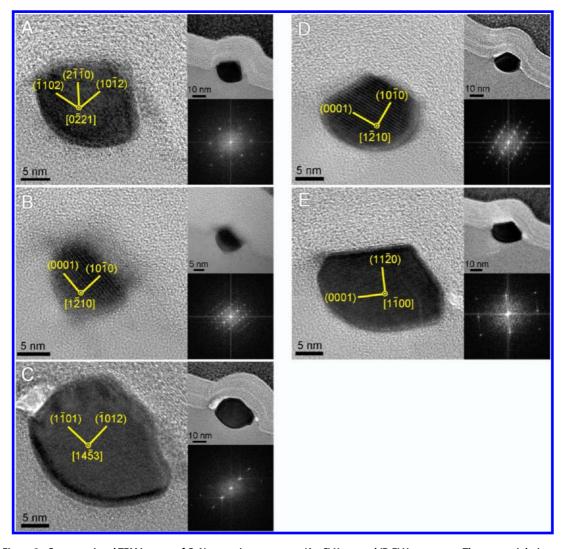


Figure 3. Cross-sectional TEM images of GaN nanowires grown on (A—C) X-cut and (D,E) Y-cut quartz. The upper-right insets show a low-magnification general view of the same cross section, and the lower-right insets show Fourier transform of the nanowires' section in the TEM image. The images exemplify the most common axial orientations of the nanowires that were observed on each substrate. See the Supporting Information for more TEM images of the less common orientations, on both X-cut and Y-cut quartz.

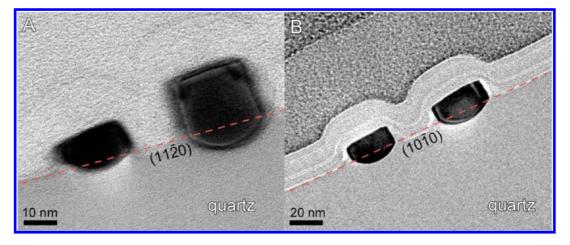


Figure 4. Cross-sectional TEM images reveal that the nanowires are slightly embedded in both the (A) X-cut and the (B) Y-cut quartz. Their shape is round at the interface with the quartz and faceted at the top. The transition between the rounded area and the faceted area occurs at the baseline of the quartz surface (indicated by the dashed red line).

In the case of guided GaN nanowires on quartz, the variety of nanowire orientations observed in the crosssectional TEM images indicates that there are no welldefined epitaxial relations between the nanowires and the substrate. Also, the quartz surface has no geometrical features (larger than lattice parameters) that can guide the nanowires along a certain direction, so the guiding force is not graphoepitaxy by definition. Based on our observations only, a detailed mechanism for the guided growth of GaN nanowires on guartz cannot be elucidated. Nevertheless, we suggest a general outline for a new guided growth mode that we can term dynamic graphoepitaxy. In this mode, the nanowires are formed via the VLS mechanism, starting with the selective absorption of Ga and N from the vapor phase into the liquid droplets of Ni catalyst, followed by the nucleation and growth of a nanowire due to the precipitation of GaN from the supersaturated droplet. During the growth, the catalyst droplet induces an anisotropic restructuration of the quartz surface, simultaneously with the GaN precipitation and the nanowire growth. Thus, the catalyst droplets actually plow aligned nanogrooves on the quartz for the nanowires to grow along them, so eventually the nanowires are grown slightly embedded into the nanogrooves that are formed in situ as the catalyst keeps being pushed forward by the growing nanowire. This dynamic graphoepitaxy mode features some of the properties of the endotaxy mode²³ and other properties of the graphoepitaxy mode;8 the GaN nanowires grow embedded in the quartz as in the endotaxy mode, but with no specific lattice match to the quartz substrate. It also shares some of the properties of the epitaxial guided growth in the sense that the nanowires grow along specific crystallographic directions of the substrate without the latter having any features larger than the lattice parameter. On the other hand, it differs from epitaxial guided growth because it does not lead to a specific crystallographic orientation of the nanowires themselves.

The absence of well-defined epitaxial relations, together with the round shape of the nanowires at the interface with the substrate, suggests that the guided growth may be driven by the maximization of the interfacial area, as in the graphoepitaxy growth mode. The control over the growth direction is not yet fully understood. We assume that the alignment is a result of surface energy differences between the quartz planes during the quartz restructuration, which are more pronounced under the synthetic conditions (i.e., substrate temperature, alloy composition at the catalyst droplet, gas environment, etc.). This is supported by our observation that, when X-cut quartz is etched in HF, the surface becomes anisotropically rough, with nanometric (~5 nm) grooves along the \pm [0001] direction (see Figures S6 and S7), which is the same direction of the guided growth of the GaN nanowires on this quartz plane. This suggests the existence of a surface instability leading to faceting along this direction. In some samples, a shallow anisotropic roughness (below 1 nm) could also be observed before etching. The generality of the model is yet to be examined for other planes of quartz as well as supported theoretically.

Transfer of Guided Nanowires to Silicon Wafers. The guided growth of horizontal GaN nanowires was previously reported on sapphire⁸ and SiC,⁹ and in this work, it is further elaborated for quartz substrates. However, such a controlled growth cannot be achieved by direct synthesis on every desired substrate, due to limitations related to the substrate properties and the specific growth conditions. For practical applications, certain properties of the substrate such as mechanical flexibility, thermal and electrical conductivity, or even low-cost and process compatibility can be essential for device fabrication and operation. Therefore, it is highly desired to develop the ability to transfer guided nanowires to a large variety of functional substrates. When the guided GaN nanowires are grown directly on sapphire or quartz, they are covalently bonded to the substrate, and their transfer is not possible without chemical intervention. Previous attempts to transfer guided GaN nanowires from sapphire failed due to the high chemical stability of the sapphire, and no etchant was found to selectively etch the sapphire while leaving the nanowires intact. Quartz, on the other hand, is a more chemically reactive substrate than sapphire. We found that it is possible to release the nanowires without damaging them, by selectively etching the quartz after the guided growth. After their release, the nanowires can be easily transferred to any other substrate.

In this work, we exemplify this concept by transferring guided GaN nanowire arrays grown on X-cut quartz to silicon wafers by selective etching of the substrate. The challenge was how to affix the nanowires to the substrate in order to maintain their relative spatial arrangement, while at the same time allowing the etchant to etch the substrate underneath the nanowires. This was successfully achieved by depositing a protective layer in a tilt angle, such that the nanowires are only coated from one side. Figure 5 displays a flowchart of the transfer process: After the nanowires are grown on quartz, a thin layer of 20 nm Cr and 80 nm Au is deposited at 60° with respect to the sample surface. By applying this tilt, the nanowires serve as a shadow mask during the deposition, and as a result, the quartz remains bare along one side of the nanowires, while the rest of the surface, including one side and the top of the nanowires, is covered with the Cr/Au film. At this state, the sample is dipped in buffered oxide etch (BOE) 1:6 (HF/NH₄F) for 3 h. The quartz is etched at the exposed areas along the nanowires and underneath them, which enables their release from the

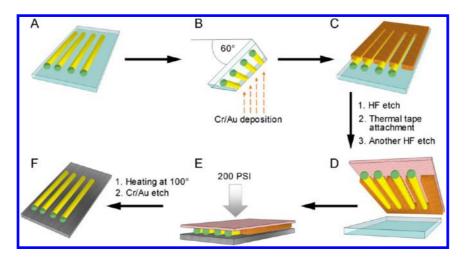


Figure 5. Schematic flowchart of the nanowire transfer process from the quartz to silicon wafers: (A) GaN nanowires are grown horizontally on X-cut quartz. (B,C) Cr/Au film is deposited at 60° so that along the nanowires the quartz remains bare and exposed to HF in the following etching process. (D) Thermal tape is attached to the sample and, after further etching, is peeled off together with the Cr/Au film and the nanowires. (E) Detached film is pressed against the Si/SiO₂ substrate, followed by the (F) removal of the thermal tape and the Au/Cr film by heating the sample and etching the Cr/Au layer in a commercial Cr etchant and a Kl/I₂ solution, respectively.

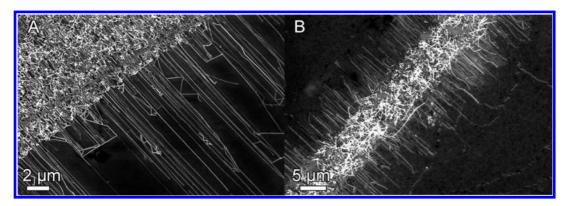


Figure 6. SEM images of GaN nanowire-transferred silicon wafers.

substrate, while at the same time, their position and alignment are fixed by the Cr/Au film. A thermal tape is then applied onto the Cr/Au film, and the sample is dipped again in BOE for 3 h. Usually, after this stage, the thermal tape is peeled off easily together with the Cr/ Au film and the nanowires, leaving the quartz surface clean. The peeled layers are then strongly pressed against a clean Si/SiO₂ substrate using a pneumatic press. The thermal tape is then detached by heating the sample at 100 °C for a few seconds, followed by oxygen plasma treatment to remove thermal tape residues. The Cr/Au film is subsequently removed by a commercial Cr etchant and a KI/I₂ etchant solution. All the etching processes are selective for the quartz and Cr/Au films and leave the GaN nanowires intact in the same geometrical arrangement of the guided growth.

Figure 6 shows SEM images of a transferred nanowire array on Si/SiO₂. The nanowires appear well-aligned, and their position is known since the catalyst pattern was designed prior to the synthesis. A clear advantage of such transfer was demonstrated by the

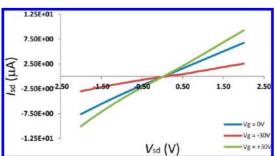


Figure 7. Performance of a back-gated FET from GaN nanowires that were grown on X-cut quartz and transferred to Si/SiO₂. The graphs of source-drain current (I_{sd}) versus source-drain voltage (V_{sd}) are displayed for different voltages that were applied to the silicon back-gate (V_{q}).

parallel fabrication of an array of back-gate field-effect transistors (FETs). The source and drain electrodes were defined on top of the transferred nanowires by photo-lithography; the thermal SiO_2 layer was used as the gate dielectric, and the degenerately doped silicon substrate is used as a back-gate. An example for the measured $\mathit{I-V}$ curves as a function of gate voltage in one of these transistors is presented in Figure 7.

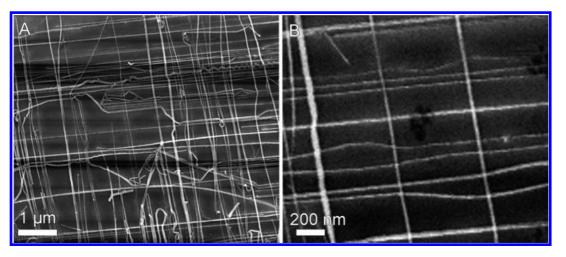


Figure 8. Nanowire crossbar arrays produced by transferring one array of guided GaN nanowires onto a similar array at 90° with one another.

The nanowires displayed a typical n-type behavior with an estimated mobility of 8 cm²/Vs.

The transfer method can also facilitate unique geometrical assemblies of nanowires that cannot be achieved directly by guided growth. For example, we demonstrate a nanowire crossbar array, which was assembled by transferring an aligned array of nanowires on top of another aligned array of nanowires on X-cut quartz. The top nanowires were transferred at 90° with respect to the nanowires that were originally grown on the X-cut quartz in the $\pm [0001]$ directions (Figure 8).

CONCLUSIONS

We have demonstrated the guided growth of horizontal GaN nanowires on different planes of quartz and their transfer to silicon wafers. We showed that horizontal GaN nanowires can have a variable degree of alignment on different planes of quartz. Under our synthetic conditions, the best aligned arrays were obtained on X-cut and Y-cut quartz. A crystallographic characterization of the aligned nanowires grown on X-cut and Y-cut quartz revealed a large variability of axial orientations. This suggests that a complex mode of guided growth, neither epitaxial nor graphoepitaxial, dominates the horizontal growth of GaN nanowires on quartz along specific lattice directions. Based on our observations, we proposed a new guided growth mode of dynamic graphoepitaxy, by which nanowires grow along nanogrooves formed in situ by restructuration of the quartz substrate in specific directions induced by the catalyst nanoparticles during the growth. The proposed mechanism of guided growth is still not fully understood and is yet to be supported by a theoretical model. Finally, we have demonstrated that using quartz as a substrate for the guided growth of GaN nanowires enables their transfer to other functional substrates, on which the direct guided growth is not possible. We developed a process to detach the nanowires from the quartz and transfer them to a receiving substrate, while maintaining their alignment and relative positions. This process was proven to be successful for the transfer of guided GaN nanowires from X-cut quartz to silicon wafers. The same process is expected to work equally well for other materials, including flexible substrates. Such experiments are planned but are currently beyond the scope of this article. A large variety of devices comprising aligned arrays of nanowires may become much easier to produce by transferring the nanowires from a highly ordered array than from a disordered suspension, as is often done in postgrowth methods. The guided growth of GaN nanowires on quartz presented in this work is not as perfect and deterministically controlled as we had previously reported for other nanowires and substrates,^{7-9,11} which was far superior to any postgrowth assembly method with regards to control of position, orientation, and length. This may be a matter of further optimization, as we have shown that the experimental conditions significantly affect the degree of alignment. In any case, the present proof-of-concept that guided nanowires can be transferred to any desired substrate paves the way to massively parallel integration of nanowires into functional systems on virtually any desired substrate via guided growth.

MATERIALS AND METHODS

Substrate Preparation. Quartz $(\alpha\text{-SiO}_2)$ wafers with six different orientations were used: Y-cut $(10\overline{1}0)$, Z-cut (0001), and R-plane $(10\overline{1}1)$ were purchased from Roditi International, ST-cut $(42^\circ45')$ Y-cut) and AT-cut $(35^\circ15')$ Y-cut) were purchased from Krystaly,

Hradec Králové, and X-cut ($11\overline{2}0$) wafers were purchased from both Quartz Unlimited and Roditi International. Before being used, all substrates were sonicated for 10 min in acetone, then rinsed in acetone, isopropyl alcohol, and distilled H₂O, and blowdried in N₂. Prior to catalyst patterning using photolithography,

the substrates were also treated with oxygen plasma (March Plasmod GCM 200, 2 min, 1 sccm of O_2 , 100 W).

Catalyst Patterning and Deposition. Ni catalyst was usually deposited by electron-beam evaporation of a thin (nominal 5—10 Å) metal layer. First, a pattern for catalyst deposition was defined using standard photolithography with negative photoresist. After pattern development, thin films (nominal 5—10 Å) of Ni were deposited by electron-beam evaporation, followed by lift-off in acetone. The thin Ni films underwent dewetting upon heating at 550 °C in air to generate the nanoparticles that serve as the catalyst for the VLS growth of the nanowires. We also performed a few experiments using Ni catalyst from nickel nitrate salt, obtaining similar results.

Nanowire Synthesis. GaN nanowire growth was carried out by a home-built chemical vapor deposition (CVD) comprising a 25 mm diameter quartz tube inside a three-zone tube furnace. Gallium was supplied from Ga_2O_3 powder (99.999%, Alfa Aesar) held at 1000 °C inside the quartz tube; the nitrogen source was ammonia gas (99.999%, Praxair), and molecular hydrogen (99,999%, Gordon Gas) was used as a carrier gas. The samples were held downstream at temperatures between 950 and 980 °C on a fused silica carrier plate. In the beginning of a typical experiment, the tube was inserted into the three-zone furnace and purged to remove oxygen by at least six cycles of pumping to 10 mbar and purging with molecular nitrogen (99.999%, Gordon Gas). During purging, the furnace was heating different zones of the tube. Once the tube was purged and the furnace reached 350 °C, ammonia gas (2.6-3.5 sccm) and H₂ gas (60-120 sccm) were streamed into the tube and pressure was maintained at 400 mbar while the furnace continued heating. When the desired temperature was achieved, the oven was moved over the Ga₂O₃ powder and turned off at the end of the growth time (25-45 min).

Microscopic Characterization. The grown nanowires were imaged using field-emission SEM (Supra 55VP FEG LEO Zeiss) at low working voltages (3—5 kV). Atomic force microscopy (AFM, Veeco, Multimode Nanoscope IV) images were acquired in air tapping mode using 70 kHz (FESP1). Thin lamellae for TEM characterization were made using a FEI Helios DualBeam microscope and inspected using a FEI Tecnai F30-UT field-emission TEM, equipped with a parallel electron energy loss spectroscopy (EELS) and energy-filtered TEM (Gatan imaging filter) operating at 300 kV. TEM digital images were recorded using a Gatan Ultrascan1000 CCD camera. TEM images were analyzed to determine crystallographic orientation using Fourier transform (FFT) from selected areas in the nanowire cross sections. Indexing of the FFT peaks was done according to crystallographic tables for bulk GaN.

Electrical Characterization. GaN nanowire field-effect transistors (FETs) were fabricated on Si/SiO₂ by defining source and drain electrodes using standard photolithography, followed by electron-beam evaporation of Ti and Au (20 and 30 nm, respectively)²⁶ and lift-off in acetone. The channel length between the source and drain electrodes was 10 μ m. The gate dielectric was the 200 nm thick thermal oxide (SiO₂) layer of the silicon wafers underneath the nanowires, and the degenerately doped silicon substrate was used as a back-gate. Two-terminal electrical measurements were performed by applying source-drain DC bias and measuring I-V curves as a function of gate voltage (V_a) . The charge carrier mobility (μ) was extracted from the transconductance, $g_{\rm m}$, which was defined as the slope of the $I_{\rm sd}-V_{\rm q}$ curve in the linear region and was given by eq 1, where V_a is the gate voltage, μ is the mobility, L is the nanowire channel length, and C is the capacitance.^{27,28} The capacitance is calculated using quasi-circular cross-section approximation given by eq 2, where h is the dielectric thickness and a is the average width of the horizontal GaN nanowire.

$$g_{\rm m} = \frac{{\rm d}I_{\rm sd}}{{\rm d}V_{\rm g}} V_{\rm sd=const.} = \mu \left(\frac{{\rm C}}{{\rm L}^2}\right) V_{\rm sd}$$
 (1)

$$C \approx \frac{2\pi\varepsilon\varepsilon_0 L}{\ln(4h/a)} \tag{2}$$

Nanowire Transfer. The transfer of guided GaN nanowires from quartz to other substrates was performed in four main

steps: (1) A thin layer of 20 nm Cr and 80 nm Au was deposited by electron-beam evaporation on the sample with the as-grown nanowires. During the deposition, the sample was tilted by 60° around the nanowire growth axis. (2) The sample was dipped in buffered oxide etch 6:1 (J.T. Baker) for 3 h, followed by a gentle wash with distilled H₂O and N₂ blow-dry. A thermal tape (Revalpha, Nitto Denko) was mounted onto the Cr/Au film before the sample was dipped once again in buffered oxide etch 1:6 for 3 h, followed by a distilled H₂O wash and N₂ blowdry. (3) The thermal tape was peeled off from the quartz together with the Cr/Au film and the nanowires. The peeled layers were strongly (200 psi pressure) pressed against a clean receiving substrate, using a homemade pneumatically operated nanoimprint setup. (4) The thermal tape was removed by heating the sample at 100 $^{\circ}\text{C}$ for a few seconds, followed by oxygen plasma treatment. The Cr/Au film was removed by the commercial Cr etchants (Technic France) and KI/I₂ solution, respectively

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: (1) Horizontal GaN nanowires that were growth on Z-cut (0001) quartz. (2) Horizontal GaN nanowires that were grown on annealed X-cut (11\overline{120}) quartz. (3) Additional cross-sectional TEM images of GaN nanowires on X-cut (11\overline{20}) quartz and Y-cut (10\overline{10}) quartz, exhibiting different crystallographic orientations. (4) EELS elemental map of GaN nanowires on Y-cut quartz. (5) AFM image of X-cut quartz before and after 40 min of etching in buffered HF, showing the spontaneous formation of nanogrooves upon etching. This material is available free of charge via the Internet at http://pubs.acs.org.

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