Review Article

Synthetic Strategies and Applications of GaN Nanowires

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GaN is an important III-V semiconductor material with a direct band gap of 3.4 eV at 300 K. The wide direct band gap makes GaN an attractive material for various applications. GaN nanowires have demonstrated significant potential as fundamental building blocks for nanoelectronic and nanophotonic devices and also offer substantial promise for integrated nanosystems. In this paper, we provide a comprehensive review on the general synthetic strategies, characterizations, and applications of GaN nanowires. We first summarize several growth techniques of GaN nanowires. Subsequently, we discuss mechanisms involved to generate GaN nanowires from different synthetic schemes and conditions. Then we review some characterization methods of GaN nanowires. Finally, several kinds of main applications of GaN nanowires are discussed.

1. Introduction

One-dimensional (1D) semiconductor nanostructures such as nanowires and nanotubes have stimulated their functional applications and are emerging as building blocks for next generation of electronic and optoelectronic nanodevices due to their unique physical and chemical properties. As a particularly important III–V semiconductor with a direct band gap of 3.4 eV at room temperature, gallium nitride (GaN) nanowires have been widely studied in past decade. The successful synthesis of GaN nanowires has been demonstrated via various methods including chemical vapor deposition [1–7], laser ablation [8, 9], metal-organic chemical vapor deposition [10–15], molecular beam epitaxy [16–18], and hydride vapour phase epitaxy [19, 20]. Researchers also proposed the possible growth mechanisms of GaN nanowires. The applications of GaN nanowires were focused on the research of photovoltaic devices, field effect transistor, light emitting diodes, lasers, photocatalyst, and nanogenerators.

In this paper, we will give a comprehensive review on the growth methods, growth mechanisms, characterizations, and applications of GaN nanowires.

2. GaN Nanowires Growth Methods

2.1. Chemical Vapor Deposition. Chemical vapor deposition (CVD) is a chemical process often used to produce high-purity, high-performance solid materials. CVD method in a conventional tube furnace is widely used by researchers to synthesize nanowires due to the advantages of facile, simple, and cheap. In the past decade, GaN nanowires have been prepared by CVD by many groups.

Synthesizing GaN nanowires using CVD method was first demonstrated by Han and coworkers [1]. In their work, carbon nanotubes (CNTs) were used as template confining the reaction in the tubes and hence leading to the nanowire morphology complementary to that of the carbon nanotubes. The reaction in the GaN nanowires growth process was carried out at high temperature in a conventional furnace with a horizontal tube and was expressed as

$$2Ga_2O_{(g)} + C\ (NTs) + 4NH_3 \longrightarrow 4GaN\ (NWs) \\ + H_2O + CO + 5H_2 \tag{1}$$
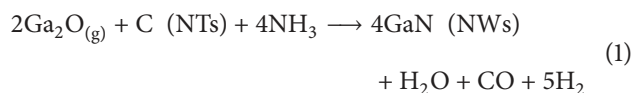
A 4 : 1 molar mixture of Ga-Ga$_2$O$_3$ powders were used as precursor of Ga$_2$O. A HREM image showed that a GaN nanowire had a diameter similar to that of the original carbon nanotubes. Besides CNTs template, other templates such as GaAs nanocolumns [2] and nanosized-pore Al$_2$O$_3$ templates [3] as well were used to prepare GaN nanowires.

Chen et al. reported an approach of synthesizing straight and smooth GaN nanowires via NiO catalyzed CVD technique [4]. The nanowires were deposited onto a single crystal LaAlO$_3$ substrate without using template. Before the deposition, the substrate was quickly dipped into Ni(NO$_3$)$_2$ ethanol solution and then heated at 900°C in a long quartz tube in a stream of Ar for 2 hours (h) to decompose Ni(NO$_3$)$_2$ into NiO nanoparticles. Then GaN nanowires growth was carried out in a long quartz tube at 920–940°C in a flow of NH$_3$ for 5–20 min. The synthesized GaN nanowires had diameters of 10–40 nm and a maximum length of about 500 μm.

Also, Johnson and coworkers [5] demonstrated that using sapphire substrate can fabricate long GaN nanowires via CVD method. Using gallium metal and ammonia as sources of Ga and N, GaN nanowires were deposited on sapphire substrate at 900°C using a nickel catalyst. The wires they prepared had lengths up to several hundred micrometres and diameters between 30 and 150 nm.

As mentioned above, the growth of GaN nanowires using template-based CVD or synthesizing on expensive single crystal substrates can only get little amounts of GaN nanowires. Chen and Yeh [6]described a simple method for large-scale production of GaN nanowires on silicon wafer by reacting gallium and ammonia using polycrystalline indium powder as a catalyst. In this report, molten gallium and powdered indium in toluene were placed on the substrates. After evaporating toluene, the substrate was transferred into a quartz tube in a furnace and kept the temperature at 910°C for 12 h under a flow of ammonia. After the reaction, large quantities of GaN nanowires with diameters ranging from 20 to 50 nm and lengths up to several micrometers were synthesized.

In the preparation of nanoelectronic devices, it is very important using nanowires with low defect density and long length. However, the processing, dispersal, and patterning techniques, such as ultrasonication and lithography, could introduce defects in nanowires. To resolve this problem, Li and coworkers [7] described a method growing nanowires suitable for in situ fabrication of nanowire devices. In this report, using "Dip-Pen" nanolithographic (DPN) techniques, a contact-mode AFM tip was dip-coated with Ni(NO$_3$)$_2$ solution and was brought into contact with the substrate to precisely deliver a small amount of Ni(NO$_3$)$_2$ as demonstrated in a sketch shown in Figure 1. The position of catalyst islands was controlled by moving the tip from location to location using the piezoelectric scanner. Then, GaN nanowires were synthesized in a horizontal quartz tube inside a tube furnace with a flow of ammonia using elemental gallium and catalyst-patterned substrates.

2.2. Laser Ablation. Laser ablation is a laser-assisted method and the key feature of this technique is that the catalyst
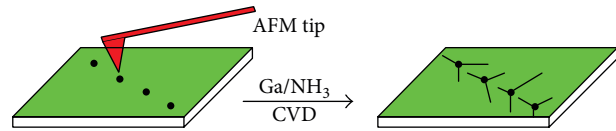

Figure 1: Schematic of the DPN process for the patterning of catalysts and growth of GaN nanowires. Reprinted with permission from [7]. Copyright 2004 American Chemical Society.

used to define nanowire VLS growth can be selected from phase diagram data and/or knowledge of chemical reactivity [8]. In this method, pulsed laser is used to vaporize a solid target containing desired material and a catalyst at high temperature, and the resulting liquid nanoclusters direct the growth and define the diameter of crystalline nanowires through a VLS growth mechanism [8, 21–23].

The famous Lieber group at Harvard University made remarkable progress in developing the laser ablation method to synthesize single-crystalline compound semiconductors [8, 21, 23].

Duan and Lieber described a laser ablation process in preparing single crystalline GaN nanowires [8]. In this report, a GaN/Fe (atomic ratio (GaN) : Fe = 0.95 : 0.05) composite target was positioned with a quartz tube at the center of a furnace. A pulsed Nd:YAG laser (1064 nm, 8 ns pulse width, 10 Hz repetition, 2.5 W average power) was used to ablate the GaN/Fe target and the resulting Fe nanoclusters that are formed at elevated temperature direct the growth and define the diameter of GaN nanowires through a VLS growth mechanism as shown in Figure 2. The grown GaN nanowires deposited at the end of the inner quartz tube wall had diameters on the orders of 10 nm and lengths greatly exceeding 1 μm [8].

Using laser ablation method, Ng et al. [9] synthesized GaN nanowires with lengths from 300 to 500 nm and diameters around 50 nm. In this report, a KrF (248 nm, 23 ns) excimer laser at a laser fluency of 2.2 J/cm^2 was used to ablate a GaN target and the produced plasma plume was delivered directly to a sapphire substrate coated with 10 nm of Au. The grown GaN nanowires had tips made up of the Au/Ga eutectic confirming the VLS growth mechanism.

2.3. Metal-Organic Chemical Vapor Deposition. Metal-organic chemical vapor deposition (MOCVD) is a chemical vapour deposition method of epitaxial growth of materials from surface reaction of organic compounds or metal-organics and hydrides containing the required chemical elements. Alternative names for this method include metal-organic vapour phase epitaxy (MOVPE), organometallic vapour phase epitaxy (OMVPE), and organometallic chemical vapour deposition (OMCVD) [10]. In the past decade, MOCVD technique has been successfully used to synthesize GaN nanowires both by metal-catalyzed [11–13] and noncatalyzed techniques [14, 15].

In 2003, the Yang group at the University of California Berkeley synthesized high-quality GaN nanowires via metal-initiated MOCVD method for the first time [11]. In their
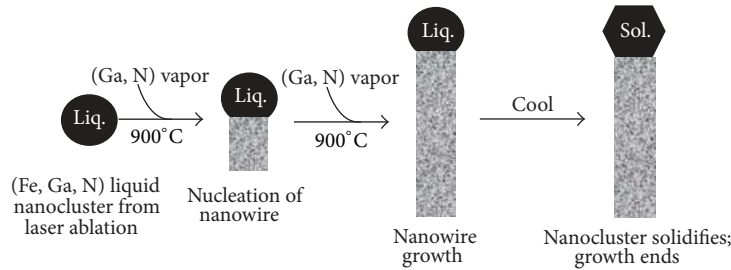
FIGURE 2: Overall evolution of nanowire growth following the generation of the catalytic nanocluster. Reprinted with permission from [8]. Copyright 2000 American Chemical Society.

report, trimethylgallium (TMG) and ammonia source materials were used as Ga and N precursors. A silicon substrate or c-plane and a-plane sapphire with thermally evaporated thin film of Ni, Fe, or Au were used as substrate for growth of GaN nanowires. The nanowires growth occurred at a substrate temperature of 800–1000°C in the form of vapor-liquid-solid growth mechanism. The reaction was carried out in an oxygen-free environment at atmospheric pressure. Nitrogen was used as a carrier gas and percolated through the TMG precursor and coupled with a second nitrogen line. The grown GaN nanowires on a gold-coated c-plane sapphire substrate had diameters of 15–100 nm and lengths of 1–5 μm. It was observed that there were preferred nanowire orientations on the substrate, indicating the epitaxial growth of nanowires on a sapphire substrate [11].

Su and coworkers [12] reported flexible synthesis of GaN nanowires and nanostructures by MOCVD via a catalytic vapor-liquid-solid (VLS) growth mechanism. In this report, sapphire, alumina, and SiO_2 were used as substrates and the substrates were dipped in $0.01 M$ $Ni(NO_3)_2$ aqueous solution and dried in air on filter paper before loading into the MOCVD reactor. It was noted that the existence of liquid-mediated, anisotropic 1D growth depends sensitively on the growth stoichiometry or V/III ratio in a MOCVD environment [12].

Stephen D. Hersee et al. demonstrated a scalable process for the growth of high-quality GaN nanowires and uniform nanowire arrays in which the position and diameter of each nanowire was precisely controlled. The approach was based on conventional MOCVD using regular precursors without additional metal catalyst.

In their report, a 30 nm silicon nitride growth-mask layer was deposited by low-pressure chemical vapor deposition (LPCVD) onto 600 nm GaN films that had been previously grown by MOCVD on sapphire, silicon carbide, and silicon (111) substrates. The growth was carried out at 1050°C, at a pressure of 100 Torr with a hydrogen/nitrogen carrier gas mixture in MOCVD reactor. GaN nanowires array emerged from the growth mask and the diameter of each nanowire remained constant during the growth process. Figures 3(a) and 3(b) show SEM images of part of a GaN nanowires array in high and lower magnification, respectively [15].

2.4. Molecular Beam Epitaxy. Molecular beam epitaxy (MBE) is a method to deposit single crystals. It was invented in the

late 1960s at Bell Telephone Laboratories by Stangl et al. [24]. The MBE method is a useful technique in the synthesis of GaN nanowires.

GaN nanowires with extremely good crystal quality have already been synthesized by MBE on different substrates.

Using plasma-assisted molecular beam epitaxy method, Calarco and coworkers prepared GaN nanowires on Si (111) substrates [25]. In their report, the nucleation process of GaN-NWs in terms of nucleation density and wire evolution with time for a given set of growth parameters was investigated. The results indicated that the wire density increased rapidly with time and then saturated [25]. Bertness et al. analyzed the spontaneous growth of c-axis GaN nanowires in MBE under a number of different growth parameters, including relative flux of N species to Ga, type of N species present, AlN buffer layer thickness, and substrate orientation. They concluded that the nucleation mechanism for nanowires included formation of nanocolumns in the AlN buffer layer, and the propagation of the nanowires in GaN growth appeared to be driven by the differences in growth rates among crystallographic planes under N-rich conditions [16].

Tchernycheva et al. [17] reported on the growth of GaN free-standing nanowires synthesized in catalyst-free mode on Si (111) substrate by plasma-assisted molecular beam epitaxy. Cylindrical nanowires with a hexagonal cross-section defined by {10$\bar{1}$0} planes and diameters down to 20 nm were observed. The growth rate in the lateral direction was studied and the result showed that the lateral over axial growth rate ratio can be tuned from ~1% to ~10% by changing the III/V flux ratio. Rafael Mata and coworkers [18] investigated the growth of GaN nanowires by means of plasma-assisted molecular beam epitaxy directly on Si (111) as a function of temperature. Through statistically analyzing SEM images of GaN nanowires grown at different temperatures, it was concluded that density, diameter, length, and length dispersion of nanowires were strongly dependent on growth temperature [18].

2.5. Hydride Vapour Phase Epitaxy. Hydride vapour phase epitaxy (HVPE) is an epitaxial growth technique often employed to synthesize semiconductors such as GaN, GaAs, InP, and their related compounds. Carrier gasses commonly used in HVPE process include ammonia, hydrogen, and various chlorides. HVPE provides a better process control

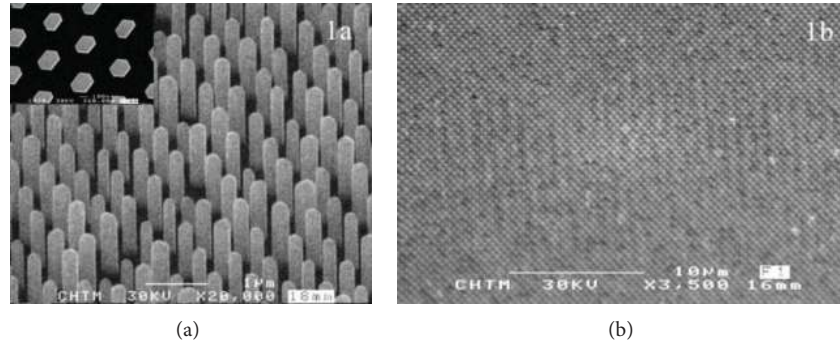(a)   (b)

FIGURE 3: (a) High magnification SEM image (inset shows plan view) and (b) lower magnification SEM image of a GaN nanowire array. Reprinted with permission from [15]. Copyright 2006 American Chemical Society.

than the commonly used CVD techniques and is of particular interest due to its high-growth rates and simplicity of basic reactor design.

Kim and coworkers [19] proposed a simple approach for the controllable growth of GaN nanorods by hydride vapour phase epitaxy technique. In their preparing process, GaCl precursor formed by the reaction of Ga metal and HCl gas was transported to the substrate area and then mixed with NH_3 to form GaN. GaN nanorods were directly grown on bare sapphire or silicon substrates without a catalyst or template layer. After the growth, a high density of straight and well-aligned nanorods with diameters in the range of 80–120 nm was formed uniformly over the entire substrate.

Seryogin et al. demonstrated the catalytic growth of GaN nanowires by the HVPE method [20]. In this work, nickel-gold was used as a catalyst and the nanowire growth was limited to catalyst-patterned areas. The growth of GaN nanowires was carried out in a custom designed HVPE rector at atmospheric pressure. The reactor consisted of 75 mm quartz tube and placed in a three-zone Mellen horizontal furnace. Two heating zones were used for hydride reactions of column-III metals with HCl gas. Only gallium was used as the source metal to form GaCl in a direct reaction between molten Ga and HCl gas diluted with nitrogen and the reaction was expressed as

$$Ga_s + HCl_g \longrightarrow GaCl_g + \frac{1}{2}H_2 \qquad (2)$$
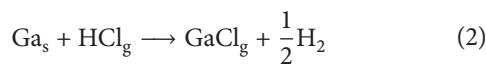
The third zone was the growth zone and ammonia was delivered to this zone to react with GaCl gas. GaN nanowires were formed via the HVPE process on catalyst-patterned silicon (111) or c-plane sapphire substrates:

$$GaCl_g + NH_{3g} \longrightarrow GaN + HCl_g + H_2 \qquad (3)$$
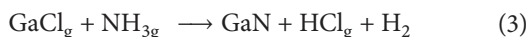
3. Growth Mechanism of GaN Nanowires

The growth of nanowires is a process involving the use of anisotropy. To obtain anisotropy many methods have been adopted, which can be roughly divided into two kinds, vapor method and solution method, leading to vapor-based mechanisms and solution-based mechanisms. While due to no

report of solution-based method for GaN nanowires by now, only vapor mechanisms have been suggested. Vapor-based mechanisms include vapor-liquid-solid (VLS), vapor-solid (VS), and vapor-solid-solid (VSS), and solution-based mechanisms include solution-liquid-solid (SLS) and solution-solid (SS).

3.1. VLS Mechanism. VLS is the most widely accepted mechanism first described by Wagner and Ellis in 1964 based on the appearance of Au nanoparticle on the top of single crystal silicon nanowire [26]. Here vapor, liquid, and solid, respectively, stand for reactant vapor, liquid metal catalyst, and solid nanowire product. In this mechanism a few key factors should be seriously considered, such as vapor supersaturation, selection of liquid, liquid-substrate interface, liquid-solid interface, and solid-substrate interface.

Vapor supersaturation should be enough to dissolve into liquid metal catalyst to form supersaturated alloy and then nanowire seed crystals crystallize out of the liquid metal. The control of vapor supersaturation can be realized by adjusting pressure, temperature, raw material, and so forth. Metal catalyst should be seriously considered, generally based on the alloy phase diagram and chemical reactivity [8].

Interface between liquid metal catalyst and substrate also should be seriously considered. Because the wettability between them will determine the distribution of liquid metal catalyst [27], which can be continuous film, porous film, connected network, isolated islands, or something else. Therefore the morphology of products can be seriously affected.

By the way, the place on where the nanowire seed crystals crystallize is under debate, maybe on the surface of liquid metal, maybe between liquid metal and substrate, or somewhere else. The most common place is between liquid metal and substrate. So in this situation two more interfaces emerge, interfaces between liquid metal catalyst and solid nanowires and interfaces between solid nanowires and substrates. Liquid-solid interface is the place where new epitaxial atom layers come about, so these interfaces will lead the growth of nanowires. Solid-substrate interface is also an important interface, because this is an interface where the crystal nucleus lands and lattice match or mismatch happens. Therefore the lattice matching and surface atom condition of

substrate should be adjusted to satisfy the epitaxial growth of nanowires.

But this mechanism also has defect, such as the inability to get metal nanowires and the pollution derived from metal catalyst.

Using laser-assisted catalytic method, Duan and Lieber synthesized single crystalline GaN nanowires [8]. In this report, a GaN/Fe composite target was ablated by a pulsed Nd:YAG laser and the resulting vapor containing Ga, N, and Fe formed a miscible liquid phase. With the saturation of Ga and N in the process, GaN crystallized and separated out. GaN nanowires growth happened in the crystallization directed by the Ga, N, and Fe liquid nanoclusters through a VLS growth mechanism. Yang group reported [11] the VLS growth of GaN nanowires by MOCVD. Seryogin et al. [20] also demonstrated the VLS mechanism growth of GaN nanowires catalyzed by nickel-gold using HVPE growth method.

3.2. VSS Mechanism. VSS is an analogous mechanism to VLS with the only difference of catalyst states. In VSS catalyst is solid-state, while in VLS catalyst is liquid-state. Here vapor, solid, and solid, respectively, stand for reactant vapor, solid metal catalyst, and solid nanowire product. It was first proposed in 2000 by Kamins et al. for Ti-catalyzed silicon nanowires [28].

Weng et al. [29] reported the growth of GaN nanowires using Ni-assisted metal-organic chemical vapor deposition method. As described in this report, a c-plane sapphire and a sputtered Ni thin film were used as substrates and trimethylgallium (TMG) and ammonia as the groups III and V precursors. During the reacting process, nickel thin film transformed into Ni_3Ga nanoparticles and the nanoparticles kept capturing Ga species and became supersaturated. Subsequently, GaN nanowires formed by reaction of extra Ga and the decomposed ammonia at the surface of the Ni_3Ga through VSS mechanism.

Hou and coworkers [30] first reported the Au-assisted GaN nanowire growths by the VSS mechanism. The control of the migration and detaching of Au seeds during the growth of GaN nanowires in the plasma-enhanced chemical vapor deposition system was realized. It was observed that at the low gallium partial pressure, GaN nanowire growth was driven by a vapor-solid-solid (VSS) process, with the Au migration rate dramatically reduced due to the slow diffusion of Au in the solid Au-Ga alloy.

3.3. VS Mechanism. VS is a totally different mechanism from VLS and VSS due to the absence of catalyst. Here vapor and solid, respectively, stand for reactant vapor and solid nanowire product. In general the synthesis temperature it needs is higher than VLS and VSS due to the absence of energetically favored catalyst sites for easier growth. But its biggest advantage is no catalyst addition, and therefore catalyst pollution is avoided. In principle so long as suitable supersaturation and nucleation sites are provided we can get one-dimensional nanomaterial of any material [30]. This mechanism contains much simpler process, because without

the use of catalyst many interfaces are avoided. Here only three interfaces are considered, vapor-substrate interface, vapor-solid interface, and solid-substrate interface. Vapor-substrate interface should be first considered because this is where nucleation happens. In this interface vapor condenses into solid to form nucleus, so the parameters provided for this suitable sites should be seriously thought over, such as deposition temperature, pressure, and substrate surface condition. After this key nucleation step finished, two more interfaces are presented, vapor-solid interface and solid-substrate interface. Vapor-solid interface is a new and different interface lying between reactant vapor and solid nanowire nucleus from vapor-substrate interface, so nucleation does not guarantee epitaxy, that is, nanowire growth. If reactant vapor cannot condense onto nucleus or condensation does not lead to one-directional epitaxy, only nanoparticles are obtained. Solid-substrate is an also important interface where the crystal nucleus lands and lattice match, mismatch, or dismatch happens.

Using high temperature transmission electron microscopy, Stach et al. [31] realized the observations of the growth of GaN nanowires. Ga liquid droplets and gallium/nitrogen vapor that are produced by thermal decomposition of GaN in a vacuum initiate VLS nanowire's growth after supersaturating the metal and creating a liquid-Ga/solid-GaN interface.

4. Characterizations of GaN Nanowires

Various tools have been used to realize the characterizations of GaN nanowires. The most common used instruments in the reported literatures are scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM), Raman spectroscopy, and photoluminescence spectra (PL).

4.1. Scanning Electron Microscope (SEM). SEM is a tool to directly watch the morphology of a nanowire sample. By scanning a sample with a focused beam of electrons, the electron microscope can produce morphology images of it. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. With the help of SEM, the length, diameters, shape, and densities of the GaN nanowires can be clearly shown. The SEM images appear in almost all the literature reports about GaN nanowires.

4.2. X-Ray Diffraction (XRD). X-ray crystallography is a valuable tool for obtaining structural parameters of GaN nanowires. In the structure of a crystal, the crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, an XRD pattern can be produced. From XRD patterns, the crystalline phase, preferred growth direction, lattice constants, and some other structural information of the nanowires can be obtained. Usually, GaN nanowires are stable in a hexagonal wurtzite phase with lattice constants of $a = 0.3186$ nm and $c = 0.5178$ nm [7, 8, 32]. The XRD patterns

of GaN nanowires have these reflection peaks: (100), (002), (101), (102), (110), and (112) indicating hexagonal wurtzite phase [7, 32]. (100), (002), and (101) peaks are the three high intensity peaks in the XRD pattern. The highest intensity peak as well as crystallographic orientation of the GaN nanowires is determined by their epitaxial relationship with the substrate [33].

4.3. Transmission Electron Microscope (TEM).

Transmission electron microscopy (TEM) is one of the most forceful and versatile techniques for the characterization of nanostructured materials. Its unique features allow researchers to achieve morphology and atomic resolution of crystal lattices as well as to obtain chemical composition of materials. As it is known to us, when a beam of electrons interacted with a solid specimen, a number of elastic or inelastic scattering phenomena will be produced. The scattering includes: backscattering or reflection, emission of secondary electrons, X-rays or optical photons, and transmission of the undeviated beam along with beams deviated as a consequence of elastic or inelastic phenomena. The TEM technique is dedicated to the analysis of the transmitted or forward-scattered beam. The low resolution TEM and high resolution TEM (HRTEM) image can be obtained by collecting central beam and diffracted beams, respectively. The crystalline phase, crystal plane, growth direction, interplanar spacing, and chemical composition of GaN nanowires have been determined through TEM analysis. In the report of GaN nanowires prepared by laser-assisted catalytic growth method in Lieber's group, TEM analysis was used to characterize the structure of the nanowires [8]. One-dimensional topography with Au nanoparticle at tip was clearly shown in low resolution TEM image. The lattice resolved HRTEM image displayed the single-crystal structure of the nanowire and the lattice planes along the [100], [010], and [−110] directions [8]. Besides the structural characterization using TEM, Stach et al. realized the real-time high temperature transmission electron microscopy observations of the growth of GaN nanowires [31]. It was the first direct observation of self-catalytic growth of nanowires via the VLS mechanism and suggested new strategies for synthesizing electronically pure single-crystalline semiconductor nanowires.

4.4. Raman Spectroscopy.

Raman scattering is a useful tool for the characterization of nanosized materials and a qualitative probe of the presence of lattice defects in solids, for example, the crystalline quality can be judged from the peak shapes and the selection rules [34]. For GaN nanowires, Raman spectroscopy provides information on the vibrational states that are sensitive to the crystalline quality, the stress, carrier concentration, and mobility and therefore can be employed for process and growth monitoring [35]. Since GaN nanowires normally crystallize in the hexagonal wurtzite structure, group theory predicts four Raman active modes: A1(LO), E1(TO), E_2^L, and E_2^H [36]. The four modes are usually at peaks near 724, 556, 143, and 568 cm^{-1}, respectively [36]. Tan et al. reported the Raman study on the influence of growth temperatures on the characteristics of GaN nanowires [37]. In their report, E2H mode experienced a blueshift at lower temperature and redshift with the rising growth temperatures. Through analyzing Raman line shape, the carrier concentration and mobility at different growth temperatures were determined which varied in the range of 4.0×10^{16} cm^{-3} to 5.27×10^{17} cm^{-3} and 158.2 cm^2/V s to 376.2 cm^2/V s, respectively [37].

4.5. Photoluminescence (PL).

Photoluminescence technique is a noncontact, nondestructive method of probing the electronic structure of semiconductor materials. When light is directed onto a sample, it is absorbed and photoexcitation process can occur. The photoexcitation causes the material to jump to a higher electronic state and will then release energy (photons) as it relaxes and returns back to a lower energy level. PL spectrum is an effective way to study the electronic structure and optical and photochemical properties of semiconductor materials, by which information such as surface oxygen vacancies and defects, as well as the efficiency of charge carrier trapping, immigration, and transfer, can be obtained [38]. The PL spectrum of GaN nanowires usually has a near band-gap emission peak blue-shift compared with the value of 365 nm of bulk GaN, which can be ascribed to the quantum confinement effect [39].

5. Applications of GaN Nanowires

As an important direct wide band-gap semiconductor material, GaN has been widely used in UV or blue emitters and high-temperature/high-power electronic devices. GaN is also a promising material for field emitters because of its low electron affinity and high carrier mobility as well as its excellent physical and chemical stabilities. For semiconductor nanowires, the cylindrical geometry and strong two-dimensional confinement of electrons, holes, and photons make them particularly attractive as potential building blocks for nanoscale electronics and optoelectronic devices [5]. The applications of GaN nanowires have been demonstrated by researchers in these fields: photovoltaic devices, light emitting diodes (LED), field-effect transistors (FETs), lasers, photocatalyst, and nanogenerators.

5.1. Photovoltaic Devices.

The global energy shortage has become more prominent and it is estimated that the annual global consumption of energy is to rise by more than 50% in the future 20 years [40]. The development of new energy has been getting high priority. Solar cells have been widely considered as one of the ways of solving this problem and the first conventional solar cell, the silicon p-n junction cell, was invented in the 1950s [41].

GaN nanowire arrays of high crystalline quality are attractive for high-performance photovoltaic (PV) devices due to the merits as mentioned above including a wide and direct band gap, high carrier mobility, high thermal and chemical stability, and capability of n- or p-type doping.

Tang et al. [42] demonstrated that the GaN nanorods/Si heterojunctions could be used for the PV applications. In their report, p-type GaN nanorod arrays were synthesized on

n-type Si substrates to form a heterostructure for fabricating p-n heterojunction PV cells by doping Mg into GaN via a CVD method using gold nanoparticles as catalyst. The cell they fabricated had a high short-circuit photocurrent density of 7.6 mA/cm^2 and energy conversion efficiency of 2.73% under AM 1.5G illumination at 100 mW/cm^2. Li and coworkers [43] reported the growth of close-packed GaN nanorod/Si heterostructures via a hydride vapor phase epitaxy (HVPE) technique and their applications for UV PV cells. The PV cell was illuminated with a UV lamp at a power of 6 W and a wavelength of 365 nm. The maximum open-circuit voltage, the short-circuit current density, and the fill factor were found to be 0.7 V, 146 μA/cm^2, and 0.38, respectively. A power conversion efficiency of about 1% was obtained [43].

5.2. Field Effect Transistor. Nanowires are attractive building blocks for nanoelectronics since their morphology, size, and electronic properties make them suitable for fabricating both nanoscale devices and interconnects [44]. GaN nanowires have been widely used to fabricate field effect transistors (FETs) by many groups [44–50].

Lieber group fabricated FETs using individual GaN nanowires in 2002 [44]. In their work, the FETs were prepared by dispersing a suspension of GaN NWs in ethanol onto the surface of an oxidized silicon substrate where the underlying conducting silicon was used as a global back gate. A layer of Ti/Au (50/70 nm) at the two ends of the nanowire was used as source and drain electrodes defined by electron beam lithography method. The electrical transport measurements were made at room temperature. Figure 4 shows schematic of a NW FET and a set of typical current versus source-drain voltage (I-V_{sd}) and source-gate voltage (I-V_g) data [44]. The results showed that the GaN NWs were n-type and the electron mobilities were as high as 650 cm^2/V·s.

Kim et al. [45] designed FET devices with individual GaN nanowires to study the electrical transport properties of the nanowires. The electrical measurements results showed a pronounced n-type field effect and an estimated electron mobility was about 2.15 cm^2/V·s. Using a unique prealignment process, the fabrication of GaN nanowire field-effect FETs with both bottom-gate and top-gate structures was demonstrated by Cha et al. in 2006 [47]. In terms of saturation and breakdown characteristics of the two FETs structures, better FET performance can be obtained using the top-gate structure [47].

5.3. Light Emitting Diodes. Light emitting diode (LED) technology was originally developed from the high-efficiency electroluminescence (EL) of semiconductor devices in early 1962 [51]. GaN nanowires are highly suitable for light-emitting diodes devices due to their direct band-gap structure and dislocation-free nature [52]. UV-blue LEDs using GaN nanowires have been fabricated, and the GaN-based LEDs are an active field of research [44, 51–56].

In Lieber group's report [44] mentioned above, p-n junctions were assembled using p-Si nanowire and n-GaN nanowire and the junctions exhibited highly reproducible rectifying behavior suggesting potential applications in LEDs.

With replacement of p-Si nanowire by p-GaN nanowire, the p-n crossed GaN nanowire junctions could be functioned as nanoscale UV-blue light emitting diodes in C. M. Lieber group's latter report [54]. The p-n junction exhibited a dominant emission peak centered at 415 nm under electroluminescence (EL) measurements.

Motayed et al. [55] reported GaN nanoscale light emitting diodes utilizing n-GaN nanowire/p-GaN substrate homojunctions. In their report, n-type GaN nanowires were placed on the surface of a p-doped GaN thin film to form GaN homojunction. Under a forward bias, detectable emission with 365 nm peak wavelength was observed from these p-n junctions.

In addition to crossing junctions or homojunction of GaN nanowire and film, core/multishell nanowire heterostructures or multiquantum-well nanorod arrays based on GaN nanowire were also demonstrated as high-brightness and high-efficiency light LEDs [52, 56]. Qian et al. [52] reported the growth of radial heterostructures with an n-GaN core and InxGa1-xN/GaN/p-AlGaN/p-GaN multishell by metal organic chemical vapor deposition and demonstrated that the heterostructures could function as LEDs, with tunable emission from 365 to 600 nm and high-quantum efficiencies. Similarly, high-brightness and high-efficiency LEDs were realized by Kim and coworkers using dislocation-free indium gallium nitride (InGaN)/gallium nitride (GaN) multiquantum-well (MQW) nanorod (NR) arrays [56]. It was found that the MQW NRA LED extraction efficiency was much higher than conventional broad area (BA) LEDs.

5.4. Lasers. A laser is a device that emits light through an optical amplification based on the stimulated emission of electromagnetic radiation. Stimulated emission from bulk GaN at low temperatures was first reported by Dingle et al. in the 1970s [57]. Two decades later, room-temperature lasing in GaN thin films was achieved by Khan et al. [58].

The emission from GaN nanowires was first reported by Yang group in 2002 [5]. In their report, a single, isolated GaN nanowire with diameter of ~300 nm and length of ~40 μm was excited using a fourth harmonic of the signal beam from an optical parametric amplifier and an optically pumped (310 nm, 4.0 eV) laser emission was observed. The radiation patterns correlated with axial Fabry-Perot modes observed in the laser spectrum [5].

Gradecak et al. [59] reported optically pumped room temperature lasing in GaN nanowires and the nanowires functioned as freestanding Fabry-Perot cavities with cavity mode spacings that depended inversely on length. The lasing threshold as low as 22 kW/cm^2 was represented [59].

Recently, Li et al. [60] demonstrated GaN nanowire lasers operating far above lasing threshold with a stable, single-frequency output. The GaN nanowires were prepared by a top-down fabrication technique that produces uniform and vertically aligned GaN nanowire arrays from c-plane GaN epilayers on sapphire with low defect density and smooth sidewalls. The devices were optically pumped at room temperature with a 10 kHz, 100 ps pulsed quadrupled YAG laser emitting at 267 nm [60].
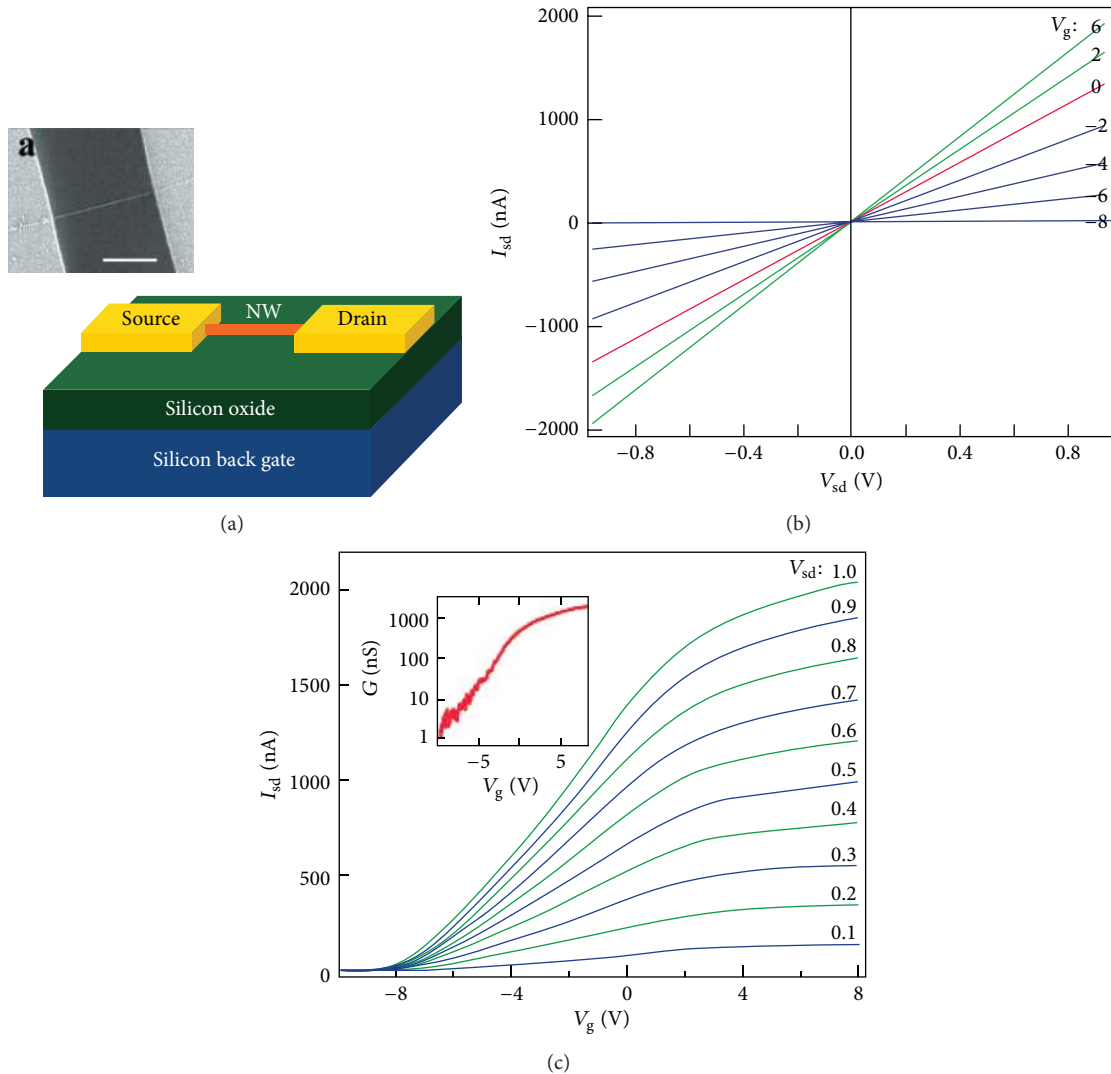
(a)

(b)

(c)

FIGURE 4: (a) Schematic of a NW FET and (inset) FE-SEM image of a GaN NW FET. (b) Gate-dependent I-V_{sd} data recorded on a GaN NW. (c) I-V_g data recorded for values of V_{sd} 0.1–1 V. (inset) Conductance, G, versus gate voltage. Reprinted with permission from [44]. Copyright 2002 American Chemical Society.

5.5. *Photocatalyst.* Photocatalyst is a kind of catalyst used in cleaning facilities, houses, and living environments and it splits water into hydrogen and oxygen with the help of natural sunlight. Although GaN nanowires have been widely researched in photoelectric fields, photocatalytic applications of GaN have rarely been reported.

In 2008, Jung et al. [61] reported the photocatalytic activity of GaN nanowires and the GaN nanowires exhibited good ability to photodegrade organic dye at various pHs, even under strong acidity and alkalinity. Also, the photocatalytic activity of GaN nanowires was compared with that of TiO_2 and ZnO nanowires. It was found that even though the surface area of the GaN nanowires was an order of magnitude lower than that of the TiO_2 nanowires, the photocatalytic activity of GaN nanowires was slightly higher. When compared with ZnO nanowires, ZnO nanowires performed better than GaN nanowires at pH 7.0, but in the strong pH region,

for example, pH 2.3, the photocatalytic activity of ZnO nanowires decreased rapidly from 70% to 33%, whereas that of GaN nanowires exhibited a 60% increase [61].

Recently, Wang and coworkers [62] demonstrated the capacity for both H_2 and O_2 evolution on nonpolar GaN surfaces. When incorporated with photodeposited Rh/Cr_2O_3 core-shell structures, photocatalytic pure water splitting was achieved on GaN nanowires for the first time.

5.6. *Nanogenerators.* The piezoelectric and semiconducting properties of GaN nanowires can be further utilized for the applications of the piezoelectric nanogenerator to extract energy from environment [63]. The Wang group from Georgia Institute of Technology demonstrated that GaN nanowire arrays could produce negative output voltage pulses when scanned by a conductive atomic force microscope in contact mode. The average of piezoelectric output voltage in their

report was about −20 mV, while 5–10% of the NWs had piezoelectric output voltages exceeding −(0.15–0.35) V [63]. In their latter report [64], a GaN nanowire-based nanogenerator and LED were fabricated using n-type GaN nanowires grown on a p-type GaN substrate. An output power around ~12.5 mW/m^2 produced by the nanogenerator lighted the GaN NWs LEDs and corresponding electroluminescence (EL) spectra was recorded and investigated [64].

6. Conclusion

This paper provides a review of achievements on the investigation of GaN nanowires in recent decade. Synthesis of GaN nanowires has been widely researched and a variety of growth methods have been developed. Several growth mechanisms including VLS, VSS, and VS have been proposed to explain the growth of GaN nanowires. Various characterization methods are presented. Finally, the applications of GaN nanowires in many fields such as photovoltaic devices, field effect transistor, light emitting diodes, lasers, photocatalyst,and nanogenerators have been reviewed.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
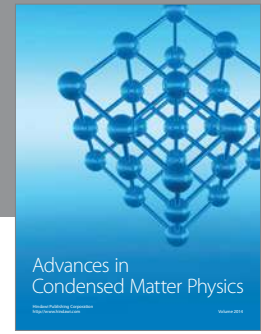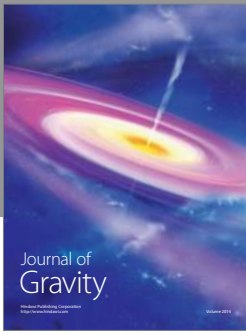
Acknowledgments

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