

Origin of Yellow-Band Emission in Epitaxially Grown GaN Nanowire Arrays

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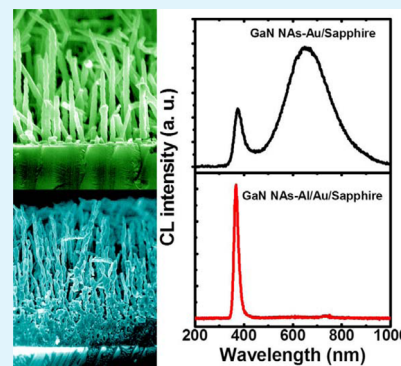
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S Supporting Information

ABSTRACT: Here, we report the origin of the yellow-band emission in epitaxial GaN nanowire arrays grown under carbon-free conditions. GaN nanowires directly grown on [0001]-oriented sapphire substrate exhibit an obvious and broad yellow-band in the visible range 400–800 nm, whereas the insertion of Al/Au layers in GaN–sapphire interface significantly depresses the visible emission, and only a sharp peak in the UV range (369 nm) can be observed. The persuasive differences in cathodoluminescence provide direct evidence for demonstrating that the origin of the yellow-band emission in GaN nanowire arrays arises from dislocation threading. The idea using buffering/barrier layers to isolate the dislocation threading in epitaxially grown GaN nanowires can be extended to the rational synthesis and structural defect controlling of a wide range of semiconductor films and nanostructures with superior crystal quality and excellent luminescence property.

KEYWORDS: GaN, nanowire arrays, epitaxial growth, interface, yellow-band emission



INTRODUCTION

The origin of yellow-band emission in gallium nitride (GaN) crystal has received extensive attention and discussion in the past years and nowadays due to its uncertainty and its damage to the performance of GaN-devices.^{1–5} A comprehensive and persuasive explanation responsible for the exact mechanism is still lacking, and several research groups have presented experimental evidence to elucidate the possible reasons for the yellow-band emission.^{4,6} Previous studies on undoped GaN films have claimed that carbon-related impurity and complex, which are introduced in a metalorganic chemical vapor deposition (MOCVD) process and are considered as an acceptor-type electron trapping center,^{7,8} are responsible for the well-known yellow luminescence band centered at 2.2–2.3 eV.^{1,9–12} The carbon-induced yellow-band emission has recently been verified by measuring the photoluminescence of polar-GaN and nonpolar-GaN nanowires in the visible range due to the relatively extensive carbon absorption of polar-GaN.⁴ In addition, the yellow-band emission of GaN has also been attributed to some point defect such as Ga-vacancy-related $V_{\text{Ga}}-\text{O}_{\text{N}}$ complex¹³ and the edge dislocation density.^{3,14}

On the other hand, the alignment of GaN nanowires or nanorods offers numerous advantages in optoelectronic nanodevice fabrication, block-building, and functionalization.^{15–19} GaN nanowires with diverse morphologies and tunable optoelectronic properties are ideal candidates for the

integrations of various functional nanodevices such as nano-field-emission transistor (FET), nanolight emitting diodes (LED), blue and ultraviolet light emitters, laser, diodes, chemical sensor, high-temperature, high-power optoelectronic devices, and nanophotonics.^{20–23} The intrinsic characteristics of GaN, known as wide band gap (3.4 eV), high melting point, large carrier mobility, higher electrical breakdown field, and chemical inertness, also make it more competitive and promising in comparison with its counterparts like ZnO and SiC. Therefore, it is definitely essential and important to understand the optical transition process (yellow band) and fabricate well-aligned GaN nanorods from the viewpoints of fundamental research and technological applications.

In this work, we demonstrated that the yellow-band emission of GaN nanowire arrays directly arises from the epitaxial growth on sapphire substrate and how the strong visible emission can be effectively depressed through the insertion of a Au barrier layer and an Al buffering layer. The epitaxial growth of GaN nanowires leads to the dislocation threading through the GaN–sapphire interface and thus deteriorates the GaN crystallinity. On the other hand, the lattice mismatching between GaN and sapphire will also induce some structural constrain that partly

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contributes to the yellow-band emission. On the contrary, the using of Au barrier layer can isolate the dislocation spreading, and the buffering Al layer can release the structural constrain. As a result, the origin of the yellow-band emission in GaN nanowire arrays can be confirmed, and GaN nanowires with strong near-band-edge emission (NBE) can be obtained. In addition, the method proposed in this work also offers more possibility for the growth of high-quality GaN nanowire arrays on a wide variety of cheap substrates as demonstrated successfully on sapphire, Si wafer, etc., and this method can also be extended to the dislocation density reduction and heteroepitaxial growth of other semiconductor film or nanostructures.

EXPERIMENTAL SECTION

Synthesis of GaN Nanowire Array. GaN nanowire arrays were directly synthesized using a feasible chemical vapor deposition (CVD) method as described in our previous work.²⁴ In a typical experiment, two types of substrates ([001]-oriented sapphire and sapphire substrate previously coated with 5 nm Au layer and 10 nm Al layer by electron beam deposition method) are used. High-purity Ga₂O₃ powders and ammonia gas are employed as the precursors for Ga and N for the formation of GaN. The growth temperature is set at 1100 °C, and stable NH₃ gas with a flowing rate of 200 mL/min was introduced into the growth chamber before the temperature was increased to 600 °C from room temperature. The growth of GaN nanowires was maintained at 1100 °C for 30 min and was then cooled to room temperature under protection of flowing Ar. The samples were collected for subsequent structural and compositional analyses.

Structural and Compositional Analyses. The as-grown GaN nanowires were analyzed and characterized using an X-ray diffraction spectrometer (XRD, RINT 2200HF) with Cu K_α as the X-ray source (λ 1.5046 Å), a field-emission scanning electron microscope (FE-SEM, INSPECT, F50) with an accelerated voltage of 20 kV, and a 200 kV Tecnai G² F20 high-resolution field emission transmission electron microscope (FETEM) equipped with an X-ray energy dispersive spectrometer (EDS). Elemental mappings of the GaN nanowires were carried out in a STEM mode.

Optical Property Measurement. The cathodoluminescence (CL) spectra of GaN nanowires and their spatially resolved CL images were measured in a field emission SEM (Hitachi, S4300) equipped with a CL system (Horiba, MP32S/M). The applied voltage and beam current in this work are 5 kV and 1000 pA, respectively. Details for the measurement can be found in previous work.²⁵

RESULTS AND DISCUSSION

To fabricate GaN nanowires with preferential orientation, it generally requires a highly crystalline foreign substrate, which has lattice matching with GaN. The smaller difference in lattice constants can allow an epitaxial growth of GaN and a decent crystallinity, and the good alignment of GaN nanowires can be guaranteed, as reported in our previous work.²⁴ So far, crystalline sapphire, SiC, and ZnO substrates are widely used for epitaxial GaN growth by various chemical vapor deposition (CVD) processes and highly cost molecular beam epitaxy (MBE) routines.²⁶ As an example, Figure 1a shows the top-view scanning electron microscope (SEM) image of GaN nanowire arrays epitaxially grown on [001]-oriented sapphire substrate. It can be seen that the majority of the GaN nanowires are vertically standing on the sapphire substrate with a small amount of GaN nanowires randomly crossing. Typically, the GaN nanowires epitaxially grown sapphire substrate exhibit a rough morphology, an average diameter of 300–400 nm, and a pyramid-like tip (inset of Figure 1a). Such pyramid-like morphology has been observed in our previous

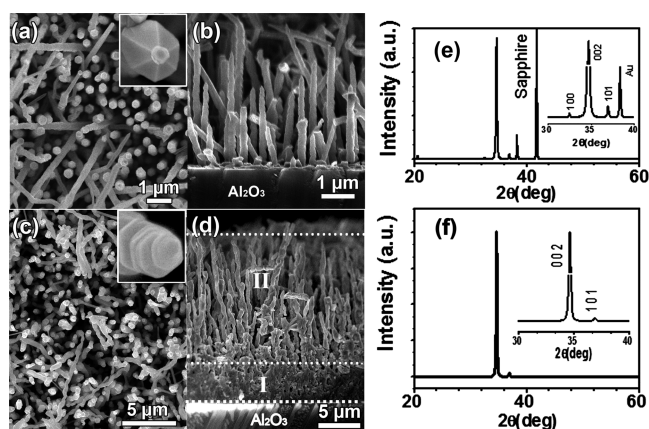


Figure 1. Top-view and cross-section SEM images of (a, b) GaN nanowires epitaxially grown on [001]-oriented sapphire substrate and (c, d) helical GaN nanowire arrays grown on Al/Au/sapphire substrate and (e, f) their corresponding XRD patterns. Insets of (a) and (c) are the SEM images of the representative tip-end of GaN nanowires; insets of (e) and (f) are the magnified XRD patterns in the range of 30–40°.

GaN nanorods and nanowires.^{24,27} The alignment of GaN nanowires can also be well confirmed from the cross-section SEM image (Figure 1b), and the epitaxial nucleation of GaN nanowires on sapphire substrate can also be supposed because no buffering layer between GaN nanowires and sapphire substrate is ahead deposited. The length of these GaN nanowires ranges from 1 to 10 μ m due to different nucleation stages and growth rates, but their preferential orientation is predominantly along the [001] direction, as verified by the strong diffraction intensity of the (002) peak in the X-ray diffraction (XRD) pattern (Figure 1e). From the magnified XRD profile in the inset, two weak peaks near the (002) peak can also be observed, which can be indexed to the (100) and (101) peaks of a wurtzite-type hexagonal GaN (see JCPDS card no. 760703) and arise from GaN nanowires randomly distributed in the nanowire arrays (Figure 1a). Distinctly different from aligned GaN nanowire epitaxially grown sapphire substrate, the insertion of a thin Al layer (\sim 10 nm) and a thin Au layer (\sim 5 nm) between GaN–sapphire interlayer leads to the obvious morphology evolution of GaN nanowires, as shown in Figure 1c,d. The GaN nanowires grown on Al/Au/sapphire substrate still show a preferential orientation with most GaN nanowires perpendicularly standing on the substrate and few nanowires dangling on the arrays (Figure 1c). The magnified SEM image on the tip of GaN nanowires reveals that the GaN nanowires possess a hexagonal cross-section morphology instead of the pyramid-like one (inset of Figure 1c). Further observation on dozens of GaN nanowires concluded that the GaN nanowires exhibit an obvious helical feature in morphology, and the tip is flat without the presence of any catalyst. Such helical GaN morphology has once been observed in ZnGa₂O₄ nanostructures.²⁸ The detailed crystallography analyses using high-resolution transmission electron microscope (TEM) will be presented later. Figure 1d shows the cross-section SEM image of GaN nanowires grown on Al/Au/sapphire substrate, and one can clearly see the uniform orientation. The preferential orientation of GaN nanowires can also be well revealed by the predominant diffraction intensity of (002) peak in XRD pattern (Figure 1f). Besides the (002) peak, the magnified XRD pattern in the range of 30–40°

(inset of Figure 1f) only shows the (101) peak with small intensity, reflecting the good alignment of GaN nanowires. Despite the obvious difference in morphology for the two-type GaN nanowires, the formation of GaN nanowire arrays on Al/Au/sapphire substrate includes two continuous stages: (1) the deposition of GaN nanoparticles and (2) the growth of aligned helical GaN nanowires via self-assembled process. In contrast to the direct epitaxial growth of GaN nanowires on sapphire substrate (Figure 1b), the GaN nanoparticle layer with a thickness of 5–10 μm will first nucleate on the surface of Al layer (in fact, the Al layer has been ammoniated to AlN layer in ammonia gas at high temperature), as shown in area I; then these GaN nanoparticles on the Al layer surface tend to evolve into helical nanowires with good alignment (area II). The absence of catalyst particles on the tip-end of these GaN nanowires suggests that the Au nanoparticles beneath the Al layer do not act as catalyst to promote the nucleation of GaN nanowires and are not responsible for the formation of GaN nanowires.

Previous studies on epitaxial GaN films and nanowires have proved that the dislocation can easily pass through the GaN–sapphire interface and spread into GaN crystal,²⁹ and thus high dislocation density was often observed in such GaN crystal. The accumulation of dislocations in epitaxially grown GaN layers or nanowires will worsen their crystal quality and thus deteriorate the performance of GaN-based optoelectronic devices. The problematic dislocations will cause the current leakage in LED,³⁰ the lifetime reduction of laser diode, and the poor efficiency of HEMTs.^{31,32} Another example of dislocation in deteriorating the GaN-based nanodevices comes from the fact that GaN nano-LED made of p-type GaN nanowire arrays and n-type Si substrate can only produce a quantum efficiency as low as 2.7%.¹⁷ Figure 2 shows the cathodoluminescence (CL)

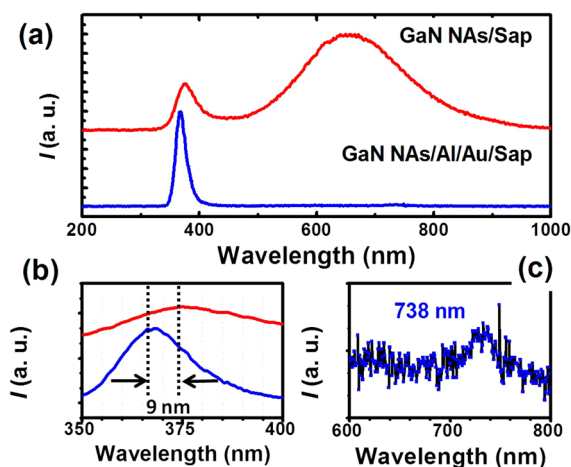


Figure 2. (a) Room-temperature CL spectra of GaN nanowires epitaxially grown on sapphire substrate and helical GaN nanowires grown on Al/Au/sapphire substrate; (b) magnified CL spectra of the two type GaN nanowires in the UV range; and (c) magnified CL spectrum of helical GaN nanowires in the visible range.

spectra of GaN nanowire arrays grown on sapphire and Al/Au/sapphire substrates, respectively. The spectra were directly collected from two types of dense GaN nanowires under an accelerated voltage of 5 kV and a beam current of 1000 pA at room temperature, and represented their general features of GaN nanowires in optics. It can be seen that the two spectra exhibited obvious differences in the investigated wavelength

range of 200–800 nm. First, the GaN nanowires directly grown on sapphire substrate have one small peak in the UV range and a strong visible luminescence band in the range of 600–800 nm, whereas the GaN nanowires deposited on Al/Au/sapphire substrate only show a sharp peak centered at 369 nm (Figure 2a). The flatness of the CL curve in the visible range indicates the superior crystallinity and higher purity of helical GaN nanowires. When the CL curve in the visible range is magnified, only one weak peak centered at 738 nm can be found, and this small band corresponds to the second order of the strong UV emission at a wavelength of 369 nm, instead of the yellow band (Figure 2c). Second, the helical GaN nanowire arrays grown on Al/Au/sapphire substrate exhibit an obvious blue-shift for the CL peak in the UV range in comparison with the GaN nanowires epitaxially grown on sapphire substrate (Figure 2b). Generally, the 369 nm UV emission of GaN nanowires can be assigned to the near-band-edge emission (NBE), whereas the origin of the yellow-band luminescence is still in debate.^{1,2,4,33,34} The significant differences in the visible emissions for these two types of GaN nanowires strongly demonstrated that the origin of yellow-band emission in GaN nanowire arrays should arise from the threading dislocation originally formed in sapphire substrate, as observed in epitaxial GaN nanorods by HRTEM.²⁹ At least in this work, the broad yellow band of GaN nanowires directly grown on sapphire substrate can be assigned to the dislocation induced by epitaxial growth. The same experimental conditions except for substrate types (sapphire and Al/Au/sapphire) have completely excluded the possibility of carbon contamination. Different from MOCVD-GaN no carbon-containing precursors were used in the whole reaction process of GaN formation, and thus any carbon-related complex contamination is excluded. Some literature pointed out that gallium vacancies are responsible for the yellow-band emission,³³ but the weak CL intensity of GaN nanowires grown on Al/Au/sapphire substrate in the range of 600–800 nm (Figure 2c) has ruled out the gallium vacancy-related assertion due to the facts that the two types of GaN nanowires are grown under the same experimental conditions (Ga_2O_3 precursor for Ga source, ammonia for N source, the same growth temperature and gas flowing rate, etc.). The sole difference comes from the different substrates. Therefore, it can be claimed that the insertion of Al/Au double layers should be responsible for the yellow-band depression in GaN nanowires. The adding of Al/Au layers also leads to the obvious peak shift toward the short wavelength direction, and a blue-shift distance of 9 nm can be identified (Figure 2b). From Figure 2a, it can also be found that the CL peak narrowing of GaN nanowire arrays and a full width of half-maximum (fwhm) value decrease from 51 to 22 nm can be obtained after the insertion of Al/Au layers. The disappearing of the yellow-band emission and the sharpness of the UV emission peak further demonstrated the effectiveness of Al/Au layers in preventing the dislocation threading and in improving the crystal quality of GaN nanowire arrays.

To further evaluate the optical characteristic and to precisely determine the spatial luminescence distribution of GaN nanowires grown on Al/Au/sapphire substrate, the monochromatic imaging of an individual GaN nanowire was carried out at room temperature. Figure 3a shows a single GaN nanowire with three consecutive broken sections dangling on the TEM grid, and the helical morphology can be observed. According to the CL spectra shown in Figure 2a, spatial monochromatic CL images were recorded in the UV (369 nm)

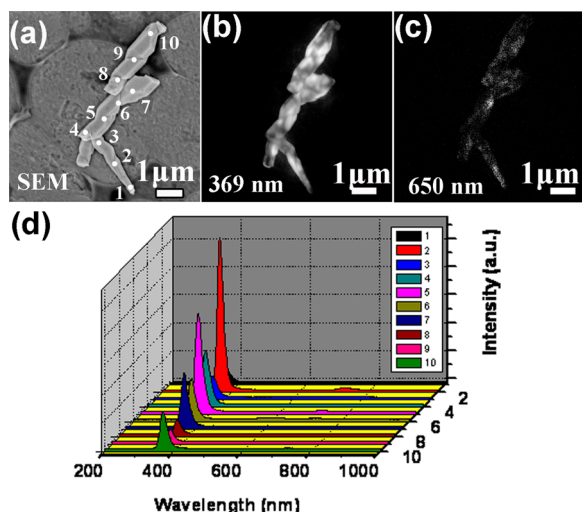


Figure 3. (a) SEM image of helical GaN nanowires dangling on the TEM grid and their corresponding spatially resolved CL images at the wavelength of (b) 369 nm and (c) 650 nm; and (d) position-dependent CL spectrum profiles collected at different areas of the helical GaN nanowire shown in (a).

and vis (650 nm, the wavelength is selected on the basis of the CL spectra in Figures 2c and 3d) ranges, respectively, under the same measuring conditions as the CL spectrum. One can see that the helical GaN nanowire shows strong UV emission under the energetic electron excitation, whereas the CL mapping in the vis range is almost dark, implying the poor luminescence of the yellow-band emission in the visible range. The distinguished contrast between these two CL images demonstrates again the superior optical properties of helical GaN nanowires and the excellent performance of Al/Au layers in depressing the yellow-band emission. Figure 3d shows the position-dependent CL profiles of helical GaN nanowire in Figure 3a. Ten CL spectra were collected from the different areas along the GaN nanowire, and one can see that all of the spectra present a predominant peak in the UV range despite the intensity differences, whereas the luminescence intensity in the visible range is almost too weak to be clearly identified. The position-dependent CL results are in good agreement with the spatial CL imaging shown in Figure 3b and c. It should be noted that the CL spectra show an obvious tendency in intensity increasing from the bottom to the growth tip-end of GaN nanowire (Figure 3d), suggesting the gradual crystallinity improvement along the growth direction of GaN nanowire arrays.

In GaN crystal, both the Ga/N ratio and the invasion of unconscious contamination/doping, as well as the structural defects, can have a strong influence on its band gap and yellow-band emissions.^{27,35} Deviation of Ga/N ratio from the standard stoichiometry will lead to the peak shift of its band gap emission,²⁷ and impurity in GaN lattice will result in the strong defect-related emission in visible range.³⁶ Therefore, it is definitely required to further clarify the purity and composition in as-synthesized GaN nanowires for a clear understanding of its optical property. The two types of GaN nanowires are examined by high-resolution energy X-ray dispersive spectrum (EDS), and it was found that the CVD-grown GaN nanowires are of high purity in composition (Supporting Information Figure S1). The quantitative analyses performed on dozens of GaN nanowires confirmed that the average ratio of Ga/N

approaches 1:1, in good agreement with the stoichiometric composition of standard GaN crystal. As an example, Figure 4a

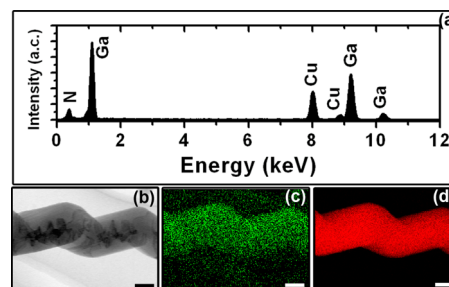


Figure 4. (a) Representative EDS spectrum of helical GaN nanowires; (b) STEM image of an individual GaN nanowire; and the elemental mapping of (c) Ga and (d) N. The scale bar is 100 nm.

shows the EDS spectrum of helical GaN nanowires grown on Al/Au/sapphire substrate, and one can clearly see the N and Ga peaks (the Cu signal is from the copper TEM grid). The peak of the other possible impurities like O and C³⁷ is not observed within the resolution limit of EDS, implying the high purity of our GaN nanowires. The spatially resolved elemental mapping of a GaN nanowire (Figure 4b–d) gives a uniform distribution of N and Ga elements inside the nanowire. From the CL and EDS results, the possibility of any carbon/oxygen-related contamination responsible for the yellow-band emission of epitaxially grown GaN nanowires can be excluded, and it can be concluded again that the yellow-band emission of GaN nanowires originates from the threading dislocation, at least in current work.

Hsu and co-workers have verified the dislocation threading in epitaxially grown GaN nanowires based on high-resolution TEM observation on the GaN–sapphire interface,²⁹ and this phenomenon has also been found in various epitaxially grown GaN films using HRTEM.³⁸ The propagated dislocations have been considered as the key factor to deteriorate the optical emissions and detrimental to the performance of GaN-based devices. In epitaxially grown GaN film or nanostructures, the matching lattices between GaN and sapphire enable an easy dislocation propagation into subsequently grown GaN crystal, whereas the insertion of Al/Au layers will destroy the lattice-matching relationship between GaN and sapphire. Sapphire and Au have different structural symmetries, and their lattice constants vary enormously. The huge lattice mismatching will allow the Au atoms to be randomly deposited on the sapphire surface without preferential crystallographic orientation within the small thickness (<5 nm). The disordering arrangement of Au atoms will block the propagation of dislocation initially formed in sapphire substrate. On the other hand, the adding of Al/Au layers will also promote the formation of a continuous void at the GaN–sapphire interface during/after the growth of GaN nanowires (Supporting Information Figure S2b). The void will undoubtedly isolate the dislocation threading and improve the crystal quality of GaN nanowires. The void-assisted method has also been used to improve the crystal quality of bulky GaN film.³⁹ As a result, the defect-related yellow-band emission of GaN nanowire arrays has been effectively depressed (Figure 2).

The microstructure and crystallinity of GaN nanowires grown on Al/Au/sapphire substrate were also well studied using a HRTEM under an accelerated voltage of 200 kV. Figure 5a shows a representative GaN nanowire with a twist-like

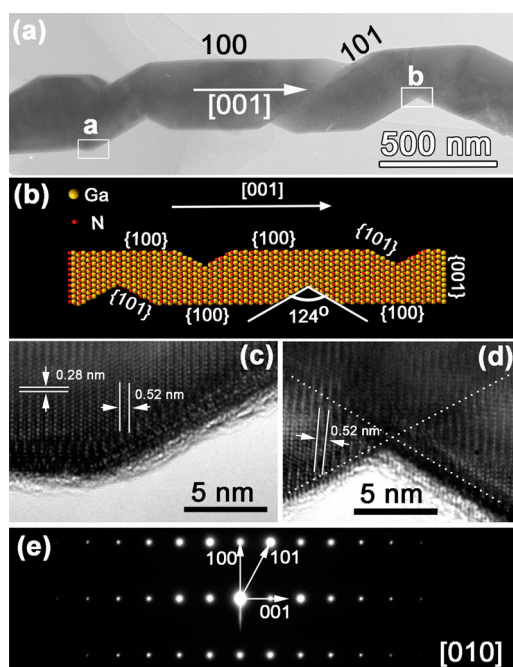


Figure 5. (a) Typical low-magnification TEM image of a helical GaN nanowire removed from Al/Au/sapphire substrate; (b) crystallographic model of the helical GaN nanowire; (c, d) high-resolution TEM images of the selected areas of “a” and “b” shown in (a); and (e) the SAED pattern taken along a zone axis of [010] direction from GaN nanowires.

helical morphology. Typically, the GaN nanowire is composed of different kinking sections linking together and exhibits a zigzag shape. It can be seen that the side walls of GaN nanowire are parallel to the axial direction and can be further indexed to the (100) facets through TEM analysis, whereas the kinking surfaces correspond to the (101) planes of a wurtzite-type hexagonal GaN, as marked in Figure 5a. The angle between two neighboring sections is measured to be 124° (Figure 5d), in good agreement with the theoretical value between (100) and (101) planes of GaN. A detailed description of the crystallography of helical GaN nanowire is schematically shown in Figure 5b. All of the crystalline planes shown in Figure 5a match well with these labeled in the crystal model (Figure 5b). To evaluate the crystallinity of helical GaN

nanowires, two representative areas labeled as “a” and “b” are studied using the HRTEM, and their corresponding high-resolution atomic images are shown in Figure 5c,d. One can see that all of the atoms are regularly arranged in the ordering of a wurtzite-type hexagonal GaN structure and the nanowire exhibits an obvious characteristic of single crystal. The selected area electron diffraction (SAED) pattern taken along the zone axis of [010] direction also shows succinct diffraction spots (Figure 5e), demonstrating again the superior crystallinity of helical GaN nanowires. The measured lattice distances between neighboring planes are 0.52 and 0.28 nm, respectively, matching well with the d -spacing values of (001) and (100) crystalline planes of a standard GaN crystal (see JCPDS 760703). From the HRTEM image and SAED pattern, the preferential orientation of helical GaN nanowires can also be confirmed to be the [001] direction (Figure 5a), in good agreement with the XRD and SEM data (Figure 1). The structural defects such as twins or stacking faults are not found from the HRTEM images of several TEM samples, suggesting the excellent crystallinity of as-synthesized GaN nanowires and well supporting the CL results. For the crystallinity of epitaxially grown GaN nanowires on sapphire substrate, our previous TEM studies have shown that they are still well crystallized and free of twin or stacking faults.²⁴

On the basis of detailed microstructure and cathodoluminescence studies on these two different types of GaN nanowire arrays, it can be concluded that the yellow-band emission of GaN nanowires indeed arises from dislocation-related structural defects in the case of carbon free. Meanwhile, the effectiveness of Au barrier layer in isolating the dislocation threading and Al buffering layer in promoting the preferential growth of GaN nanowires has been successfully demonstrated. To fully understand the possible mechanism accounting for the block of dislocation threading (or the depression of the yellow-band emission), a schematic diagram describing the different growth processes of GaN nanowires with/without Al/Au layers was plotted (Figure 6). For GaN nanowires epitaxially grown on Au-coated sapphire substrate, the GaN nanowires directly nucleate on sapphire surface and grow under the catalytic assistance of Au particles, as schematically described in Figure 6a. In this case, the formation of GaN nanowires follows the well-known vapor–liquid–solid (VLS) growth mode, and the Au layer serves as catalyst. Most importantly, the lattice matching between GaN nanowires and sapphire substrate is

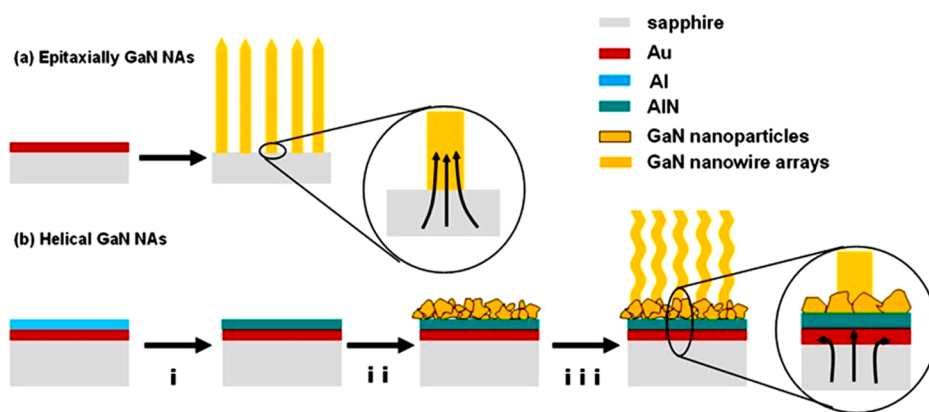


Figure 6. Schematic diagrams for the formation of (a) GaN nanowires epitaxially grown sapphire substrate coated with Au layer and (b) helical GaN nanowires grown on Al/Au/sapphire substrate. The magnified schematics in (a) and (b) illustrate the different dislocation threading processes at the interfaces.

well maintained, and thus the dislocation can easily pass through the GaN–sapphire interface and penetrate into GaN nanowires (as presented in magnified schematic diagram). Therefore, it is reasonably understood that why the yellow-band emission with strong intensity is observed in epitaxial GaN nanowires (Figure 2a). Such dislocation threading at GaN–sapphire interface has been observed in various epitaxially grown GaN layers³⁸ and nanostructures.²⁹ When thin Al/Au layers were inserted into the GaN–sapphire interface, the growth mechanism and process of GaN nanowires exhibit a totally different feature. First, the Al layer at the top surface will be ammoniated into AlN layer, as described in process I, Figure 6b. The AlN matches well with GaN in structural symmetry and lattices, acting as the buffering layer to release the lattice constrain of subsequently grown GaN crystals. It should be noted that the introduction of ammonia gas should start from a temperature below the melting point of Al (663 °C) to ensure the formation of AlN layer, whereas the beneath Au layer still maintains its initial state. When the temperature approaches the reaction temperature (1000–1100 °C), the GaN will nucleate on the AlN surface and accumulate into some nanoparticles with a thickness of $\sim 5 \mu\text{m}$ (Figure 1d), as schematically shown in process II, Figure 6b. Because of the chemical inertness and higher melting points of AlN and sapphire, the Au layer will be confined in the AlN–sapphire interlayer and will not participate in the GaN nucleation. With the continuous supplying of Ga and N precursors, the GaN nanoparticles at the top layer prefer to evolve into wire-like morphology with uniform orientation via a self-assembled process and finally form the helical nanowire arrays as shown in Figure 1b (process III, Figure 6b). It should be highlighted that the Au layer plays a critical role in blocking the dislocation threading. Because of the huge lattice mismatching of Au with AlN and sapphire, no epitaxial growth relationship among them can be established. Furthermore, some continuous void will also be simultaneously generated during/after the formation of GaN nanowire arrays, spatially preventing the dislocation propagation. As a result, any possible dislocation threading in the GaN–sapphire interface has been completely isolated, as schematically described in the magnified diagram in Figure 6b. In addition, it should be noted that the Au layer thickness also plays a key role in controlling the growth of GaN nanowire arrays, as well as Al layer thickness. Different Au/Al layer thicknesses have been tested, and it was found that the thickness of Au (or Al) layer should be at least 5 nm or more to isolate the dislocation threading and to enable an epitaxial growth of GaN. The smaller thickness of Au layer will lead to partial epitaxial growth of Al (AlN) with sapphire substrate, and thus the dislocation can penetrate into the subsequently formed GaN crystal, while the smaller thickness ($< 5 \text{ nm}$) of Al layer will cause the beneath Au layer to pass through Al layer to serve as catalyst for GaN nanowire growth. Last but not least, different from the directly epitaxial growth of GaN nanowires on sapphire substrate (Figures 1a and 6a), the helical GaN nanowires were homoepitaxially deposited on GaN nanoparticles previously nucleated on AlN buffering layer. The AlN layer and the GaN nanoparticles have completely released the structural constrain subjected by the difference in lattice matching. Therefore, well-crystallized GaN nanowires with perfect crystallinity and negligible yellow-band emission can be achieved.

The Al/Au bilayer has been proved successful in isolating the dislocation threading of epitaxially grown GaN nanowires on

sapphire substrate and their crystallinity improvement. It is also expected that such a method can also be extended to the synthesis of high-quality GaN nanowire arrays on other substrates. The same preparation processes of GaN nanowire arrays grown on Al/Au/sapphire substrate, including the Al/Au thickness and synthetic parameters, were also transferred to Si substrate. Interestingly, aligned GaN nanowires with helical morphology can also be achieved (Supporting Information Figure S2), and the GaN nanowires exhibited the same growth behavior as those grown on Al/Au/sapphire substrate (first GaN nanoparticle layer with a thickness of several micrometers will be deposited, and subsequently helical GaN nanowire arrays will form via a self-assembled process, as described in Figure 6b). It should be noted that large lattice mismatching exists in wurtzite GaN and cubic Si, and the growth of aligned GaN nanowires on Si substrate has rarely been reported and still remains challenging.¹⁷ The realization of GaN nanowire arrays on Si substrate demonstrated the universal applicability of the method proposed in this work and thus can be applied to the fabrication of GaN nanowire arrays on a wide range of substrates, as well as the crystallographic growth design of other semiconductor nanostructures. In addition, continuous voids with a separation distance of $\sim 100 \text{ nm}$ have also been found in the GaN–Si interface (as marked in Supporting Information Figure S2a and magnified in Supporting Information Figure S2b), showing features similar to those of the GaN nanowire arrays grown on Al/Au/sapphire substrate. Therefore, the Al/Au bilayer not only promotes the growth of aligned GaN nanowires on various cheap substrates, but also opens more opportunity for the industrial applications of GaN nanowire arrays due to their significantly technological importance in the fields of optoelectronics.

In summary, we have experimentally demonstrated that the yellow-band emission of well-aligned GaN nanowires originated from the dislocation threading in GaN–sapphire interface in the case of carbon free. The insertion of Al/Au layers in GaN–sapphire interface played a critical role in preventing the propagation of dislocation and the improvement of optical emission, as well as the growth process of GaN nanowires. It is believed that the large lattice mismatching between Au–sapphire destroys the epitaxial growth relationship of GaN on sapphire and isolates the dislocation threading, while the top Al layer (AlN) contributes to the preferential growth of GaN nanowires and crystallinity improvement. Without Al/Au bilayers, the GaN nanowire arrays are epitaxially grown on sapphire substrate and show a strong yellow-band emission in the visible range; the adding of Al/Au layers induced the self-assembled formation of aligned GaN nanowires with helical morphology and the significant enhancing of cathodoluminescence. In addition, the Al/Au layers will also lead to the simultaneous formation of continuous voids between GaN–sapphire interlayer during/after the formation of GaN nanowire arrays, further blocking the dislocation threading and partly contributing to the optical enhancement. This work not only elucidates the origin of yellow-band emission in epitaxially grown GaN nanowire arrays, but also provides a feasible way to improve the crystal quality of bulky GaN films by HVPE or MOCVD methods, and will undoubtedly open more opportunity for the utilization of GaN crystals in optoelectronic fields.

■ ASSOCIATED CONTENT

● Supporting Information

EDS spectra recorded from GaN nanowires epitaxially grown on sapphire substrate and Al/Au/sapphire substrate and SEM images of GaN nanowire arrays grown on Al/Au/Si substrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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