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Growth of large-scale vertically aligned GaN nanowires and their heterostructures with high uniformity on SiO_x by catalyst-free molecular beam epitaxy†

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The catalyst-free molecular beam epitaxial growth of GaN nanowires and their heterostructures on a SiO_x template is studied in detail. It was found that by optimizing the growth temperature, highly uniform and vertically aligned GaN nanowires and InGaN/GaN heterostructures with excellent optical properties can be obtained on a SiO_x template in a large-scale. This work provides an entirely new avenue for GaN nanowire based optoelectronic devices.

Dislocation-free semiconductor nanowire structures are a promising route to scale down the size of future electronic and photonic devices.[1–5] In this regard, III-nitride nanowires, due to their tunable energy bandgap from the ultraviolet (~6.2 eV for AlN) to the near-infrared (~0.65 eV for InN), as well as the large electron mobility and saturation velocity, have been intensively investigated.[6–8] To date, GaN nanowire based devices are generally achieved on single crystalline substrates, which have several downsides including high cost and limited performance for optoelectronic devices due to the light absorption by substrates. Therefore, to drastically reduce the device fabrication cost[9–11] and further improve the device performance, as well as to achieve seamless integration with other device components for the emerging flexible photonics and electronics,[12,13] it is of practical interest to develop high-quality GaN nanowires and their heterostructures, as the building blocks for future optoelectronic devices, on transparent and/or flexible substrates.

Previous efforts on the growth/synthesis of semiconductor nanowires and their heterostructures on transparent substrates are largely related to amorphous substrates (*e.g.*, SiO_x), and a foreign metal catalyst is typically utilized, which in general leads to a significant level of impurity incorporation, as well as uncontrolled structural, electrical and optical properties.[14–21] Development of catalyst-free processes to further improve the semiconductor nanowire quality on amorphous and/or transparent substrates is urgent.

Recently, in the catalyst-free spontaneous formation process of high-quality GaN nanowires on Si(111) substrates, a thin (~2 to 3 nm) SiN_x amorphous layer was found to exist in the nanowire–substrate interface, indicating that the nanowire nucleation and growth might start from this thin amorphous layer.[22–24] This, however, cannot lead to a conclusive argument that GaN nanowires can be spontaneously grown on amorphous substrates due to the incompletely removed influences from the Si(111) substrate, *e.g.*, the epitaxial relationship. Meanwhile, the spontaneous formation of GaN nanowires on a thick SiO_x buffer layer deposited on a Si(100) substrate has been investigated, wherein such an *ex situ* deposited amorphous layer can remove any potential influence from the Si substrate. In this case, the nanowire formation starts from SiO_x directly.[22] The resulting GaN nanowires, however, generally exhibit random orientations (with respect to the surface of the underneath SiO_x template), which is believed to be related to the local surface roughness of the underneath amorphous layer.[22]

Therefore, the realization of catalyst-free, electronically pure GaN nanowires on an amorphous substrate with controlled orientation, and superior crystalline and optical qualities on a large scale has remained elusive. In this communication, we report a detailed investigation of the catalyst-free molecular beam epitaxial (MBE) growth and characterization of GaN nanowires and their heterostructures on SiO_x (deposited on both Si(111) and Si(100) substrates). It was found that the substrate temperature plays a *significant* role in tuning the nanowire density, orientation, and uniformity; while there is no difference between using Si(111) and Si(100). Transmission electron microscopy (TEM) studies further indicate that the GaN nanowires grown at the optimized substrate temperature are nearly free of dislocations and stacking faults. Such GaN

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nanowires also exhibit strong photoluminescence (PL) emission at room temperature with the *absence* of yellow luminescence, further confirming the negligible level of defects. Furthermore, we demonstrate that high-quality InGaN/GaN heterostructures can also be achieved on a SiO_x template, the optical performance of which is as good as, if not better than that of the same structure but grown directly on a Si substrate. This demonstration of high-quality GaN nanowires and their heterostructures on an amorphous substrate provides great promise to move current GaN nanowire based optoelectronic devices to other transparent and/or flexible substrates.

The GaN nanowires/heterostructures were grown on a SiO_x template by radio-frequency (RF) plasma-assisted MBE. The SiO_x, with a thickness of ~100 nm, was deposited on a 2-inch Si(111) or (100) substrate by plasma-enhanced chemical vapour deposition (PECVD), and serves as an amorphous template for the nanowire formation. For the InGaN/GaN heterostructures, the thickness of the underneath SiO_x is ~1.5 μm. The growth conditions for the GaN nanowires include a substrate temperature (measured by a thermocouple) of ~780 to 830 °C, a Ga flux of $\sim 7 \times 10^{-8}$ torr, a nitrogen flow rate of ~0.6 to 1.4 sccm (1 sccm $= 1$ mL min^{-1}), and a RF plasma forward power of ~350 W.

PL measurements were performed in a homemade micro-PL setup. The GaN nanowires and InGaN/GaN heterostructures were optically excited using laser sources with $\lambda = 325$ nm and $\lambda = 405$ nm, respectively. The laser beam is focused onto the sample through a 100× objective, with a beam size of ~5 μm. The emitted light (collected through the same 100× objective) was spectrally resolved using a high-resolution spectrometer, and was detected by a liquid N_2 cooled CCD camera.

In order to determine the optimum growth conditions, GaN nanowires grown at different substrate temperatures were first investigated (in this case, the N_2 flow rate was kept at ~1.0 sccm, and the SiO_x layer was deposited on the Si(111) substrate). The scanning electron microscopy (SEM) images taken with a 45 degree angle are shown in Fig. 1; (a) to (c) correspond to ~830 °C, ~808 °C, and ~780 °C, respectively. It can be seen that as the substrate temperature decreases, the nanowire density increases dramatically. Meanwhile, the orientation of the nanowires changes from being random/tilted to almost 100% vertically aligned (the statistics of the nanowire angle with respect to the underneath SiO_x is shown in Fig. S1a†). Moreover, the uniformity, in terms of the nanowire diameter and length, increases significantly (the statistics of the nanowire diameter and length are shown in Fig. S1b and c,† respectively). Figure 1d clearly demonstrates such highly uniform and vertically aligned GaN nanowires (with diameters in the range of 50 to 60 nm, and lengths of ~600 nm) on a large scale. The 100 nm-thick SiO_x can also be seen as marked. Growth experiments were also performed by changing the N_2 flow rate from ~0.6 sccm to ~1.4 sccm, while keeping the substrate temperature fixed at ~780 °C. In this case, however, no significant changes in the nanowire density, orientation, and uniformity were observed. Furthermore, with similar growth conditions, changing the substrate from Si(111) to Si(100) while using the same SiO_x on top of the Si substrate does not affect the afore-described properties.

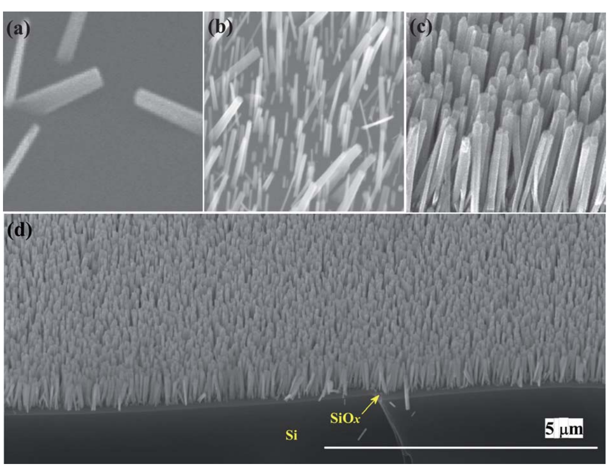

Fig. 1 SEM images of GaN nanowires grown on a SiO_x template (thickness ~ 100 nm) at different substrate temperatures taken with a 45 degree angle, of (a) ~830 °C, (b) ~808 °C, and (c) ~780 °C, respectively; the SEM images are of size 1 μm × 1 μm. (d) Same growth parameters as in (c) but shown on a large scale, with the SiO_x layer marked by an arrow.

These results clearly indicate that the substrate temperature is of critical importance to control the nanowire morphology. We propose that such substrate temperature dependence can be understood by the following. At relatively high substrate temperature, the Ga adatom desorption rate is high, and therefore the nucleation process is severely suppressed. As a result, the nanowire density is low (Fig. 1a). In this case, the orientation of the GaN nanowires depends strongly on the surface roughness of the underneath SiO_x template, thereby leading to random orientations for such low-density GaN nanowires.[22] Similar is the case for GaN nanowires with moderate density when the substrate temperature is decreased (Fig. 1b). Although some vertically aligned GaN nanowires are present, the nanowire orientation is still fairly random and highly dependent on the surface roughness of the underneath SiO_x template.

This situation is changed with further decreasing the substrate temperature. The much-reduced Ga adatom desorption rate (which in turn enhances the nucleation process) results in GaN nanowires with a very high density ($\sim 10^{10-11}$ cm^{-2}), and in this case the GaN nanowires are almost 100% vertically aligned (Fig. 1c). This can be ascribed to, with a high nanowire density, the number of Ga adatoms that can impinge onto the non-vertically orientated nanowires is significantly reduced, due to the shadow effect of the surrounding nanowires. As a consequence, the growth of non-vertical nanowires is suppressed, thereby promoting the formation of vertically aligned and nearly uniform GaN nanowire arrays. These results indicate that, besides the role of surface flatness, maintaining a high nanowire density is critical to achieve vertically aligned GaN nanowires on SiO_x, and this can be realized by optimizing the substrate temperature.

The excellent size uniformity and controlled orientation can also be maintained for relatively long GaN nanowires. Figure 2a shows the SEM image (taken with a 45 degree angle) of the GaN nanowires grown on a SiO_x template (deposited on a Si(111) substrate) at ~780 °C with a N_2 flow rate of ~0.6 sccm for a

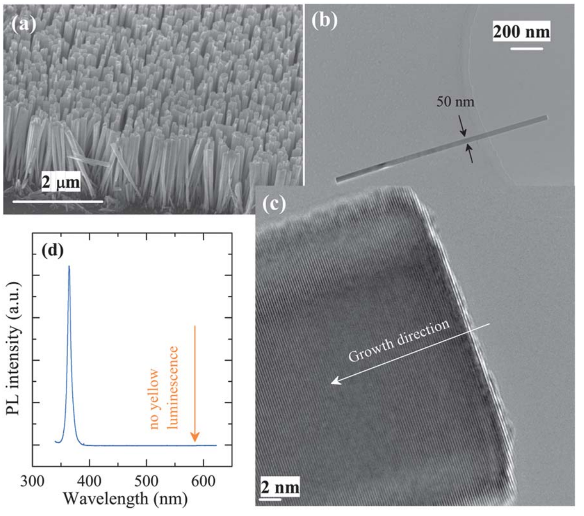

Fig. 2 (a) A SEM image of GaN nanowires grown on SiO_x (thickness ~ 100 nm) for a longer growth duration, taken with a 45 degree angle. (b) A low-magnification TEM image of a *typical* GaN nanowire. (c) A high-resolution TEM image of the bottom region of a *typical* GaN nanowire. (d) The PL spectrum measured at room temperature with a λ = 325 nm laser.

longer growth duration. It can be seen that the resulting nanowires maintain high uniformity and vertically aligned orientation. Figure 2b shows a low-magnification TEM image of a *typical* GaN nanowire with a length of ~1.8 µm and a diameter of ~50 nm. As can be seen, it exhibits a non-tapered morphology, *i.e.*, equal sizes in nanowire top and bottom. Figure 2c shows a *typical* high-resolution TEM image of the root of a single GaN nanowire, which exhibits clear atomic planes, and is free of stacking faults. Detailed studies further confirm that the entire nanowire is also free of dislocations. The PL spectrum measured at room temperature is shown in Fig. 2d, and no defect-related yellow luminescence is observed. The peak at ~363 nm (with a linewidth of ~6 nm) could be ascribed to the band-to-band carrier recombination, which is consistent with the bandgap energy of GaN. Again, whether using Si(111) or Si(100) for the SiO_x template deposition makes no difference to the nanowire qualities.

These results solidly indicate that high-quality (both structurally and optically) vertically aligned GaN nanowires can be grown on an amorphous template *on a large scale*, and the quality is comparable to that of GaN nanowires grown directly on a Si substrate,[22,23,25–29] due to a possibly similar nanowire formation mechanism.[22,23] More importantly, this work clearly indicates that the growth of GaN nanowires does *not* rely on the epitaxial relationship between the nanowire and the Si substrate. Therefore, we propose that the nanowire formation can be essentially achieved on *any* substrate *as long as* the 2D nuclei, which often rely on (but may not be limited to) the presence of an amorphous interface (*e.g.*, SiN_x, SiO_x), can be formed.[22,23] The subsequent shape transformation is driven by the anisotropies of surface free energies, surface stresses, as well as the interface barriers.[23]

In the next step, we have further investigated the growth and characterization of InGaN/GaN dot-in-a-wire light-emitting-diode (LED) heterostructures on a thick (~1.5 µm) SiO_x template (defined as "sample A"). The structure consists of Si-doped GaN, 10 vertically aligned InGaN/GaN quantum dots, and Mg-doped GaN. Each dot has a height of ~3 nm and is covered by a ~3 nm GaN barrier. The detailed growth process and characterization of such dot-in-a-wire LED heterostructures grown directly on a Si substrate were described elsewhere.[30] The schematic plot of this structure is shown in Fig. 3a. The corresponding SEM image is shown in Fig. 3b, from which it can be seen that the InGaN/GaN nanowires are almost 100% vertically aligned with high uniformity (the statistics of the nanowire diameter, length, and angle with respect to the underneath SiO_x template is shown in Fig. S2†).

The room temperature PL spectrum of sample A is measured (shown as the solid blue curve in Fig. 3c). The emission peak wavelength is ~650 nm, with a spectral linewidth of ~100 nm. This linewidth is comparable with the state-of-art values of planar structures[31] and nanowire structures[32–35] formed on crystalline substrates. The relatively broad linewidth in such a dot-in-a-wire InGaN/GaN heterostructure is directly related to the composition and size variations of the dots.[30] The PL spectrum of the same structure but grown directly on a Si(111) substrate (defined as "sample B") is also shown (the dashed red curve in Fig. 3c). It can be seen that sample A has a comparable or even stronger PL emission intensity compared with that from sample B. The stronger emission from sample A could be

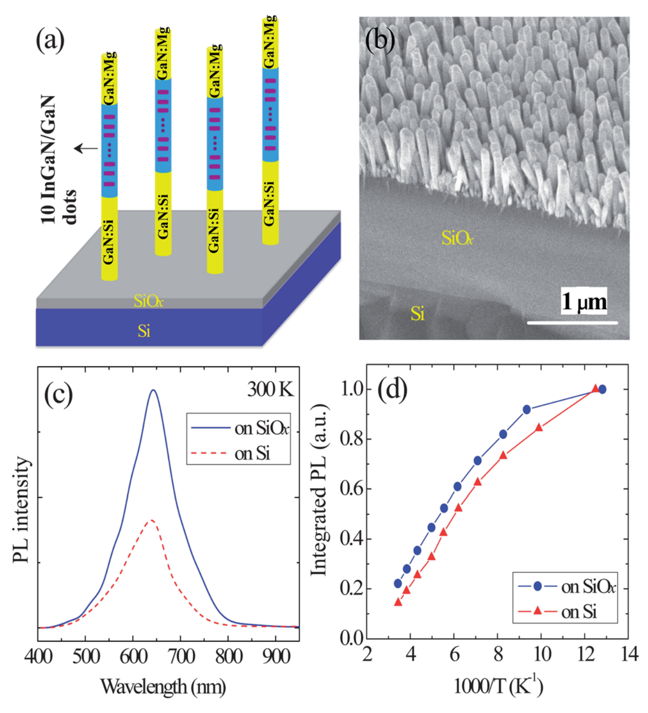

Fig. 3 (a) Schematic plot of the InGaN/GaN dot-in-a-wire LED heterostructures on SiO_x (thickness ~ 1.5 µm). (b) The corresponding SEM image taken with a 45 degree angle. (c) PL spectra for such LED heterostructures grown on SiO_x (solid blue curve) and directly on a Si substrate (dashed red curve), measured with a λ = 405 nm laser at room temperature. (d) Normalized integrated PL intensities as a function of the inverse temperature for samples A and B, measured from 74 K to 300 K.

ascribed to the *reduced optical absorption* by the SiO_x template. In addition, as illustrated in Fig. 3d, the integrated PL intensities at 300 K are about 20% and 15% of those measured at 74 K for sample A and sample B, respectively.

These PL measurements suggest that the optical performance of InGaN/GaN nanowire LED heterostructures on SiO_x is as good as, if not better than that of the same structure but grown directly on a Si substrate. In addition, for device applications, demonstrating high-quality nanowire structures on a transparent substrate is critical; therefore the "coupled" optical properties (of a nanowire–substrate system) are also of practical importance.

Up to here, highly dense and uniform GaN nanowires and their heterostructures with excellent optical properties have been demonstrated on an amorphous template, which is of crucial importance for realizing practical large-area optoelectronic devices, such as LEDs. This could provide another solution for achieving high-efficiency green and red LEDs based on GaN nanowires.

Although planar structure InGaN/GaN LEDs with extraordinary performance have been demonstrated in the blue and blue-green wavelengths, the efficiency of these devices in the deep green to red wavelength range has been extremely low due to the increased strain and dislocation densities.[36] Nanowire structures, on the other hand, promise high performance long-wavelength LEDs due to the much more efficient strain relaxation to the large nanowire surface. Recently, significant progress has been made in GaN nanowire based LEDs in the blue, green and red spectral range, with performance comparable to, or even better than that of conventional planar structure LEDs.[11,30,32–34,37] However, the external quantum efficiency has been severely limited by the optical absorption of the Si substrate in many cases.[30]

Therefore, further improving the LED performance requires the removal of the Si substrate, which can be alternatively satisfied by the growth of LED structures on a conductive transparent substrate or directly on a transparent electrode, considering the electrical injection. This becomes possible from the afore-discussed growth mechanism (*i.e.*, the growth of GaN nanowires and their heterostructures is essentially substrate *independent as long as* the 2D nuclei can be formed), as well as the demonstration of high-quality GaN nanowires and their heterostructures on a SiO_x template.

In summary, this work clearly demonstrates that high-quality (structurally and optically) GaN nanowires and InGaN/GaN heterostructures can be grown on an amorphous template on a large scale. This could further extend to other transparent substrates and/or electrodes, thus fundamentally enhancing the performance of GaN nanowire based optoelectronic devices. It also enables the integration of these devices to flexible substrates for the emerging flexible electronics and photonics.

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