InGaN-based nanowires development for energy harvesting and conversion applications

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ABSTRACT
This tutorial teaches the essential development of nitrogen-plasma-assisted molecular-beam-epitaxy (PA-MBE) grown InGaN nanowires as an application-inspired platform for energy harvesting and conversion applications by growing dislocation- and strain-relieved axial InGaN-based nanowires. The tutorial aims to shed light on the interfacial, surface, electrical, and photoelectrochemical characteristics of InGaN nanowires through nanoscale and ultrafast characterizations. Understanding the interrelated optical-physical properties proved critical in the development of renewable-energy harvesting and energy conversion devices. Benefiting from their unique aspect ratio and surface-to-volume ratio, semiconductor properties and piezoelectric properties, the group-III-nitride nanowires, especially InGaN nanowires, are promising for clean energy conversion applications, including piezotronic/piezo-phototronic and solar-to-clean-fuel energy-conversion.

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I. Introduction
Group-III-nitrides compound semiconductors consist of binary GaN, InN, and AlN with their ternary compounds, which can emit and absorb light across a wide solar spectrum. In the optical domain, light-emitting diodes (LEDs) and laser diodes are in high demand due to their applications in solid-state lighting, optical data storage, pico-projectors, and displays.1,2 In the electronic domain, the group-III-nitrides are used in high-power/high-frequency electronics, sensors, and so on. These applications are enabled by the excellent optical properties of these materials, such as tunable direct bandgap, electrical characteristics, such as high dielectric breakdown voltage and electron mobility, and their excellent chemical stability.

Although group-III-nitrides have been widely implemented as photonic or electronic devices, another significant application category has garnered momentum in the past decade, namely, energy harvesting and conversion devices. These applications utilize and produce renewable and clean energy. Two major applications that have been reported in the literature are piezotronics/piezo-phototronics and photoelectrochemical (PEC) hydrogen generation devices. Owing to their superior absorption of solar light, electrical conductivity and unique piezoelectric properties, the group-III-nitride materials, particularly (In,Ga)N materials, are capable of harvesting, converting and coupling three forms of energy: solar energy, mechanical energy, and electrical energy. Moreover, inspired by their advanced material characteristics and relatively mature technologies, the group-III-nitride nanowires ensemble is a promising material platform for next-generation energy- and environment-related devices.

The absence of a cost-effective free-standing GaN substrate wafer for homoepitaxy inevitably introduces heterogeneous substrates, such as sapphire and silicon, to grow group-III-nitride planar thin film. This leads to a high density of dislocations and defects in GaN epitaxy on the substrates.

In place of the planar layer platform for group-III-nitrides, nanowires grown by molecular beam epitaxy (MBE) can be used to circumvent part of the aforementioned obstacles, as single-crystal
nanowires ensemble can be grown with less strain on various kinds of unconventional substrates, such as Si, metal or even amorphous glass. Any threading dislocations generated from the semiconductor substrate interface are largely eliminated at the bottom of the nanowires, as threading dislocations can be terminated at the m-plane sidewall. Hence, this allows the adoption of heterostructures while decoupling the need for a favorable epitaxial relationship or a small lattice mismatch between the nanowires and the substrates. A self-assembled growth mechanism in plasma-assisted MBE (PA-MBE) can provide wafer-scale nanowires without requiring metal-induced seed nucleation on unconventional substrates. The resulting nanowires ensemble of high crystalline quality can be grown uniformly at a high density of up to $10^{10}$/cm$^2$.

In addition, axial nanowire heterostructures are preferred for optoelectronics because the metal-contact fabrication process for conventional planar devices can be easily adopted on the ensemble. Although MBE process can be tuned to produce co-axial nanowires, i.e. a core-shell structure similar to that typically produced using metal organic chemical vapor deposition (MOCVD), it is also capable of producing axial segments along the c-plane growth direction. Techniques for nanowires-based solid-state lighting devices have been adequately documented in previous articles and therefore do not need to be repeated here.

As indicated in Fig. 1, this tutorial delves into the fundamental kinetics of the ensemble growth of nanowires and key characterization techniques. Further, it elucidates the lessons learned from PA-MBE-grown InGaN-based nanowires. We also inspect the piezoelectric properties of group-III-nitride materials for energy-autonomous device realization. This is followed by renewable-energy-related applications, such as hydrogen generation using PEC water splitting. The present tutorial is meant to be broad-based to benefit a broader scientific community interested in non-conventional applications of (In)GaN-based nanowires beyond solid-state lighting. Hence, the article incorporates a balance of basic and specific know-how and knowledge.

In Section II, general overviews of catalyst-free, self-assembled growth and selective area growth are presented for InGaN-based nanowires ensemble and nanowires array, respectively. GaN nanowires growth is discussed with specific reference to PA-MBE. Section III contains various methods of characterization for (In,Ga)N nanowires. The high aspect ratio of (In,Ga)N nanowires is favorable for piezotronic energy conversion, and the associated large surface-to-volume ratio is highly attractive for PEC water splitting and related renewable energy processes. Positioning the InGaN-based nanowires as an application-inspired platform, Sections IV and V introduce the working principles of piezotronics/piezophototronics, as well as renewable energy harvesting, specifically in hydrogen generation through PEC water splitting method. In Section VI, the prospects for InGaN-nanowires-based energy-related applications are further discussed for piezotronic devices. Moreover, by optimizing the doping concentration and indium composition of InGaN nanowires, the bandgap can favorably straddle the redox potential to facilitate PEC carbon dioxide reduction reaction (CO$_2$RR) and nitrogen reduction reaction (NRR).

![FIG. 1. Development of group-III-nitride nanowires (Section II), detailed characterization (Section III) and potential applications for piezotronics/piezophototronics toward energy-autonomous micro-devices (Section IV) and solar-energy harvesting PEC water splitting (Section V).](https://doi.org/10.1063/5.0035685)

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**II. Development of Group-III-nitride nanowires**

### A. PA-MBE growth of catalyst-free GaN nanowires

PA-MBE can produce axially grown nitrogen-polar (N-polar) and metal-polar nanowires on bare and patterned substrates, respectively, using a bottom-up approach. In Fig. 2(a), the growth of nanowires is governed by a diffusion-induced growth mechanism of Ga adatoms under overpressure of nitrogen plasma species and nitrogen molecules. On a bare substrate (Fig. 2(a)), Ga adatoms migrate on the substrate surface and form a wetting layer. Seed GaN is nucleated on the surface through a combination of diffusion, desorption, and adsorption for the elongation (vertical growth) of the nanowires through an appropriate growth regime to be discussed below.

To better establish the growth kinetics of self-assembled nanowires ensemble, the kinetic parameters of GaN nanowires growth on Si(111) were simulated by Consonni et al. The effective diffusion lengths of the Ga adatoms on a spontaneously formed amorphous Si$_x$N$_{1-x}$ surface ($\lambda_0$) and a GaN-nanowire’s m-plane sidewall ($\lambda_m$) for the particular study were found to be 100 nm and 45 nm, respectively. During the elongation process of GaN nanowires ensemble that populated the substrate, the contribution from Ga adatom diffusion on Si$_x$N$_{1-x}$ reduces while the Ga adatom diffusion process on m-plane sidewall becomes dominant. In addition, because the nucleation energy on the m-plane sidewall is larger than that on the c-plane top surface, GaN elongation is preferentially much faster in the axial c-direction than in the lateral m-direction.

In the case of selective area growth, there is an open dielectric-mask window area that exposes the underlying GaN surface. The nanowires array are then preferentially nucleated in the window areas through a combination of impinging fluxes on the top of the nanowires ($J_{top}$), impinging fluxes on the sidewall ($J_{sid}$), and diffusion fluxes from the surface of the substrate ($J_{sub}$), as shown in Fig. 2(b). As the Ga adatoms migrate on the mask and get...
incorporated into the favorable sites of the window-area, the GaN nanowires grown on patterned substrate exhibit a distinct hexagonal faceting, and possess uniform lengths and diameters. Gotschke et al. deduced the effective diffusion length of the Ga adatoms on a periodically patterned surface (λ-eff ∼ 400 nm) from the analyses of diameters and periods of the nanowires.20 The λ-eff is found to be larger than the λs (for the self-assembled growth case).15,20 Also, the lateral size of GaN nanowires can be controlled by the window-area pitch distance. If the pitch distance becomes larger and exceeds the effective diffusion length, the lateral size of the nanowires stops increasing and remains constant. Fig. 2(c) and (d) show the scanning electron microscope (SEM) morphologies of randomly grown or self-assembled nanowires ensemble and the hexagonal shape of the nanowires array grown by selective area growth, respectively. Because there are no favorable sites for the growth of GaN nanowires on a bare substrate, the self-assembled nanowires are seeded and grown in random positions (Fig. 2(c)). In contrast, nanowires grown by selective area growth exhibited better controlled nucleation and elongation only in the mask-window positions (see Fig. 2(d)).

![Diagram](image_url)

FIG. 2. (a) PA-MBE growth process of self-assembled GaN nanowires ensemble through adatom migration, diffusion, nucleation, and desorption. (b) Schematic of GaN nanowires array on a patterned mask template by selective area growth.19 Reprinted from Journal of Applied Physics 115, 163104 (2014), with permission of AIP publishing. (c) SEM elevation view of a self-assembled nanowires ensemble on a bare substrate, and (d) SEM top view of the selective area grown GaN nanowires array.21 Reprinted from Appl. Phys. Lett. 112, 091105 (2018), with permission of AIP publishing.

B. GaN nanowires growth window and bulk polarity

For the epitaxial growth of group-III-nitride planar layer, Heying et al. suggested three growth regimes for GaN, as shown in Fig. 3(a).22 The Ga-droplet, intermediate and N-stable regimes are determined by the Ga/N flux ratio.22,23 If a planar GaN epilayer is grown in the Ga-droplet regime (φ_GaN > 1), the surface accumulates micrometer-scale Ga-droplets.24 The N-stable regime (φ_GaN < 1) resulted in semi-insulating characteristics with the heavily pitted morphologies of the GaN layer. In the intermediate regime (φ_GaN = 1), a thin Ga adlayer is formed on the surface without Ga-droplets.25,26 The Ga-droplet regime and intermediate regime are utilized for the growth of the planar layer. On the other hand, a N-stable (or N-rich) growth regime is suitable for the growth of nanowires because it suppresses the random movement of the adatoms and promotes adatom accumulation on either the nucleation sites or in the open mask-area.27 During the growth of GaN nanowires on a Si substrate, the sample surface is irradiated with nitrogen plasma along with group-III flux. However, due to the reactive plasma species, an amorphous Si3N4 layer (< 5 nm) is inevitably formed on the Si substrate before the random nucleation of GaN island on the Si surface, as mentioned earlier (Fig. 3(b)). The lateral size and the corresponding density of the resulting GaN nanowires can be controlled through the Ga/N flux ratio and the Si3N4 layer thickness. As one of the examples on the relationship between the nanowires lengths and lateral size (diameters), Debnath et al. has shown that the dependence is governed by the kinetic models related to the Ga adatom diffusion process on nanowire sidewalls toward the nanowire tip. For slender nanowires, the adatom diffusion on the nanowire sidewall gives a noticeable contribution to the axial growth rate, while direct impingement at the top of the nanowire contributed to thicker lateral size nanowires. Fig. 3(c) shows an inverse relationship between the nanowire length and lateral size (diameter) of the GaN nanowires at a given time after surface nucleation. The inset shows the higher aspect ratios of the slender GaN nanowires.14

![Diagram](image_url)

Fig. 3(d) shows the lattice structure of Wurtzite GaN crystal of Ga-polarity with the conventional crystal directions indicated as the +c and -c, respectively.28,29 The polarity discussed herein is a bulk property and not a surface property, and the lattice is best investigated as stacks of Ga-on-N or N-on-Ga bilayers rather than an alternating Ga and N layer (see Fig. 3(e)).30 The former stacking is easily recognized as Ga-polar GaN. However, the latter may still consist of a monolayer of group-III coverage at the top-terminating surface and can therefore be described as N-polar GaN with Ga-terminated surface.30,31

In general, self-assembled nanowires grown on the aforementioned Si3N4 under N-rich growth conditions can result in N-polarity along the growth direction. N-polar GaN nanowires can also be achieved by selective area growth using an optimized underlying N-polar AlN interlayer with small window opening of a Si3N4 mask (smaller than the effective Ga adatom diffusion length, λ-eff).34,35 Scanning transmission electron microscopic (STEM) observation allows the Ga and N lattice-order to be determined along the growth direction to identify the polarity (Fig. 3(e)). The polarity can also be identified through a wet chemical etching process, as the chemically stable Ga-polar surface of GaN tends to be resistant to wet etching in heated KOH and NaOH solutions, while the N-polar surface of GaN is readily etched into sloping surfaces or pyramidal shape in the solutions.36
C. InGaN-on-GaN axial nanowires

In the PA-MBE growth of InGaN, highly reactive nitrogen radicals in conjunction with impinging indium and gallium atoms govern the group-III/V flux ratio, thereby influence the incorporation of indium in InGaN nanowires. The growth temperature can also be used to tune the indium composition of InGaN. Adjusting these parameters allows the PA-MBE grown an InGaN nanowire to show a continuous visible-wavelength span from blue to red, which implies that a high indium composition can be achieved. Furthermore, because the laterally strain-relieved GaN nanowires are largely free from dislocations, the subsequently grown bulk InGaN nanowires or InGaN quantum-disc-in-a-wire structures can have less dislocations and can potentially yield high quantum efficiency. Fig. 4(a) shows the general features of axially grown bulk InGaN on GaN nanowires through self-assembled growth, where the indium composition is mainly tuned by flux ratio and the growth temperature. Similar to high-density binary, ternary or heterostructure group-III-nitride nanowires, bulk InGaN nanowires can also form an inverted taper due to the shadow effect and low growth temperatures that promoted lateral growth toward the tip of the nanowires.

To shed light on the optical and structural characteristics of InGaN nanowires, a spatially resolved cathodoluminescence (CL) spectrum was investigated, as shown in Fig. 4(b). The dominant peak energy (wavelength) of the CL emission varies from the InGaN/GaN interface to the top of the nanowire, i.e., from 2.84 eV (437 nm) to 2.36 eV (525 nm), 2.16 eV (574 nm), 2.03 eV (611 nm), and 1.98 eV (626 nm). This is caused by two mechanisms related to the nanowire strain and indium segregation. First, the initial strain at the bottom of the selective area grown InGaN/GaN interface is high due to the large lattice mismatch between InGaN and GaN. However, as the bulk InGaN nanowire length increases toward the tip, the lateral strain relief comes to favor a higher indium composition incorporation. In addition, indium segregation plays a crucial role in varying the indium composition. Since InN decomposes at the typical InGaN nanowires growth temperatures, partial InGaN decomposition happens, thus supplying more indium for achieving higher indium composition at the top of the nanowires.

It should be noted that in selective area growth of InGaN-on-GaN axial nanowires, the indium composition is also affected by the lateral size and pitch distance (p) of the nanowires. When p is smaller than the effective diffusion length of the Ga adatoms (l_P) (p < l_P), it was found that Ga incorporation reduces while indium composition increases. If p > l_P, the indium composition of InGaN nanowires depends on the lateral size of the nanowires. As the lateral size of nanowires increases, indium incorporation from lateral diffusion decreases, resulting in lower indium composition relative to that of the nanowires with smaller lateral size.

In practical devices, a well-controlled composition or composition gradient is essential in improving the performance of energy-related applications. For piezotronics and piezo-phototronics, this can assist the creation of a desired piezoelectric enhancement and solar absorption. For PEC water splitting, it also helps to achieve the desired bandgap that can drive the chemical reaction, enable efficient solar absorption, and benefit carrier transportation by better band alignment. These will be discussed in Section IV and V of this tutorial.

FIG. 3. (a) PA-MBE growth-regime diagram of Ga-flux vs. substrate temperature for Ga-droplet, intermediate, and N-stable regimes under a constant N-flux. Reprinted from Appl. Phys. Lett. 77, 2885 (2000), with permission of AIP publishing. (b) SEM cross-sectional image of GaN nanowires grown on Si substrate with SiN_x layer at the interface. Reprinted from Appl. Phys. Lett. 98, 071913 (2011), with permission of AIP publishing. (c) Nanowire length vs. diameter plot. Reprinted from Appl. Phys. Lett. 90, 123117 (2007), with permission of AIP publishing. (d) Different polarities of GaN crystal along the c-plane direction, i.e., +c (Ga-polar or group-III-polar) and -c (N-polar), respectively. The red dashed line indicates one Ga-centered tetrahedron unit. Adapted with permission from Progress in Crystal Growth and Characterization of Materials 48, 42-103 (2004). Copyright 2004 Elsevier. (e) STEM images of Ga-polar and N-polar GaN with schematics showing the models for the Ga-/N-polarity. Ga and N atoms are shown as green and blue spheres, respectively. Adapted with permission from Cryst. Growth Des. 16, 2 (2016). Copyright 2016 American Chemical Society.

FIG. 4. (a) Schematic of the axially grown bulk InGaN on GaN nanowire by self-assembled growth. (b) Cathodoluminescence (CL) spectrum of selective area grown bulk InGaN on GaN nanowire at 10 K.
from Journal of Applied Physics 113, 114306 (2013), with permission of AIP publishing.

III. Characterizations

It is essential to understand the characteristics of nanowires, such as their morphology, crystal quality, optical properties, band structures, carrier dynamics, and so forth, before utilizing the materials for specific applications. Here, we briefly summarize the commonly used characterization tools, along with two ultrafast characterization methods. The tools to characterize optical properties, such as photoluminescence (PL) spectroscopy and Raman spectroscopy, were introduced to investigate the composition of InGaN ternary compounds and the strain relationship between material and substrate. For structural characterizations, X-ray diffraction (XRD) tools can provide information, including crystalline quality and the epitaxial relationship between substrate and epitaxy. X-ray photoelectron spectroscopy (XPS) also provides an insight into the elementary composition and chemical states of various atoms. Hence, it can be used to investigate band-alignment and surface chemical bonds, which is of great interest to electrochemical applications. In morphological studies, SEM, transmission electron microscopy (TEM), and atomic force microscopy (AFM) are used in relation to their capabilities in morphological inspection, elementary mapping, and electrical characterization of a single nanowire. Moreover, we highlight electrochemical impedance spectroscopy (EIS) as a practical approach for the study of the interfacial charge-carriers transport. For advanced ultrafast characterizations, we discuss the use of THz spectroscopy and four-dimensional (4D) scanning ultrafast electron microscopy for non-contact studying of the electrical properties and the carrier dynamics in nanowires ensemble.

A. Optical characterizations

1. Photoluminescence spectroscopy

PL spectroscopy is a useful tool for extracting information on the optical properties of semiconductors. Unlike a spectrophotometer, which can probe the optical bandgap by measuring wavelength-dependent light absorption, PL spectroscopy measures band-to-band or excitonic emission during carrier transition. In a PL system, a laser beam with energy greater than the semiconductor bandgap is used to excite carriers from the ground state to an excited state. Then photoexcited carriers recombine and emits spontaneous emission photons, which can be captured by a photodetector. The PL system records the relative intensities of the emitted photons over an energy (wavelength) range, which can usually be fitted by Gaussian functions.\textsuperscript{52,53} For semiconductors with acceptable crystal quality, the prominent PL peak reflects the direct bandgap of a semiconductor, from which the compound composition can be estimated. The dominant indium composition ($x$) of In$_x$Ga$_{1-x}$N nanowires can be estimated by a quadratic function from PL peak energy (see Fig. 5(a)). The composition can be fitted as

\[ E_g = 3.42 - 2.74x - bx(1-x)eV \]  

(1)

, where GaN bandgap is 3.42 eV, and $b$ is the bowing parameter, estimated in Fig. 5(a) to 1.77 eV, which is suitable for the high indium composition range of InGaN.\textsuperscript{54-56} For nanowire-based quantum confined structures, multiple PL peaks may originate from the faceting of small bandgap quantum-disk, which are embedded in the quantum-barrier of larger bandgaps.\textsuperscript{57,58} Spatial measurements, such as PL mapping, are usually performed to map the uniformity of the compound composition and the crystal quality of a nanowires ensemble wafer for growth optimization.

However, the composition estimation might not be accurate since the direct bandgap emission can be shifted by strain, Stark shift, doping, and so forth.\textsuperscript{59,60} For certain poor quality materials, the defect peak intensity may exceed the band-to-band recombination peak intensity. On the other hand, inhomogeneous broadening and/or splitting of PL spectrum may coexist for many reasons, such as deep-level defects, dopant related Fermi levels shifting, alloy disordering, and interface roughness in quantum confined structures.\textsuperscript{51,62} In nanowires, the non-optimized growth of ternary compounds may lead to severe inhomogeneous broadening along with the appearance of multiple overlapping dominant peaks,\textsuperscript{5,63} which results in optical reabsorption losses. Hence, the technique is also commonly utilized to identify defect states and to evaluate the carrier concentrations in semiconductors.\textsuperscript{62,64}

In the case of fully elongated long nanowires, numerous surface defect states on the sidewall exist that create additional charge-trapping centers.\textsuperscript{55} This causes nonradiative recombination, indirect recombination, and Fermi level pinning, which leads to surface band bending.\textsuperscript{66-68} Due to this built-in electric field in band bending, the electron-hole pairs segregate, and holes accumulate at the near-surface for n-type GaN nanowires. This spatial separation is large enough to reduce the overlap between electron and hole wave functions. It can also result in local potential fluctuations of the InGaN nanowires. The combination of band bending and local potential fluctuations causes a radial Stark effect leading to indirect transitions.\textsuperscript{68-70}

Thus, surface passivation is essential for reducing surface defect states and compensating for the band bending. PL emission intensity can be compared to anticipate the effects of passivation on (In)GaN nanowires. Fig. 5(b) compares the room temperature PL spectra of pristine $p$-GaN and $p$-GaN nanowires passivated by the organic-sulfide chemical 1,2-ethanedithiol (EDT). The EDT-passivated $p$-GaN nanowires show a 24-fold increase in PL intensity over the pristine $p$-GaN nanowires. EDT can therefore effectively passivate the surface defect states for recovering the band-edge emissions.\textsuperscript{67}

The temporal evolution of PL through ultrafast laser spectroscopy is essential in understanding the dynamics of charge-carriers and the surface passivation effects. Time-resolved photoluminescence (TRPL) spectroscopy uses femtosecond laser pulses at a high repetition rate to excite the semiconductor, and PL intensity decay is recorded over each pulse-duration period. The time-decay spectra can help to understand the dynamics of carrier recombination in semiconductors.\textsuperscript{1,71,72} Fig. 5(c) shows a comparison with TRPL on the pristine $p$-GaN and EDT-passivated $p$-GaN nanowires with the
fitting curve of a TRPL spectrum using the stretched exponential decay model.

\[ I(t) = I(0) \exp \left( \frac{t}{\tau} \right)^{\beta} \]  

(2)

where \( I(t) \) is the PL intensity at time \( t \), \( I(0) \) is the PL peak intensity at \( t = 0 \), \( \tau \) is the photoexcited carrier lifetime, and \( \beta \) is the stretching parameter, which is relevant to the effects of high-excitation carrier density and/or disorders within the materials, such as compositional variation in the nanowires. \( \tau \) and \( \beta \) can be obtained by linear fitting of the logarithm of the TRPL intensity vs. decay time.\(^{5,67}\) From the fitting results, see Fig. 5(c), the fast and slow decay times (\( \tau_1 \) and \( \tau_2 \)) for pristine \( p \)-GaN nanowires were found to be 16 ps and 40 ps, while the EDT-passivated \( p \)-GaN nanowires showed slower decay times of 22 ps and 65 ps, respectively. This indicates that EDT passivation successfully eliminated surface defect states, and PEC efficiency can be enhanced.\(^{67}\)

A further detailed treatment of the time-integrated and transient PL properties of GaN nanowires should take into account the effect of surface recombination, coalescence, or both surface recombination and coalescence.\(^{37,52}\) Hence, structural information will also be useful in PL analysis.

Beyond the temporal evolution of PL, temperature dependent PL (TDPL) evolution can provide additional information on photon-to-electron conversion. The recombination mechanisms can be investigated by analyzing the peak shifts and intensity change of the PL peaks. A fitting example of TDPL spectra on InGaN nanowires of indium composition ~32% is shown in Fig. 5(d).\(^{42}\) From the integrated intensity of the PL peak (\( I_I \)) and temperature (\( T \)), the evolution of the spectra can be described with an Arrhenius equation, expressed as

\[ I_I = I_0 e^{\frac{-E_T}{k_B T}} \]  

(3)

where \( I_0 \) and \( k_B \) are the integrated PL intensity close to 0 K and the Boltzmann constant, respectively. \( A \) and \( B \) are fitting parameters, and \( E_1 \) and \( E_2 \) are the activation energies related to different recombination channels or mechanisms.\(^{76,77}\) Smaller activation energy (\( E_2 = 6 \) meV) indicated a weaker carrier-localization effect, potentially originated from a N-rich region of the InGaN nanowire perimeter, and a larger activation energy (\( E_1 = 58 \) meV) may correspond to defect-levels or traps that cause fast thermal quenching of luminescence in InGaN nanowires.\(^{42}\) The TDPL energy peak (\( E_T \)) can also be fitted using the extended Varshni’s equation as

\[ E_T = E_B^0 - \frac{\sigma T^2 \alpha^2}{k_B T + \beta^2} \]  

(4)

where \( E_B^0 \) and \( E_B^0 \) are the energy bandgaps at temperature \( T \) and close to 0 K, and \( \alpha \) and \( \beta \) are Varshni’s fitting parameters. The value of \( \sigma \) indicates the degree of localization effects.\(^{78,79}\)

TDPL has been applied to estimate internal quantum efficiency (IQE) (the conversion efficiency of electron-hole pair generation due to absorbed photons) for group-III-nitride-based nanowires, typically by calculating the integrated PL intensity ratio (area under the PL spectrum) at room temperature and low-temperature.\(^{57,71,80,81}\) This assumes that defects related to non-radiative recombinations were frozen out at a low temperature of <10 K, but this is not always true. It was found that the integrated PL intensity may increase beyond 10 K before it shows a normal decreasing trend with increasing temperature in both planar epitaxy and nanowires.\(^{57,81}\) The initial increasing trend is related to the decreasing Shockley-Read-Hall non-radiative recombination or sidewall-related excess carrier losses, and the transition toward efficient bimolecular radiative recombination. Thus, care should be taken when the photons-to-carriers conversion efficiency is analyzed at low temperatures.

The TDPL spectrum can also be used to understand the molecular gas adsorption and surface chemical reactions on the nonpolar sidewalls of (In,Ga)N nanowires ensemble. For instance, at elevated temperatures of up to 200°C and in chemical reactive synthetics air environments, hydrocarbons can enhance PL responses due to the removal of quenching oxygen adsorbates and the enhancement of water-related adsorbates from surface oxidation reactions.\(^{52}\)

![FIG. 5.](image-url) (a) PL bandgap vs. indium (In) composition estimation of In\(_{x}\)Ga\(_{1-x}\)N at room temperature (R.T.).\(^{54}\) Reprinted with permission from Physica Status Solidi (a) 201, 12, 2850-2854 (2004). Copyright 2004 from Wiley. (b) Room-temperature PL spectra of pristine \( p \)-GaN and EDT-passivated \( p \)-GaN nanowires, respectively. Inset shows the normalized pristine and EDT-passivated \( p \)-GaN nanowire spectrum for comparison. (c) TRPL comparison between pristine \( p \)-GaN and EDT-passivated \( p \)-GaN nanowires. Fast and slow decay times (\( \tau_1 \) and \( \tau_2 \)) are indicated.\(^{67}\) Adapted with permission from Nano Lett. 17, 3 (2017). Copyright 2017 American Chemical Society. (d) Integrated PL intensity vs. inverse temperature (the continuous line shows the Arrhenius fitting). Inset shows the PL peak energy vs. temperature and the Varshni’s empirical equation fitting.\(^{42}\) Adapted

2. Raman spectroscopy

Raman spectroscopy is used to study the vibrational and rotational modes of materials through the interaction between incident photons and chemical bonds within material. Raman scattering is an inelastic scattering process, in which photons can be scattered to a virtual state and then re-emitted to a vibrational energy state that is either higher or lower than the initial state. Where the energy level of the final vibrational state is lower than that of the initial states, it is called the anti-Stokes effect, and where it is higher, it is called the Stokes effect. A Wurtzite GaN primitive cell has four atoms, and the group theory predicts a set of acoustic modes (A_1 + E_1) and optical modes (1A_1+2B_1+1E_1+2E_2)\(^{83-85}\) (see Fig. 6(a)). Among these optical modes, the B_1 modes are Raman inactive. A_1 and E_2 modes are both IR and Raman active (polarized) modes because of the crystal anisotropy of the Wurtzite material, which are split into transversal optical (TO) and longitudinal optical (LO) components with different frequencies due to the long-range Coulomb interactions. The two E_2 modes, namely, the low-frequency mode (E_2(LO)) and high-frequency mode (E_2(NG)), are Raman active (unpolarized) and can be used to study strain conditions in nanowires.\(^{84-85}\) Fig. 6(b) and (c) shows the typical Raman spectra of (In,Ga)N nanowires on Si and sapphire substrates, respectively. The E_2(high) mode of (In,Ga)N nanowires on Si substrates is located at ~567 cm\(^{-1}\), which is similar to strain-free GaN, while that of (In,Ga)N nanowire grown on sapphire showed a blueshift to 571 cm\(^{-1}\) due to the compressive stress in InGaN.\(^{3}\)

In nanowire structures, light scattering in the nanowires ensemble and the surface depletion layer in the nanowire structures resulted in more complex Raman spectra. Some have resorted to novel Raman techniques to characterize a single nanowire, which are summarized herein. The strain distribution of AlGaN/GaN core-shell single nanowire has been studied by resonant Raman spectroscopy.\(^{88}\) Polarized-confocal Raman spectroscopy has been applied to a single GaN nanowire to determine the crystalline phase and crystallographic orientation.\(^{89}\) In addition, the Raman system can be coupled with an AFM system to conduct tip-enhanced Raman spectroscopy on a single GaN nanowire.\(^{90}\) Moreover, the carrier concentrations of the group-III-nitride nanowires can also be estimated by analyzing the Raman spectra because they are related to the frequency shifts of the coupled longitudinal phonon-plasmon mode.\(^{65,91}\) All of the aforementioned Raman techniques are beneficial for non-destructive and in-situ characterizations,\(^{92}\) and can potenially be applied to group-III-nitride nanowires.

B. X-ray structural analyse and chemical bond characterizations

XRD is a classical approach to identify and characterize the crystalline structures of materials. The diffraction pattern contains information on the crystal phase, lattice constant, composition of ternary compound semiconductors, and so forth. XRD can also be applied to understand the strain distribution in nanowire structures.\(^{93}\) Specific to nanowires ensemble, XRD pole figure measurements can be applied to reveal the preferential orientation of constituent nanowires or the crystallographic information related to the texture of grains.\(^{94,95}\) Here, a pole is an equivalent crystal-plane normal. As noted in the earlier section, axially grown nanowires on silicon generally show a preferred c-plane orientation at the out-of-plane direction. For the in-plane orientation of GaN nanowires, it depends on the symmetry of the substrate. As shown in the schematics in Fig. 7(a), two types of hexagonal GaN nanowires ensemble appear on the surface of Si(100), arbitrarily termed the GaN I and GaN II ensembles, which are rotated by 30 degrees for the equivalent Miller indices. Nevertheless, there is only one dominant type (GaN II) on Si(111) substrate.\(^{96}\)

The two types of GaN originate from the different structures of underlying Si substrates. First, Si(100) substrate surface has fourfold symmetry. However, due to the presence of a thin Si$_3$N$_4$ amorphous layer on the Si(100) surface, two types of hexagonal GaN are preferentially nucleated. In contrast, GaN II nanowires ensemble is dominant on Si(111) since the lattice structures of GaN and Si(111) are both hexagonal, which promotes alignment in their epitaxial relationship. To confirm this, the GaN I and GaN II nanowires grown on Si(100) and Si(111) substrates were analyzed by selecting the GaN(1015) asymmetric reflection for XRD pattern, i.e., substrate rotation scan (see Fig. 7(b)). For GaN nanowires grown on Si(111), the intensity ratio of GaN II to GaN I nanowires ensembles is approximately 1000:1. Here, we intentionally use the plural form of ensemble to indicate the two distinct types of nanowires groups. On the other hand, the GaN nanowires grown on Si(100) show an almost identical intensity distribution of GaN I and GaN II.
GaN II nanowires ensembles separated by an azimuthal angle of 30 degrees. Thus, the XRD pole figures of GaN nanowires on Si(111) exhibited six-fold symmetry, as shown by the six distinct spots radially spaced out by 60 degrees in Fig. 7(c); while that grown on Si(100) showed 12-fold symmetry, as shown by 12 high-intensity spots in Fig. 7(d), which is due to the superposition of the respective 6-fold symmetries from each of the GaN I and GaN II types of nanowires ensembles.

![Schematic illustrations of GaN I and GaN II types of nanowires ensembles grown on Si(100) (top) and Si(111) (bottom) substrates by Wang et al.](image)

FIG. 7. (a) Schematic illustrations of GaN I and GaN II types of nanowires ensembles grown on Si(100) (top) and Si(111) (bottom) substrates by Wang et al. Copyright (2016) The Japan Society of Applied Physics. (b) XRD phi-scan of GaN(10/15) asymmetric reflection of GaN nanowires grown on Si(100) and Si(111) substrates as reported by Bertness et al. Reprinted with permission from Journal of Crystal Growth 310, 13, 3154-3158 (2008). Copyright 2008 Elsevier. XRD pole figure of GaN nanowires on (c) Si(111) and (d) Si(100) substrates, respectively, for GaN(10/14) asymmetric reflection studied by Geelhaar et al. © [2011] IEEE. Reprinted, with permission, from IEEE Journal of Selected Topics in Quantum Electronics 17.4, 878-888 (2011).

XPS is a surface-sensitive tool (operating at depths in the nanometer range) for elementary, chemical state, and electronic state analyses, which is based on the photoelectric effect. When an X-ray beam of sufficient energy irradiates the surface of a material, the X-ray photons can interact with the material, break the nucleus attraction force to the electrons, and excite the electrons in specific bound states, in the so-called photoelectric effect. The kinetic energy of the photoelectrons can be measured simultaneously, in a way that depends on the energy of the X-ray photons and the binding energy of the electrons. The binding energy reflects the elements near the material surface and the chemical states of the atoms that eject photoelectrons. The XPS spectrum records the energy spectrum of photoemission intensity vs. binding energy. In favorable cases, each prominent peak corresponds to a specific element, and the area under each peak is proportional to the number of those specific elements, which allows XPS to quantify the chemical composition at the surface of a material. In the spectrum, the core-level energy shifts reflect the outer valence configuration of the material, and thus, the chemical states or possible bonds can be investigated. Detailed descriptions of the principle can be found in the literature. For planar structures, XPS is often utilized to study depth profiling, surface chemical bonds, and interfacial band alignment. Similarly, it can analyze the near-surface band structure of nanowire structures, which can significantly facilitate relevant PEC study on the charge-carriers transport properties of the photoelectrodes. XPS has been utilized to investigate the near-surface band structure of the m-plane (lateral plane) of MBE-grown GaN nanowires by analyzing the surface Fermi level shifts relative to the valence band maximum. It was also applied to investigate the band alignment in a GaN/MoS2 core-shell nanowire structure. Similarly, it is helpful to understand the surface chemical bonds of photodeelectrodes with appropriate surface states passivation and co-catalyst loading. In addition, XPS spectra are capable of investigating molecular water adsorption on the surface of thin-film group-III-nitrides. Molecular water can be introduced by the backfilling step of XPS, which is dissociatively adsorbed onto the exposed GaN(0001) surface. Monitoring the O1s level helps determining the formation of different oxygen-related components formed on the surface, and the corresponding surface band bending on GaN can be calculated. These XPS studies under operando condition are of great interest for understanding the dynamic interfacial chemical behavior, not only in water-splitting reaction but for other reactions as well, such as carbon dioxide reactions.

C. Interfacial structural and morphology characterizations

SEM can provide cross-sectional visualization and a morphological overview of nanostructures. By raster-scanning a specimen using a high-energy electron beam, SEM can detect secondary electrons (SE) or backscattered electrons (BE) that are emitted through electron-matter interactions in the bulk of the materials. Different imaging signals can lead to different spatial resolutions of SEM images. Usually, an SE image is used to analyze nanowires ensemble because of its high resolution, smaller than or at a similar scale to the nanowire size of about tens of nm. SEM provides an overview of the morphology of the nanowires ensemble, which can perform at different angles by tilting the stages. Fig. 8(a) and (b) show a cross-section view and top view of SEM images of an InGaN nanowire grown on a Ti-coated substrate. SEM can greatly assist in understanding the growth uniformity, geometry scale and coalescence of the nanowires ensemble. The samples for SEM should be clean and electrically conductive to prevent the thermal damage that would result from electron accumulation on the samples. Energy-dispersive X-ray spectroscopy (EDX) is often installed in an SEM or TEM system for the elementary analyses of nanowires.

However, TEM is better equipped to image the tiny features within the nanowire or the nanowire/substrate interface and to reveal the lattices as it is a high-spatial-resolution (sub-nanometer) and high-magnification electron microscopy technique. Focusing a high-energy electron beam onto a material specimen, it collects
transmission electrons as the imaging signal. It provides important information for crystal quality and structural defects (dislocations, vacancies, and so forth). Because the thickness of the observed sample can greatly influence the mass thickness contrast of TEM, the samples must be carefully prepared before being transferred to metallic or carbon grids. The nanowires samples can be prepared by simply scratching off and dispersing the broken-off nanowires onto a TEM grid or by slicing thin lamella using the focused-ion-beam (FIB) technique. The latter approach is most useful for observing the cross-section view at the heterointerface. Electron energy loss spectroscopy (EELS) mapping with fast Fourier transform imaging techniques can be coupled with high-resolution TEM (HR-TEM), which measures the change in electron kinetic energy caused by inelastic scattering. The EELS offers elementary analyses, including assessments of valence and conduction band electronic properties, chemical bonding, and so forth. Analyzing the atomic composition of the nanowires helps to understand the interfacial layer, the dopant concentrations, surface treatment and further assists in growth optimization.

Fig. 8(a) and (b) show the SEM elevation and plan views, respectively, of InGaN nanowires grown on Ti-coated substrate, and the corresponding TEM image and EELS mapping are shown in Fig. 8(c) and (d). A closer view and the detailed elementary mapping reveal the formation of conductive TiN between the GaN and Ti layer. This is due to the nitridation of Ti during the initial growth of GaN. The implemented Ti as the starting growth surface eliminated the formation of an insulating Si$_3$N$_4$ layer for nanowires directly grown on the Si substrate, as evident in the TEM and EELS mapping of Fig. 8(e) and (f). Directly observing the nanowire/substrate interface is of great importance for investigating the origin of interfacial impedance. This will be highlighted for PEC process in Section III.D along with the electrochemical impedance measurements.

**Fig. 8.** Structural characterization of group-III-nitride nanowires: (a) elevation view of a cross-section SEM image, (b) plan-view SEM image of InGaN nanowires grown on a Ti-coated Si substrate. HR-TEM image (c), and EELS elementary mapping (d) of GaN nanowires grown on a Ti-coated Si substrate. HR-TEM image (e) and EELS elementary mapping (f) of InGaN nanowires directly grown on Si substrates. Reproduced by permission of The Royal Society of Chemistry.

AFM-based morphological characterization is also a powerful tool that relies on interactions between the tested material and a micrometer-sized cantilever having a tip with a radius-of-curvature in the nanometer size. This can be performed in the contact mode, the tapping mode and the non-contact mode in an ambient environment. The conductive AFM (c-AFM) can simultaneously scan a three-dimensional (3D) morphology/conductivity profile of a given sample. Further, c-AFM has been explicitly used in piezotronic studies at nanoscales. A metallic tip forms a Schottky contact when it is in contact with nanowires, and the tip can be used to apply a force onto a structure as small as a single nanowire to extract the current-voltage (I-V) characteristics. The optimization of InGaN nanowires and AlGaN nanowires structures has been reported using nanoscale electrical characterization. Further use-inspired investigations of nanowires related to piezotronic and piezo-phototronic applications will be discussed in Section IV.

**D. Analyses of electrical properties with electrochemical impedance spectroscopy**

As mentioned in Section III.C, c-AFM can image the 2D conductivity profile of the nanowires ensemble and establish the I-V characteristics of a single nanowire. Other than this, some conventional electrical measurements, such as Hall effect measurements and field-effect transistor (FET) measurements have been modified for studying a single nanowire, particularly for the estimation of resistivity or carrier concentrations. However, Hall effect measurements and FET measurements for a single nanowire require a complex and elaborate nanofabrication process, which failed to provide information for the entire nanowires ensemble.

In this regard, EIS is a practical approach for analyzing the interfacial electrical performance of nanowires structures. EIS measurements are usually conducted by using a potentiostat. The potentiostat applies an alternating voltage superimposed on a bias voltage to the electrochemical cell. By measuring the corresponding current signal, the electrochemical impedance can be calculated by the ratio of the voltage to the current in the frequency domain. Drawing on EIS measurements, the Nyquist plot is a complex plane plot which plots the imaginary components of the impedance vs. the real components at different frequencies. The real part of the impedance represents the resistance of the system, and the imaginary part of the impedance is related to capacitance or inductance in the system, introduced by an undesired contact or an existing insulating layer. The impedance introduced by different parts of the nanowires can be identified by fitting the plot with suitable
equivalent circuits. The relevant studies on the interfacial impedance of the nanowires/substrate interface through Nyquist plots have been reported in existing literature.\textsuperscript{107,112,121} The principle is further described in the following.

MBE-grown nanowires on Si substrates, when exposed to a nitrogen-plasma environment, will inevitably form an insulating Si$_x$N$_y$ thin layer at the interface between the nanowires and the Si substrate, as mentioned earlier. The Nyquist plots thus form two half-circles (see Fig. 9(a)), which can be fitted with an equivalent circuit that consists of resistance in the electrolyte ($R_s$) and two RC constant-phase elements (CPEs) induced by the nanowires and the insulating Si$_x$N$_y$ layer, respectively.\textsuperscript{120,122} On the other hand, the Nyquist plots of nanowires grown on metallic substrates (see Fig. 9(b)) showed only a single half-circle and thus fitted using one RC-CPE, i.e., the Randles model, due to the insulating materials at the nanowires/metal interface. The observation is due to the nitridation of Ti on a Ti/Mo substrate as discussed in Section III.C, which eliminated the impedance related to the insulating Si$_x$N$_y$.\textsuperscript{111}

Another possible use of EIS is to estimate the statistical ionized carrier concentrations over the whole nanowires ensemble.\textsuperscript{111,122} A Mott-Schottky plot demonstrates the inverse square of the capacitance density with applied bias $V$. It has been commonly applied to estimate the carrier concentrations of planar semiconductors. The opposite slopes for Mott-Schottky plots of $n$-type (see Fig. 9(c)) and $p$-type semiconductors (see Fig. 9(d)) are attributed to opposite surface band bending at the semiconductor/electrolyte interface. A modified Mott-Schottky equation was introduced by solving Poisson's equation in 3D, taking the geometry of the nanowires-based electrodes into account.\textsuperscript{65,122,123} This modified equation considers the cylindrical symmetry of the depletion region from the surface to the center of the nanowire. The dopant distribution inside the nanowires is assumed to be homogeneous for simplicity. At a distance $x$ from the nanowire surface with radius $R$, the potential difference in the space charge region $V_{sc}$ can be given by equation 5, where $\varepsilon$, $N$, and $q$ are the semiconductor dielectric constant, the ionized carrier concentration of the semiconductor electrode, and unit charge, respectively. The total charge in a single cylindrical nanowire of length $L$ can then be calculated as $Q = eN\varepsilon\pi R^2 (R^2 - x^2)$, such that the expression for the total capacitance of the nanowires ensemble can be obtained as follows, where $L$ and $A$ are the length of the nanowires and the surface area of the electrode, respectively. $D_{NW}$ is the density of nanowires and $v_s$ is the relative dielectric constant. The relative dielectric constants of InGaN and AlGaN used in Fig. 9(c) and (d) are 12 and 8, respectively, by referring to the values of their bulk materials.\textsuperscript{111,122}

$$V_{sc} = -\frac{Nq}{2\varepsilon}\left[\frac{1}{2}(R^2 - x^2) + R^2\ln\left(\frac{x}{R}\right)\right]$$

$$C_{total} = \frac{2\pi\varepsilon\kappa LAD_{NW}}{\ln\left(\frac{x}{R}\right)}$$

From these equations, $V_{sc}$ and $C_{total}$ can be calculated for specific positions with the same distance (radius) to the center of the nanowire. Thus, the ionized dopant concentration ($N$) is the only fitting parameter for the experimental data in the Mott-Schottky equation for nanowires. The sign of $N$ is positive for hole concentrations in $p$-type semiconductors and negative for electron concentrations in $n$-type semiconductors, respectively. Previously published papers have shown that this modified Mott-Schottky model fits the EIS data of nanowires structures well, and provides a relatively accurate estimation of the concentrations over the nanowires ensemble compared to the conventional methods.\textsuperscript{117,118} Figure 9(c) shows the experimental data of $n$-type GaN nanowires ensemble, which can be best fitted with a carrier concentration of $2.8 \times 10^{18}$ cm$^{-3}$. For the $p$-type AlGaN nanowires, the best-fitted experimental data yielded a hole concentration of $1.2 \times 10^{19}$ cm$^{-3}$ when the Mg effusion cell of an MBE system was set to $360$ °C, as shown in Fig. 9(d).\textsuperscript{111}

In summary, EIS provides a statistical estimation of the effective carrier concentrations of nanowires ensemble. Obtaining the effective carrier concentration, which is related to the doping concentration, is essential in designing energy-conversion devices.

![Nyquist plots of nanowires grown on metallic substrates](image)

**FIG. 9.** EIS measurements of group-III-nitride nanowires: Nyquist plots of: (a) $n$-type InGaN on Si,\textsuperscript{122} and (b) $p$-type AlGaN on Ti/Mo.$^\text{111}$ where $R_s$ and $CPE$ are electrolyte resistance and constant-phase elements, respectively. The measured Mott-Schottky curves and fitting curves of: (c) $n$-type InGaN on a Si substrate,$^\text{122}$ and (d) $p$-type AlGaN on a Ti/Mo substrate.$^\text{111}$ (a) and (c) are adapted from Journal of Applied Physics 124, 083105 (2018), with permission of AIP publishing. (b) and (d) are reproduced by permission of The Royal Society of Chemistry.

**E. Advanced ultrafast characterizations**

1. **Terahertz spectroscopy**

THz spectroscopy is an advanced non-contact and non-destructive technique for accurately measuring the carrier lifetime, mobility, carrier concentration, and surface recombination velocity, while shedding light on the carrier dynamics. The low photon energies of THz radiation (0.4–40 meV or ~0.1–10 THz) are suitable for generating an electric field to stimulate quasiparticles, such as free-carriers, excitons, and so forth, and to excite collective excitations.
such as optical phonons. The THz frequency has a similar order of magnitude in carrier scattering rates. Thus, the THz spectroscopy is able to probe low-energy electronic processes and reach a sub-picosecond temporal resolution at room temperature.

**THz time-domain spectroscopy (THz-TDS)** typically uses a femtosecond laser as the pump source, which generates an ultrashort duration optical pulse (e.g., 800 nm, 100 fs). The optical pulse beam is split into two: one THz generation beam and one optical gate beam. The gate beam is collected by the detector as a reference. The generation beam is focused on a THz emitter (e.g., GaAs) and to excite a THz pulse. The emitted THz pulse irradiates and interacts with the sample and then collected by the THz detector. The detector measures the THz electric field within a short temporal window, where the optical gate pulse overlaps with the THz pulse, which can be controlled by delay components. The THz-TDS can be used to study electrical conductivity in nanowires ensemble in equilibrium, such as measuring the electron density and mobility of InN nanorods. Also, by applying THz-TDS, a recent study revealed a difference in the resultant orientations for GaN nanowires grown on Si(111) and Si(100) substrate.

If there is crystal symmetry or birefringence, such as GaN nanowires grown on Si (111) substrate, the THz signal can be detected, while the THz signal diminished from textured-like GaN nanowires grown on Si (100). The intensity of the THz signal reflects how well the crystal structure is aligned. For the examples of the application of optoelectronic and energy conversion devices, the study can guide the proper growth of intentionally induced coalesced GaN nanowires for easing device fabrication.

**Optical pump-THz probe (OPTP) spectroscopy** is a variant of THz-TDS. Instead of using a below-bandgap optical pump to measure the electrical conductivity at equilibrium, it uses an ultrashort optical pulse having an above-bandgap energy that results in photoexcitation. The photogenerated carriers increase the absorption of the delayed THz probe. Hence, the relative changes in transmission can be measured and converted to photoconductivity which can be related to carrier density and mobility. Therefore, a photoconductivity decay curve can be obtained and the frequency-averaged mobility can be estimated. Readers are referred to a detailed review from Joyce et al. for various physical models of THz photoconductivity in nanowires. It needs to be chosen accordingly to fit the photoconductivity spectrum. By applying OPTP spectroscopy to nanowires, Parkinson et al. extracted the electron mobility of GaN nanowires at 820±120 cm²/V·s, and the photoconductivity lifetime at 2.5±0.5 ns. Kar et al. also applied the technique to study the carrier dynamics and relaxation times of GaN/AlGaN core-shell nanowires. Moreover, near-field techniques can help to break the spatial resolution limit of conventional THz spectroscopy caused by the diffraction effects of the THz probe so that THz spectroscopy can also be applied to single-nanowire characterizations.

2. **Four-dimensional scanning ultrafast electron microscopy**

Although ultrafast transient absorption/transmission microscopy can be used to investigate carrier dynamics, it is difficult to achieve high spatial resolution, even for the aforementioned OPTP spectroscopy. On the other hand, conventional electron microscopies, including TEM and SEM, have been widely used to observe the morphology and structure of nanomaterials. Ultrafast electron microscopy can offer a time resolution at the femtosecond level and the spatial resolution down to the atomic level to study the surface dynamics and structural transitions. Also, the acceleration voltage of scanning ultrafast electron microscopy can operate at ~1-30 kV, which makes the technique suitable for surface/interface characterizations and for materials sensitive to electron beams alteration.

In this regard, four-dimensional (4D) scanning ultrafast electron microscopy, where the 4D includes x, y, z, and time dimensions), can map the surface dynamics with sub-picosecond temporal and nanometer spatial resolutions by observing the SE energy changes. The technique can be used to analyze InGaN nanowires after surface passivation. Synchronized femtosecond laser and electron pulses generate wave packets for studying the nanowire carrier dynamics. It can help visualizing the surface recombination processes by analyzing the time regimes between the electron and optical pulses (Fig. 10(a)). In one study, the time-resolved SE signal intensity recovered at a slower rate for octadecylthiol (ODT) passivated InGaN nanowires relative to the unpassivated counterpart, suggesting the suppressed carrier leakage or nonradiative recombination at the surface of the nanowires (see Fig. 10(b)). This is attributed to the presence of a polymer-like layer on the InGaN nanowire sidewall by ODT passivation (Fig. 10(c)).
FIG. 10. (a) Schematic of four-dimensional scanning ultrafast electron microscopy set-up for measurement of nanowires ensemble.\textsuperscript{135} Reprinted with permission from Advanced Materials 28,25, 5106-5111 (2016). Copyright 2016 from Wiley. (b) Real-time SE intensity for as-grown and ODT passivated InGaN nanowires. (c) High magnification TEM image of a ODT-passivated nanowire. The polymer-like deposition (layer below the red dashed-line) at the nanowire sidewall can be observed.\textsuperscript{135} Reprinted with permission from Small 12, 17, 2313-2320 (2016). Copyright 2016 from Wiley.

IV. Piezotronics and piezo-phototronics

As described in Sections II and III, proper growth optimization and characterization will ensure nanowires ensemble has the proper uncoalesced morphology (in general), doping, and bandgap properties for eventual applications in electronics and optoelectronics. The prefix piezo is derived from Greek, and the entailing term with the prefix is associated with “strain-affected.” Electronic devices that use strain-induced piezopotential to control or tune the charge-carriers transportation properties are piezotronics. If the device is based on semiconductor optoelectronics, it can couple the piezotronic effect together with the semiconductor and photonic properties, and hence called piezo-phototronic device. For such a device, the piezopotential can be applied to control charge-carriers generation, transportation, and recombination. Focusing on the development of InGaN nanowires-based devices, this section first presents the piezoelectric properties of group-III-nitride material, originating from the asymmetric crystal structures, in the form of polarization effects. The discussion then extends to the piezotronic/piezo-phototronic effects in a single nanowire, primarily based on AFM studies. Further piezotronic and piezo-phototronic applications are introduced in Section IV.C.

A. Piezoelectric properties of Wurtzite materials

Piezoelectric effects broadly exist in non-centrosymmetric materials. The mechanical strain causes deviated centers of positive and negative charges so that they introduce accumulated polarized charges on the surface of the material. The piezoelectric properties of semiconductors are well documented in the literature.\textsuperscript{136} The terminology, piezotronic effects, was coined by Wang et al. in 2006, for such a combination of semiconducting properties with the piezoelectric effects,\textsuperscript{139} inspiring a plethora of applications, including nanosensors, nanogenerators, and piezotronic transistors, among others. The effect is distinctly from the insulating perovskite materials, such as lead zirconate titanate, which exhibits a sufficiently high piezoelectric coefficient for making mechanical sensors and actuators, while their wide bandgap and insulating characteristics make it difficult for electronic or phototronic applications.\textsuperscript{140} Wurtzite structure semiconductors, such as ZnO and group-III-nitride materials,\textsuperscript{141,142} which benefit from their coupled semiconducting and polarity-dependent piezoelectric properties, are suitable and promising for piezotronic and piezo-phototronic energy-conversion applications. In this subsection, the origin of the piezoelectric properties of Wurtzite materials is discussed in detail, particularly for group-III nitrides.

Spontaneous polarization exists due to the inherent non-centrosymmetric crystal lattices and the difference in the electronegativity of group-III elements and N, which lead to polar covalent bonds. As shown in Fig. 3(d), in this structure, the constituent atoms form a tetrahedron coordinated by four nearest neighboring atoms. In reality, the group-III nitride structure slightly deviates from the ideal tetrahedral coordination, with a ratio of lattice constants ratio (c/a) smaller than $\sqrt{3/8}$.\textsuperscript{143} Therefore, within a tetrahedron unit, the Ga-N bond along the c-axis has a longer bond than the sum of vertical components of inclined Ga-N bonds, resulting in a net vertical dipole moment and spontaneous polarization, which is the volume density of dipole moment. The spontaneous polarization direction depends on the stacking order of the closest packed group-III metal and N diatomic planes in the structure (see Fig. 3(e)).\textsuperscript{144} In a metal-polar structure (designated as [0001], see Fig. 3(d) and (e)), the growth direction points from the basal plane of the Ga-centered tetrahedron toward the apex (+c), and the direction of spontaneous polarization ($P_s$) is opposing the growth direction (Fig. 11). In an N-polar structure (designated as [000-1], the growth direction points from the apex of the Ga-centered tetrahedron towards the basal plane (−c), while the $P_s$ direction is the same as the growth direction (Fig. 11).\textsuperscript{145}

The polarization fields may originate not only from spontaneous polarization but also from piezoelectric polarization. When a strain is introduced onto the lattice,\textsuperscript{146} it displaces the centroid of the anions and cations and leads to an electric-field dipole-moment that causes piezoelectric polarization. The strain can be introduced by crystal pseudomorphic growth at a heterointerface and/or applied external force onto a crystal.\textsuperscript{147} The former is due to the lattice mismatch between group-III nitride layers of different composition,\textsuperscript{1} as shown in Fig. 11. When a larger lattice is grown on a pristine substrate (e.g., InGaN grown on GaN), the strained InGaN layer suffers from a compressive strain, which results in a piezoelectric polarization ($P_{pe}$), which is opposite to the $P_s$ orientation, regardless of crystal polarity. When a smaller lattice is grown on a pristine substrate (e.g., AlGaN grown on GaN), the strained AlGaN layer suffers from a tensile strain and results in a $P_{pe}$ of the same orientation to the $P_s$. Detailed calculation of the polarization fields will be discussed later. Apart from heteroepitaxial growth, external mechanical deformation can also introduce strain on a lattice. The collective effects of the polarized dipoles of all unit cells lead to a macroscopic strain-induced piezopotential in the crystal, which can be measured or extracted experimentally so that the piezoelectric properties, i.e., the polarization effects, enable the conversion from mechanical energy to electrical energy. The crystal structure anisotropy of Wurtzite GaN and related material is well documented in a number of numerical simulations\textsuperscript{147,148} as well as in experimental work.\textsuperscript{149-151}
The total polarization field is the sum of spontaneous polarization and piezoelectric polarization. The detailed calculations for Wurtzite nanowires can be found in the literature. The piezoelectric polarization \( P_{pz} \) is proportional to the strain \( \epsilon \) as
\[
P_{pz}(i) = \sum_{j} e_{ij} \epsilon_{j}, \quad (i = x, y, z; j = 1, 2, \ldots, 6)
\]
(7)

The strain \( \epsilon \) can be calculated as \( \epsilon_{j} = \frac{e_{ij} - e_{ij0}}{e_{ij0}} \), where \( e_{ij0} \) is the pristine lattice constant and \( e_{ij} \) is the strained lattice constant. The tensor \( e \) is the piezoelectric strain coefficient tensor, which can be denoted by a 3x6 matrix. The Voigt notation stands for the tensor components in-plane polarization directions, \( j = (1, 2, 3) = (xx, yy, zz) \), and shear deformations, \( j = (4, 5, 6) = (yx, yz, xy) \). The 3D geometry of a nanowire makes it exhibiting a 3D piezoresponse. Therefore, both the in-plane piezoelectric strain coefficients \( \epsilon_{33} \) and \( \epsilon_{35} \) and the shear-strain-related tensor \( \epsilon_{35} \) need to be included when calculating the piezoelectric polarization field. Readers may find that another piezoelectric coefficient tensor, the piezoelectric stress coefficient tensor \( (d) \), is also frequently mentioned in the literature to compare the piezoelectric properties of different materials. Piezoelectric polarization can also be given by
\[
P_{pz}(i) = \sum_{j} d_{ij} \sigma_{j}, \quad (i = x, y, z; j = 1, 2, \ldots, 6)
\]
(8)

where stress tensor \( (\sigma) \) can be related to strain as \( \sigma_{j} = \sum_{k} C_{jk} \epsilon_{j} \), where \( C_{jk} \) is the elastic stiffness constant at a constant electric field. The piezoelectric stress coefficients can be determined via the converse piezoelectric effect, through which mechanical stress is generated in a material arising from an applied electrical field, and measured by optical interferometry on planar structure, or piezoresponse force microscopy (PFM) for a single nanowire.

The group-III-nitride nanowires showed similar properties as compared to the piezoelectric properties of ZnO (out-of-plane piezoelectric stress constant, \( d_{33} = 0.9-9.5 \text{ pm/V} \)), i.e., GaN with \( d_{33} = 12.8 \text{ pm/V} \), AlN with \( d_{33} = 4.0 \text{ pm/V} \), and InN with \( d_{33} = 4.0 \text{ pm/V} \), respectively. A single InN-nanowire nanogenerator was reported to exhibit a large output voltage of up to 1 V, which is more than ten times that of conventional ZnO nanowires. Remarkably, a carefully engineered single axial InGaN/GaN nanowire nanogenerator can produce an average output voltage up to 330±70 mV and a maximum output power 223 pW per nanowire. The demonstrated devices for eventual practical implementation promise an energy conversion for self-powering of nomad, remote, or implanted devices. Although ZnO is the most commonly reported material for piezotronic applications and it is relatively easy to produce, the advantages of InGaN-based nanowires will become apparent if one considers the favorable properties that InGaN-nanowires have relative to ZnO, such as their comparable piezoelectric coefficient, higher electrical conductivity, and tunable bandgap absorption.

B. AFM study on a single nanowire

I. Piezotronic effect

Many techniques can be used to characterize piezoelectric-related performance of a single nanowire. In-situ SEM/TEM can equip with micromanipulators to reveal the electrical response of small mechanical strain simultaneously. PFM is a variant of AFM that is obtained by applying an AC voltage and using a lock-in amplifier to track the converse piezoelectric response (electricity to mechanical energy) from the oscillation of the sample surface in the picometer range. It can be used to measure the piezoelectric stress coefficient, especially \( d_{31} \), of a single nanowire, as mentioned briefly in Section IV.A. However, those studies are more relevant for understanding the converse piezoelectric effects or for extracting the physical parameters of the material, instead of revealing the direct piezotronic effects in semiconductor nanowire structures.

As mentioned in the previous section, the piezotronic effect is constituted by semiconducting properties and piezoelectric effects. It appears in a piezoelectric semiconductor when it contacts another material, either a metal or a heterostructure semiconductor. Due to the semiconductor properties, when piezoelectric polarized charges appear at the contact junction, the internal electrical field, contact energy barrier, and band structure of the semiconductor change. These will affect carrier transportation, generation, and recombination processes. Unlike the broadly defined piezoelectric effect that appears in the bulk dielectric or semiconductor materials, the piezotronic effect discussed here is only an interfacial property of semiconductors. It persists so long as the force is loading on the semiconductor nanowire without obvious decay. Therefore, the c-AFM is of great interest to study the piezotronic effect. A c-AFM uses a conductive cantilever to contact and scan the sample surface to detect the topographical map and the electric current simultaneously. In a c-AFM, the deflection force of the conductive cantilever can reflect the variance in surface height of the sample in the topography map, and it can also be intentionally controlled to apply an external force upon contact. Thus, the metal-semiconductor Schottky-barrier height (SBH) change can be monitored by extracting the localized current in the c-AFM, either directly in a short-circuit AFM setup or by measuring the voltage change across an external loading. Two typical configurations are vertical compression and lateral bending of a nanowire, as shown in Fig. 12(a) and 12(b), respectively.

FIG. 11. Spontaneous polarization and piezoelectric polarization in group-III nitride, using strained AlGaN or InGaN grown on GaN as an example with Ga face (Ga-polar) or N face (N-polar). Copyright from Cambridge University Press, 2006.
FIG. 12. Schematic representation of AFM setup in two configurations using n-type N-polar GaN\textsuperscript{166}. (a) Vertical compression configuration, and (b) lateral bending configuration. The red color and blue color represent tensile strain and compressive strain, respectively. The band diagrams of the nanowire/AFM tip contact at the stretched side (position 1) (c) and compressed side (position 2) (e), respectively. (d) I-V characteristic. Readers should note that the behavior (piezopotential and diode forward/reverse bias quadrant) are opposite to the above for p-type N-polar GaN and n-type Ga-polar GaN\textsuperscript{145,166} Adapted from Appl. Phys. Lett. 90, 179901 (2007), with permission of AIP publishing.

In a vertical compression configuration, the AFM probe tip touches the c-plane nanowire at the top and creates a metal/nanowire Schottky contact. Various tip materials can form different SBHs with the nanowire, and the contact radius can also affect the actual force applied onto the nanowire.\textsuperscript{113} A Pt/Ir-coated AFM tip is preferred over a Pt/In tip or diamond-based tip for a GaN nanowire because of its relatively smaller SBH of \(-0.38\pm0.09\) eV,\textsuperscript{113} which allows effective carrier extraction and ensure observable SBH changes. When the metallic tip applies a constant normal force onto an N-polar n-type nitride nanowire in the c-AFM scanning mode from position 1 to 2 in Fig. 12(a), it simultaneously applies a lateral force component because of the local bending of a slender nanowire.\textsuperscript{167,168} This local bending results in a tensile strain on the initially exposed side of the nanowire and a compressive strain on the other side of the nanowire in the scanning direction. On the stretching surface, the piezoelectric polarization of the n-type N-polar GaN nanowire is parallel to the growth direction, and more positive polarized charges are accumulated at the tip/nanowire interface (see Fig. 12(a)). Thus, the piezoelectric field is antiparallel to the growth condition, and a positive piezopotential (given in red in Fig. 12(a)) is generated. The positive piezopotential lowers the SBH (\(\Delta \phi_B > 0\)) at the heterointerface (see the red dashed line in Fig. 12(c)), which enables the carrier flow from the nanowire to the metal tip. In this case, the Schottky heterojunction can be considered as under forward bias, and the corresponding I-V curve is shown in the first quadrant in Fig. 12(d). On the compressed side, the orientation of the piezoelectric polarization and its induced electrical field are opposite to that on the stretched side. As a result, the corresponding piezopotential is negative (in blue in Fig. 12(a)), which raises the SBH (\(\Delta \phi_B < 0\)) that hinders the carrier flow at the nanowire/tip interface. The I-V characteristic is shown in Fig. 12(d).

Depending on the position of the AFM tip, the I-V curve (Fig. 12(d)) can be extracted from the stretched side (Fig. 12(a), position 1) as a forward-biased metal/nanowire Schottky junction, and from the compressed side (Fig. 12(a), position 2) as a reverse-biased junction.\textsuperscript{145,166} The rectifying characteristic of the current-voltage curve is attributed to the Schottky junction between the nanowire and the metallic tip.

The alternate configuration, i.e., the lateral bending configuration (see, Fig. 12(b)), fixes the nanowire onto a vertical stage with the AFM tip approach the desired position on the nanowire sidewall to assert a lateral force (perpendicular) to the nanowire.\textsuperscript{169} However, this configuration only allows the tip to touch the stretched facet of the nanowire, and one can only measure the forward-biased characteristic of the Schottky junction.

Sometimes the aspect ratio of the nanowires is relatively small, so that when the AFM tip applies the compressive force, the whole tip of the nanowire is axially compressed instead of getting bent.\textsuperscript{42,169} Therefore, only a weak current signal can be detected in the c-AFM scanning mode. In this case, one could first perform a general c-AFM mapping over the nanowires ensemble to locate nanowires with favorable metal/semiconductor contact and showing adequate current conduction. Pinning the AFM tip on one of those chosen locations with a controlled force still allows the SBH to change accordingly because of the piezotronic effect. With an applied bias, the current-voltage characteristics can also be measured, which still render the rectifying characteristics.\textsuperscript{155,169} Regarding the nonuniformity of the morphology and physical properties of nanowire over the wafer, it is essential to conduct statistical measurements over the whole wafer on various nanowires to establish the representative dispersion (scattering) of the piezotronic results obtained.\textsuperscript{115,146,168}

After obtaining the I-V characteristics, it is essential to calculate the change in SBH to verify and evaluate its potential for piezotronics applications. Many models have been established to fit the current-voltage characteristics. For lightly-doped nanowires, the Schottky junction performance can be described by a thermionic-emission-diffusion model since the tunneling effect is negligible.\textsuperscript{170} Assuming that the SBH is larger than the thermal energy \(k_B T\), the I-V characteristics can be given by:

\[
I = A A^* T^2 \exp \left(-\frac{\varphi_B - \varphi_T}{k_B T}\right)
\]

where \(A\) is the area of the Schottky barrier, \(T\) is the temperature, \(\varphi_B\) is the SBH, \(k_B\) is the Boltzmann constant. \(A^*\) is the effective Richardson constant, which can be expressed as equation 10, where \(q\) is the unit charge, \(h\) is the Planck’s constant, \(m^*\) is the effective electron mass of the material. \(\varphi_T\) is the image correction force, and \(N, V, V_a,\) and \(\epsilon\) are the ionized carrier concentration, applied voltage, built-in potential, and dielectric constant, respectively.

\[
A^* = \frac{4 \pi q \hbar m^*}{h^2}
\]
\[ \phi_f = \sqrt{\frac{q}{4\pi\epsilon}} \cdot \sqrt{\frac{2q^2 h}{e} \left( V + V_{bi} - k_B T \right)} \]  

(11)

For heavily-doped nanowires, current may increase dramatically after a threshold voltage related to the excess tunneling currents through the Schottky barrier. The total current density thus involves both thermionic emission and tunneling current. Equation 9 can be modified into equation 12, where \( n \) is the ideality factor.

\[ I = A A^* T^2 \exp \left( -\frac{(\phi_f - \phi_0)}{k_B T} \right) \exp \left( \frac{qV}{n k_B T} \right) - 1 \]  

(12)

When the deflection force of the AFM tip increases, the current of a given bias decreases significantly, either for forward bias or reverse bias. From the I-V characteristics, given the currents \( (I_F, I_{Fo}) \) and the corresponding SBH \( (\phi_{Bi}, \phi_{Bo}) \) at two different applied forces, the change in SBH usually can be calculated as:

\[ \ln \left( \frac{I_F}{I_{Fo}} \right) \approx -\frac{\phi_{Bi} - \phi_{Bo}}{k_B T} \]  

(13)

It is noteworthy that the mathematical model can be further modified according to the specific experimental set-up. A back-to-back dual Schottky junction model can be used to describe the nanowire-AFM set up by considering the Schottky junctions at the bottom contact of the nanowire and at the nanowire/tip interface. A full quantitative fitting for the back-to-back Schottky barriers for nanowire structures can be found in the literature, which includes the shunt and series resistance. Another model raises the concern that the nanoscale contact radius between the AFM tip and nanowire may result in a Schottky diode size smaller than the depletion width. The effective SBH becomes a function of the diode size, and the tunneling current contributes to the conductance.

The first AFM study on piezotronic effects of group-III-nitride nanowires was conducted by Su et al. in 2007 using GaN nanorods. Since then, other binary group-III-nitride nanostructures have been studied, such as InN, AlN, GaN nanocones, and InN nanowires. Obviously, the corresponding ternary group-III-nitride nanowires will also demonstrate piezotronic effects. Similar experiments were conducted on MBE-grown InGaN/GaN nanowires on Si substrate, MBE-grown InGaN nanowires on a Ti/TaN/Si substrate, and MBE-grown AlGaN nanowires on a Ti/Mo substrate. It is essential to understand the I-V characteristics to develop piezotronic devices for self-powered nano-energy generation, taking advantage of converting mechanical energy to electrical energy.

2. Piezo-phototronic effects

Piezo-phototronics can be introduced by coupling piezoelectric polarization and semiconductor properties with photoexcitation properties, such that charge-carriers behaviors of materials are modulated by the wavelength and intensity of the light as well as by the applied mechanical strain. Although ZnO is mostly used due to the simplicity of solution process, the material suffers from oxygen-vacancy-related defects that affect the quality of the Schottky contact with metals and limited absorption of the solar spectrum in the visible-wavelength range. Group-III-nitride materials offer compositional tunability and broad absorption throughout the ultraviolet to the visible light spectrum. Thus, group-III-nitrides are more promising for piezo-phototronics in terms of broad-band light absorption.


For piezo-phototronics, both light illumination and mechanical stress are stimuli for the piezoelectrical field. The piezophototronic effect of group-III-nitride nanowires has been identified for MBE-grown n-type InGaN nanowires in an AFM study. As shown in Fig. 13(a), the c-AFM tip applies constant compressive force at a fixed deflection set point on the tip of the nanowire and measures the I-V characteristic. Based on a standard c-AFM setup, a 405-nm laser source is installed inside the c-AFM chamber to illuminate the sample at the point of interest for piezo-phototronic effect study. The InGaN nanowires are grown on a Ti/TaN-coated substrate, where the back contact between the Ti and semiconductor is a Schottky contact at the interface while another Schottky contact is formed between the InGaN nanowire with the Pt/Ir AFM tip. Here, the change in SBH in response to light and/or strain is the difference between the two SBH where the SBH of the nanowire/AFM tip contact dominates.

The I-V curve is first obtained without deflection force. The initial SBH is shown in Fig. 13(b) as the color band diagram. With only light illumination on the nanowire and without any applied force, electrons in the valence band gain sufficient energy to transit to the conduction band and generate electron-hole pairs. Due to the nature
of the initial Schottky contact between the nanowire and the tip, an upward band bending forms at the nanowire/AFM tip interface leading to holes accumulation. This will lower the SBH and the carriers get extracted from the AFM tip leading to a higher current flow as compared to the dark condition, under the same bias conditions (see Fig. 13(c)). This is primarily the light response of an InGaN nanowire, which is the fundamental mechanism of a photodiode.

When applying an external compressive strain onto the n-type N-polar nanowire but without illumination, the SBH will be increased (as shown in Fig. 13(b) with a short dashed line). The corresponding I-V characteristic will be suppressed because of the piezotronic effect, as discussed in the previous section. However, when further coupling UV illumination with the applied force, the nanowire absorbs the illuminated light, and thus resulting in photogenerated electron-hole pairs that screen the piezoelectric field and reducing the strain-induced SBH (see the long dashed line in Fig. 13(b)). This study proved that external stress could affect the carrier transportation of InGaN nanowire in dark conditions or under illumination, i.e., piezo-phototronic effect. In particular, when the tip force exceeds 6 nN in this study, the I-V characteristics in the dark and with illumination overlap with each other, indicating elimination of photoresponse, as shown in Fig. 13(c). Hence, the external force can be utilized as a switch for a photodiode, such as a solar cell or photodetector.

Although the c-AFM study only reveals the existence of piezophototronic effects of n-type N-polar InGaN nanowire, one could potentially investigate the piezo-phototronic effects of n-type metal-polar or p-type N-polar group-III-nitride nanowires. The compressive force applied onto these nanowires may reduce the SBH and assist in carrier transportation. Thus, they could be used to enhance the performance of many optoelectronic devices, such as photodetectors or solar cells.

C. Piezotronic and piezo-phototronic applications

1. Piezotronic applications: piezoelectric nanogenerator

The c-AFM studies confirm that the piezopotential in a group-III-nitride nanowire can control or modulate the carrier flow, and therefore is suitable for use in piezoelectric nanogenerators (PENGs). Single-nanowire-based PENGs are usually demonstrated by an AFM setup. Several factors may affect the piezoresponse of a single-nanowire PENG, such as doping, dimensions, and crystallographic orientation of the nanowire.

Doping can effectively increase the free carrier concentrations and the screening effect on the piezoelectric potential. However, if the carrier concentration is too high, the SBH change might be significantly suppressed, which may deteriorate the performance of a piezotronic device. Thus, the doping level should be optimized to achieve a compromise between these two effects. Wang et al. investigated the effects of carrier concentrations of nanowires on its piezotronic potential and fabricated a nanowires-ensemble-based device with optimized doping levels.174,175

As some literature indicated, dimensions strongly influence the piezoelectric coefficient of ZnO nanowires.176-178 Similar effects can be expected for Wurtzite group-III-nitride nanowires. However, it is difficult to directly measure and conduct a systematic comparison of piezoelectric properties between individual nanowires. Several simulations have suggested a strong small-scale effect on the physical properties of nanowires in the range of nanometers owing to the large surface-to-volume ratio and surface effect, which include elastic properties (Young’s modulus), dielectric coefficient, and piezoelectric coefficient.179-181 Since the surface atoms have fewer bonding neighbors compared to the bulk counterpart, the nonpolar sidewalls of the nanowires undergo surface reconstruction that can be characterized by bond length contractions. The elastic properties can be sensitive to this interatomic distance change which results in a change in surface stiffness in nanowire structures. In addition, the surface effect affects the piezoelectric properties of nanowire structure, which is attributed to the atomic polarization of surface atoms.179,180 A first-principle work concludes that the piezoelectric coefficients increased by around two orders of magnitude if the GaN nanowire diameter shrinks to less than 2.5 nm.180 With reference to the surface effect, Jiang et al. developed a core-shell model for DFT and molecular dynamics simulation of various piezo-related properties. The results show that hexagonal GaN nanowires with a diameter smaller than 70.5 nm can exhibit a much larger piezopotential than bulk materials.180

Apart from doping and the dimensions, nanowires grown along different crystalline orientations demonstrate different sensitivities to the applied force in terms of the force direction and intensity. Finite element analyses can be used to simulate the piezoresponse of GaN nanowires grown on different planes.149 As mentioned in Section IV.A, the piezoelectric coefficients, either the piezoelectric strain coefficient or the piezoelectric stress coefficient, are tensors with the largest values for the corresponding in-plane component (ε13 or d13).149 The output voltage of a single c-plane nanowire mainly originates from the in-plane piezoelectric coefficients. By contrast, those of a-plane and m-plane nanowires depend greatly on the shear piezoelectric coefficient. Comparing the piezoresponse of nanowires under normal force and transversal (lateral) force by experiment, Wang’s group discovered that the piezopotential-controlled SBHs of m-plane InN nanowires are more sensitive to a transversal force acting on nanowires than a normal force.168 A similar phenomenon can be observed on m-plane GaN nanowires by fixing the nanowires on a vertical stage (lateral bending configuration), which was found to have a ~254 meV SBH change at 1.3 μN lateral force but with a negligible response to a normal force.166 To make full use of the anisotropic piezotronic response of different facets of group-III-nitride nanowires, a PENG device was fabricated using InGaN nanowires grown on pyramid-textured Si substrate.182 Nanowires-ensemble-based PENGs have also been demonstrated.174,183,184 Fig. 14 demonstrates three typical configurations for group-III-nitride nanowires-ensemble-based PENG structures. One configuration (see Fig. 14(a)) can be implemented by embedding the vertically grown nanowires on Si substrate in a spin-on hydrogen silsesquioxane (HSQ) photore sist matrix. The force cycles are applied from the backside of the Si
substrate at different frequencies (1-6 Hz) with extra care, avoiding any cracks or cleavages to the substrate. This GaN-nanowires-based device can generate a maximum output power density of 12.7 mW/cm². The only caveat for this configuration is that the control of the applied force is difficult, as one would avoid producing interfacial defects at the back contact, which may lead to reverse leakage current at the bottom Schottky barrier, i.e., nanowire/substrate interface. This issue can be mitigated by having a PENG constructed with a metal/insulating polymer – nanowire/metal structure. Usually, the nanowires ensemble is embedded in a polymer matrix such as polydimethylsiloxane (PDMS) or polymethyl methacrylate (PMMA), and then exfoliated from the original rigid substrate before it is sandwiched in two metal contacts (Fig. 14(b) and (c)).

The above flexible polymer matrix allows the nanowires ensemble to be gently deformed by compression, stretching, or bending, while the metal/insulating polymer (dielectric)/nanowire contact forms a capacitive coupling between the top and bottom metal layers. Through cyclic applied force, the piezoelectric polarization charges accumulate at the two polar faces of the nanowire. Due to the surface band bending and Fermi-level pinning at the nanowire/dielectric interface, carriers tend to separate and accumulate at that interface instead of being distributed inside the nanowire. Thus, the dielectric layer suppresses the free carriers screening effects inside the nanowire and enhances the PENG piezoresponse. In this case, the nanowires ensemble can be embedded either vertically (see Fig. 14(b) or laterally (see Fig. 14(c)) in the polymer matrix, depending on the growth orientation of the nanowires and its applications.

![FIG. 14. Schematics of: (a) Group-III-nitride nanowires-ensemble-based PENG on rigid Si substrate. (b) Vertically-aligned nanowires-ensemble-based flexible PENG for nanowires grown along the c-axis. (c) Laterally-aligned nanowires-ensemble-based flexible PENG for nanowires grown perpendicular to the c-axis. Examples are from the references indicated.]

2. Piezo-phototronic applications: piezoelectric-assisted optoelectronic devices.

The previously mentioned AFM study in section IV.B.2 reveals the piezotronic/piezo-phototronic effect on the relative change in SBH in a metal/semiconductor/metal structure. However, the piezoelectric/piezo-phototronic effect can also occur at the semiconductor heterojunction interface. Supposing that the nanowire is an axial p-n piezo-junction, when an external strain is applied to the structure, the piezoelectric charges can expand the depletion region of the p-n junction, and thus making it possible to tune/control the carrier separation, transportation, and recombination. A strain sensor was used to demonstrate this idea based on axial p-GaN/InGaN/n-GaN microwire arrays. A similar concept was applied to a p-n junction between the nanowire and planar structure. In the work, a flexible piezo-assisted light-emitting diode (LED) uses an MOCVD-grown a-axis GaN microwire on a p-GaN thin film. When applying a compressive strain normal to the p-n junction interface, the piezoelectric field increases in the p-GaN film and reduces the barrier height of the junction, thus promoting the hole-injection efficiency. Besides, an electron-potential dip forms and confines electrons in the depletion region, thus greatly enhancing the radiative recombination rates. With a -0.12% compressive strain, the efficiency droop can be reduced from 46.6% (without external force) to 7.5%.

Apart from light-emitting devices, this effect is also essential for further enhancing the photoresponse of other nanowires optoelectronics, like photodetectors and solar cells. With an illumination of energy larger than the semiconductor bandgap, the photogenerated carrier in a nanowire p-n (piezo) junction can also be affected by the existing built-in electrical field. By coupling the piezotronic effect, strain-induced piezopotential can tune or control the built-in electrical field and influence the separation and transportation of the photocarriers, and hence enhance photoresponse. Thus, the piezo-phototronic effect can be utilized to tune the PL intensity of light emission from group-III nitride multiple quantum wells nanowires array and forms a dynamic optical pressure imaging device.

One promising energy-related application can be piezo-assisted solar cells. Based on the piezo-phototronic effects of a p-n junction nanowire, a simulation based on a ZnO nanowire envisioned the possibility of using it as a piezo-assisted solar cell. However, the wide bandgap of ZnO limited its light absorption capability to only the UV region. Because InGaN material can benefit from visible light absorption, it is expected to demonstrate even better performance as a piezo-assisted solar cell. Although not many nanowire-based piezo-assisted solar cells have been described in the literature, the potential of the idea has been confirmed by using flexible devices based on planar (In,Ga)N structures.

Piezo-assisted photodetector is another example. For instance, a MoS₂-GaN nanowire-based piezo-enhanced photodetector has been reported. The unique band alignment between a GaN nanowire and MoS₂ forms a p-n-junction-like contact. When the lateral GaN nanowire is used as the top-gate of the flexible device, the piezopotential induced by external force can significantly enhance the photoresponsivity to 734.5 A/W, which is more than 50% higher than the photoresponsivity of the same devices grown on a rigid substrate. The tunable direct bandgap of InGaN benefits its broadband absorption, especially in the visible light spectrum. It thus has an advantage over ZnO or GaN nanowires, in which the associated wide-bandgap limits light absorption in the UV region. This demonstrates the advantage of InGaN-based devices for converting ultraviolet/visible light to electrical energy, in the form of photodetectors and solar cells. One might envisage that the piezo-phototronic effect in these InGaN-based devices can improve the photoresponse, thus facilitating effective mechanical-to-electrical energy conversion, especially the piezo-assisted solar cell. Other
future applications can include piezo-assisted photodetectors, light-emitting devices, or even pressure imaging.\textsuperscript{189}

V. Solar-to-hydrogen energy applications

Since Fujishima and Honda first proposed the idea of PEC hydrogen production using TiO\textsubscript{2} photoelectrodes,\textsuperscript{196} the field has attracted considerable interest in the hopes of improving solar-to-hydrogen (STH) energy generation. Conventional electrolysis requires a large bias to drive the redox reaction (> 1.23 V at the equilibrium potential). Photocatalysis demands efficient catalysts to overcome the large redox potential and overpotential in reactions. The PEC process combines the advantages of the two approaches using semiconductor materials with the aid of a small bias or self-powered pathway for sustained solar hydrogen generation. Various semiconductor materials have been studied for this specific application, including silicon (Si), transition-metal oxides (TiO\textsubscript{2},\textsuperscript{196} ZnO,\textsuperscript{197} hematite,\textsuperscript{198} and so forth), nitrides, and other materials (BiVO\textsubscript{4}, and CdS). In particular, group-III nitrides, especially (In,Ga)N material, are a major and possible branch for eventual sustainable hydrogen energy generation. This field has emerged in 2005 since Fujii \textit{et al.} first quantified hydrogen gas generation from a GaN thin-film-based photoelectrode,\textsuperscript{199} and then it has gained an application boost in nanostructured-InGaN PEC devices, particularly in nanowires structures.\textsuperscript{200} This section covers the fundamental working principle and reaction kinetics of the PEC hydrogen production, which is relevant to InGaN-based nanowires. Further, we provide a brief outlook on the performance and the opportunities in efficiency enhancement.

A. Working mechanism and efficiency definition of photoelectrochemical water splitting

The working setup of PEC water splitting experiments is shown in Fig. 15(a). In general, laboratory evaluation prefers a three-electrode system for accurate measurements. In such system, the working electrode (WE) is usually the photoelectrodes (\textit{p}-type or \textit{n}-type), and the counter electrode (CE) is usually a conductive electrode (glassy carbon, graphite or metal electrodes, such as Pt mesh/rod). The reference electrode (RE) is utilized as a known standard to confirm the absolute potential of the WE and CE. In general, a three-electrode configuration has numerous advantages over the two-electrode configuration in terms of studying the specific properties of photoelectrodes. In addition, separating the two half-cells with an ion-exchange membrane makes it possible to perform half-cell measurements for analyzing the standalone photoanode or photocathode. All three electrodes are kept immersed within the
electrolyte for the effective transfer of charge carriers. Usually, a quartz cell is preferred for PEC analyses due to its high transparency, which can prevent photon loss. Further, a mercury-based light source is used in conjunction with an Air-Mass 1.5 Global (AM 1.5G) filter to ensure the light source approximates the chosen standard solar spectrum. In general, 1 Sun AM 1.5G illumination (100 mW/cm²) is used as a standard for the PEC measurements, although multiple-Sun illumination is also reported in the existing literature.

When preparing a nanowire wafer as a WE specimen, only the active area (the nanowires) should be exposed to the illumination. Other than the active area of the photoelectrode, the remaining area (exposed substrate and the metallic contact areas) should be isolated with chemical-resistant epoxy resin to prevent any undesired current leakage. During PEC measurements, the photoelectrode should be fully immersed in the electrolyte and fully illuminated by incident light. Only the physical area exposed to the electrolyte (the active area) and illumination is considered as the surface area for subsequent analysis.

A potentiostat/source meter is used to establish a three-electrode system for electrochemical analyses and investigations of gas evolution. Once the PEC reaction occurs, the hydrogen and oxygen are evolved from the electrode surfaces, and they can be analyzed and quantified with gas chromatography (GC). A syringe or autosampler is utilized to sample and inject the generated gas into the GC through a septum. In general, GC uses a carrier gas to transport the injected sampling gas toward the analytical column. The analytical column is located in a column oven which is heated during the analyses to vaporize the sample mixture and elute the volatile components. The analytic columns are coated with certain stationary phases (porous solid) so that the mobile phases of the sampled gas mixture can be separated depending on their reactions with the stationary phases. Following that, the separated gas from the column will be detected by a detector and be recorded as a chromatogram. The detailed working principle and gas analyses can found in existing literature.201

The whole PEC process that happens in the reactor is mainly divided into the following three steps: (1) light absorption, (2) carrier migration, and (3) chemical reaction. The detailed PEC process of an n-type semiconductor and a p-type semiconductor are shown in Fig. 15(b) and (c), respectively.

(1) Light absorption: For a semiconductor, when the energy of the illuminated photon (yellow curly arrow) is larger than the bandgap of a material, i.e., ħν > Eg, light gets absorbed and electrons (black circles) get excited to the conduction band (Ec) leaving behind holes (hollow circles) in the valence band (Ev), following the orange arrow in Fig. 15(b) and (c). The generation of the electron-hole pair leads to quasi-Fermi level splitting (Ev,Ec), and a photovoltage is generated, which is the difference between Ev and Ec.

(2) Carrier migration: As a result of the inherent band-bending, the photogenerated minority carriers accumulate at the semiconductor/electrolyte interface. Simultaneously, the photogenerated majority carriers flow to the counter electrode through the back contact and the external circuits. The green arrows in Fig. 15(b) and (c) shows the directions of carriers flow. The n-type (p-type) material’s majority carriers are electrons (holes) and the corresponding minority carriers are holes (electrons).

(3) Chemical reaction: Reactions occur when photovoltage straddles the water-splitting redox potential. The water splitting redox reactions can be considered as two half-reactions: water oxidation reaction (oxygen evolution reaction, OER) and hydrogen evolution reaction (HER), as given in equations 14 and 15, respectively. The standard potential of the half-reaction is relative to a reversible hydrogen electrode (RHE) at pH 0.

For an n-type photoelectrode (semiconductor photoanode), the holes (h⁺) accumulate at the surface and combine with the water molecules to generate oxygen and protons (H⁺) (equation 14), and these protons get transferred to CE through the conductive ionic liquid and then combine with electrons (e⁻) to form hydrogen as shown in Fig. 15(b) and equation 15. Fig. 15(c) shows the HER reaction occur on a p-type photoelectrode (semiconductor photocathode) system.

\[ \text{OER: } 2H_2O + 4h^+ \rightarrow O_2 + 4H^+; \quad E_{\text{RHE}}^{\text{OER}/0} = 1.23 \text{ V vs. RHE} \] (14)

\[ \text{HER: } 4H^+ + 4e^- \rightarrow 2H_2; \quad E_{\text{RHE}}^{\text{HER}/0} = 0 \text{ V vs. RHE} \] (15)

Numerous factors may affect the PEC performance of semiconductor-based photoelectrodes, such as photogenerated electron-proton recombination, interfacial defects and traps, and improper band positions for the oxidation/reduction process. In the literature published in the early years, there are several commonly used efficiencies terminologies for evaluating the performance of the photoelectrode cell at each step.

The incident photon-to-current efficiency (IPCE) represents the photocurrent generated per incident photon flux that corresponds to a particular wavelength. The IPCE can determine carrier loss in the solid-electrolyte interface and semiconductor/contact interface, and evaluate the effectiveness of the photoexcitation process. During experimentation, a calibrated monochromatic light source should be used as the illumination at a particular wavelength for chronocoulometry (photocurrents measurements over a period of time). The calculation of IPCE follows the below form.

\[ \text{IPCE} = \frac{j_{\text{ph}} \times \lambda}{P_{\text{mono}} \times \lambda} \] (16)

where jph is the photocurrent density (mA/cm²), Pmono and λ are the illumination power and wavelength of the monochromatic light, respectively, and h and c represent the Planck’s constant (4.1357 × 10⁻¹⁸ eV/s) and the speed of light (3×10⁸ m/s), respectively.

Another essential concept here is the applied bias photon-to-current efficiency (ABPE). ABPE is often used in a biased PEC system, in which a broad-band solar illumination (AM 1.5G) and external bias (< 1.23 V) can both serves as the input. ABPE can be calculated by equation 17, where jph, V applied, ηf, and P light stands for the photocurrent density (mA/cm²), applied bias (V vs. RHE), Faradaic efficiency and light power density (mW/cm²), respectively. The thermodynamic water-splitting potential (ΔE°) is 1.23 V at the
equilibrium condition. It is essential to note that the applied bias ($V_{\text{applied}}$) in the equation should be the potential difference between the WE and CE, instead of the potential relative to the RE. The measurement of ABPE should correspond to a complete water-splitting reaction (both HER and OER) occurring at both WE and CE.\textsuperscript{202} Also, to avoid the influence of additional chemical bias, WE and CE should be placed within the electrolytes at the same pH value, without any sacrificial donor or acceptor. The Faradaic efficiency ($\eta_F$) can be experimentally calculated using equation 18, which reveals the number of photogenerated charge carriers converted into H$_2$ through an electrochemical reaction.

\[
ABPE = \frac{\int_{t_0}^{t} |V_{\text{applied}}| - |V_{\text{bias}}| \times n_{\text{light}}}{P_{\text{light}}} \times 100\% \tag{17}
\]

\[
\eta_F = \frac{n_{\text{H}_2} \times n_{\text{F}}}{A \times [\text{H}_2]_{\text{ion}} \times dt} \times 100\% \tag{18}
\]

where $n$ is the number of moles of H$_2$ evolution measured by GC, $z$ is the number of electrons participated in HER ($z=2$), $F$ is the Faraday constant ($F=96485$ C/mol), $A$ is the effectively exposed area of the photoelectrode (cm$^2$), and $t$ is time. In some publications, the H$_2$ evolution is not experimentally quantified by GC but theoretically estimated from the measured photocurrent density with equation 18 by assuming a $\eta_F$ value.\textsuperscript{199,203}

The ultimate goal of a PEC system is to realize non-biased or zero-biased water splitting that is only driven by solar energy. In order to establish an accurate standard for evaluating the overall PEC water splitting process, particularly for an ideal zero-biased system, the STH efficiency is considered to be the benchmarking efficiency, where $R_{H_2}$ and $J_{SC}$ are the hydrogen generation rate (mmol/s) and short-circuit current density (mA/cm$^2$), respectively. The Gibbs free energy ($\Delta G_{\text{H}_2}^0$) for every mole of hydrogen is 237 kJ/mol at 25 °C.

\[
STH = \frac{R_{H_2} \times \Delta G_{\text{H}_2}^0}{P_{\text{light}} \times \lambda \times \eta_F} = \frac{|J_{\text{SC}}| \times \Delta \phi \times \eta_F}{P_{\text{light}}} \tag{19}
\]

It is worth emphasizing that the STH calculation is only valid for experiments that are conducted with broad-band solar irradiance (AM 1.5G, 1 Sun), under zero-biased or non-biased conditions, and keeping the WE and CE in the electrolyte without any sacrificial carriers. Theoretically, InGaN can achieve maximum STH efficiency of 27% for indium compositions up to 50%, but it is not easy to achieve the maximum value for many reasons.\textsuperscript{204}

### B. Enhancing efficiencies

Various methods can be applied to semiconductor photoelectrodes to enhance the system efficiencies at each step of the PEC process, as shown in Fig. 16.

**FIG. 16.** Methods of enhancing the PEC performance.

1. **Improving light absorption**

The effective absorption of the photons plays a significant role in improving renewable H$_2$ generation. Light absorption can be accomplished by selecting proper band edge positions, improving the effective exposed area to the solar light, and enhancing the visible region absorption by modifying bandgap and increasing ionized carrier concentrations. As mentioned in the previous section, InGaN materials can absorb a wider range of the solar spectrum from UV, through visible light, and potentially, to the near-infrared spectrum (see Fig. 17(a)) due to its tunable bandgap (see Fig. 17(b)). The visible light absorption is particularly important since it constitute the main portion of the solar energy. The band edge position of the material could be carefully selected by tuning the indium composition so that it can straddle the water splitting redox potential (1.23 V) and drive the reaction, as shown in Fig. 17(c). The exact conduction band minimum and valence band maximum may vary, depending on the doping type, doping concentrations, and strain in the structure. The actual band structure of the material can be investigated with PL and XPS, as mentioned in Section III. Generally, the indium composition in InGaN should be as high as possible while keeping the band edge positions straddling the water splitting redox potential. However, it should not exceed ~50%, theoretically, to ensure effective visible light absorption while having sufficient energy to overcome the kinetic barrier (overpotential) for triggering the reaction.\textsuperscript{205} The overpotential refers to the energy difference between the quasi-Fermi levels of the minority carriers to the redox Fermi level of the electrolyte. Another investigation improves the visible solar spectrum absorption in InGaN nanostructures by utilizing a multi-bandgap segmented nanostructure. Such variation in indium composition throughout the InGaN nanowires increases the degree of freedom in tuning the bandgap absorption in the visible region.\textsuperscript{21}

In addition, compared to the planar structure, the nanowire/nanorod structures significantly increase the surface-to-volume ratio and provide more reactive sites for chemical reactions. Besides, vertically-aligned nanowires ensemble is capable of enhancing the light absorption efficiency since light may scatter in the nanowires ensemble or among adjacent wires through multiple scattering by the substrate or electrolyte.\textsuperscript{206} Also, growing nanowires-ensemble on a textured substrate can further enhance light trapping. This has been identified in a study based on growing InGaN nanowires on a pyramid-textured Si substrate.\textsuperscript{207} These facts make InGaN nanowires ensemble a highly efficient and promising light absorption medium for solar-to-hydrogen generation applications.
**Enhancing carrier separation and migration**

Besides improving solar absorption and carrier generation, it is also critical to reduce carrier loss in the separation and migration process. The loss of photogenerated carriers can generally be attributed to rapid recombination. At the photoelectrode/electrolyte interface, a high density of surface states can trap the generated carriers, as shown in Fig. 18(a). These surface states cause Fermi level pinning at the interface, which means the degree of band bending in the semiconductor is fixed regardless of the change in applied bias.\(^{215}\) This phenomenon violates the requirement on effective carrier separation in the semiconductor. Instead, the applied bias gives rise to a non-negligible potential drop within the electrolyte in the vicinity of the semiconductor/electrolyte interface, i.e. the Helmholtz layer, and creates an energy barrier for carrier transport between the photoelectrode and electrolyte, which even deteriorates the reaction kinetics.\(^{216,217}\) Further, photocorrosion is another crucial factor limiting the PEC-based renewable energy systems for real-time applications. In this regard, a protection layer is needed to safeguard the host photoelectrode from harsh electrolyte conditions.

The surface protection material is needed to be highly conductive and transparent in order to conduct the photogenerated charge-carriers without compromise solar absorption. The commonly used protection materials are TiO\(_2\), Al\(_2\)O\(_3\), and NiO. Currently, two-dimensional (2D) materials are used as co-catalysts for PEC water splitting. 2D transition metal dichalcogenides hold the prerequisites for a better co-catalyst which provides the active sites for significant charge transport from the host to the electrolyte. The 2D materials also protect the solar absorption photoelectrodes from harsh electrolyte conditions.\(^{218}\)

Specifically, InGaN photoanodes suffer from surface oxidation during the reactions, which becomes unstable in an acidic electrolyte environment. Effective surface passivation can suppress surface states, assist in charge separation and transfer, and prolong the stability of the photoelectrodes (Fig. 18(b)), as shown by the 4D scanning ultrastand electron microscopy study in Section III.E.\(^{135,217}\) Common passivation methods include depositing an ultra-thin surface oxide layer and treating the surface with organic chemicals. Neuderth et al. deposited a 5 nm-thick TiO\(_2\) layer onto InGaN/GaN nanowires photoanode by atomic layer deposition (ALD), and achieved an enhanced photocurrent by a factor of 2.5.\(^{20}\) Varadhan and Ebaid et al. introduce EDT as a bifunctional surface treatment to protect the surface states while linking metallic co-catalysts with potent organic ligands.\(^{67}\) This effective passivation substantially eliminates surface states and prolongs the GaN photocathode stability up to 50 hours and beyond.\(^{67,219}\)

In addition, carrier loss can also occur at the interface between the nanowires and conventional substrates such as Si as mentioned previously, due to the formation of an ultra-thin Si\(_2\)N\(_2\) layer in an MBE growth environment, which acts as an interfacial trap that hinders the photogenerated majority carrier transport toward the CEs through the Si substrate, as shown in Fig. 18(a). Hence, the growth of group-III-nitride nanowires on various conductive substrates has been demonstrated to eliminate the Si\(_2\)N\(_2\) layer and to promote carrier transportation (see Fig. 18(b)).\(^{5,6}\) The nanowires were grown on polycrystalline-Ti-coated molybdenum substrates,\(^{219}\) and the
InGaN-nanowire-photoanode can achieve a maximum ABPE of 1.9%. The photocurrent density of the InGaN-nanowire-ensemble/Mo substrates improved from ~2 mA/cm² to ~8 mA/cm² at a bias of 1 V vs. RHE with EDT-Ir treatment. The interfacial impedance was significantly suppressed by a conductive titanium nitride layer, as confirmed with EIS. Scaling up the technique, a Ti/TaN-coated Si substrate was developed to substitute the Ti/Mo substrate. The maximum ABPE of the nanowires on the Ti/TaN/Si substrate reaches 2.2% at ~0.6 V vs. RHE, which is 12 times higher than that of nanowire/Si substrates. Following the idea, a flexible membrane photocathode was fabricated by transferring InGaN nanowires onto a gold-coated polymer substrate, which helps in efficiently extracting carriers at the ohmic InGaN/Au contact interface. The free-standing, flexible membrane showed a 10-fold increase in the generated photocurrent and a 0.8 V cathodic shift in onset potential.

This tutorial only explains the working mechanism of co-catalysts in general and enumerates commonly used co-catalysts for group-III-nitride nanowires photoelectrodes. A deeper understanding of the working mechanism of the co-catalysts can be found in the literature. HER is a relatively simple two-electron transfer reaction with only one intermediate H*. The selection of the co-catalysts for HER entails a compromise between hydrogen adsorption and desorption step so that the catalyst can activate and attain the intermediate reactions while releasing the hydrogen product. A classical volcano plot that depicts the exchange current densities with hydrogen adsorption Gibbs energy is shown in Fig. 19(b). In the plot, the exchange current density reflects the HER rates at the equilibrium potential. The peak of the curve is located near to that of platinum (Pt), where the hydrogen adsorption Gibbs energy is close to neutral zero and achieves the maximum HER rate. Pt is the best HER co-catalyst because of its negligible overpotential in acidic electrolytes for HER. Other important alternative co-catalysts for HER can be Ru/Cr2O3, Ir, among others.

In contrast, OER is a more complicated process compared to HER. OER is a four-electron transfer reaction, which involves a multistep reaction, proton-coupled electron transfer and generates various intermediates, including HO*, O*, and HOO*. The formation and stabilization of the surface-confined intermediates are critical in OER. The binding energies of these intermediates correlate by scaling relations so that if one reaction energy changes, the others change as well. This makes it difficult to decouple these intermediates. For oxides catalysts, the scaling relation between the adsorption energies of HO* and HOO* are almost constant, reported at ~3.2 eV or ~2.44 eV on oxide surface regardless of the binding site, and they always result in a non-negligible overpotential of at least ~0.4-0.2 V. Thus, the variation in OER overpotential (ηOER) on the oxide surface is mainly introduced by the adsorption energy of O*. The volcano plot in Fig. 19(c) lists metal oxides for OER catalysis, showing ηOER on a metal oxide surface vs. the free energy cost from HO* to O* intermediates, taking into account the scaling relation of HOO* and HO* level. An effective OER catalyst is expected to reduce the ηOER. For group-III-nitride photoanode, many oxide-based co-catalysts have been used for OER, including, IrO2, RuO2, NiO, Co3O4, and so forth.
Experimentally, the performance of different co-catalysts can be evaluated by checking the onset potential of the photocurrent curve and compare the overpotential at a certain photocurrent (e.g. 10 mA/cm²). It is worth noting that in different pH environments, the intermediates can be different. Thus, the selection of the co-catalysts for HER and OER reactions varies in electrolytes of different pH values.

Owing to their broadband absorption and appropriate band edge position, InGaN nanowires have been widely applied in PEC water splitting devices to convert solar energy toward clean hydrogen fuels. To further enhance the conversion efficiency, the nanowires can be optimized with improved band alignment design, interfacial impedance optimization, and surface modifications. It is worth noting that InGaN nanowire-based PEC devices are not confined to driving the water-splitting reaction. They can be further expanded to drive other reactions, including but not limited to carbon dioxide reduction and nitrogen fixation.

FIG. 19. (a) Co-catalyst-assisted PEC process. (b) Volcano plot of catalysts for HER (exchange current density of HER vs. hydrogen adsorption energy). Adapted with permission from Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 39(1), 163-184 (1972). Copyright 1972 Elsevier. (c) Volcano plot of catalysts for OER (overpotential of OER on metal oxide surface vs. the free energy difference between HO* and O* intermediates energy level). Adapted with permission from ChemCatChem 3.7, 1159-1165 (2011). Copyright 2011 Wiley.
VI. Prospects and summary

A. Materials growth on alternate substrates

The (In)GaN nanowires ensemble can be grown on a variety of substrate platforms while retaining single-crystallinity semiconductor properties. Along with their unique aspect ratio and surface-to-volume ratio, it can enable a plethora of energy harvesting and conversion applications. Beyond the rigid single-crystal bulk substrates, the unique design of substrate-platforms that satisfy electrical conductivity and visible light transparency have attracted many energy conversion and harvesting applications. For instance, 2D materials and transparent conducting oxide (TCO) can be suitable platforms for group-III-nitride nanowires. 2D materials could provide the preferred orientations for epitaxial growth, and their epi-structures can be exfoliated into a thin membrane for flexible device applications with favorable charge transport characteristics. Also, the low growth temperature process of PA-MBE can effectively incorporate high indium content InGaN nanowire-heterostructures without temperature-induced degradation of TCO stoichiometry.

B. Piezo-phototronic devices and hybrid devices

The tutorial introduced the origin of the piezotronic effect and the piezo-phototronic effect in group-III-nitride nanowires as well as explained the mechanism of AFM characterization on a nanowire. Given the merits of the piezotronic and piezo-phototronic properties of a single group-III-nitride nanowire, many promising applications for conversion of mechanical energy to electrical energy can be achieved and scaled up by using nanowires ensemble, including but not limited to PENGs.

The directional strain has an improved dipole alignment due to the reduced radial size of the nanowires, thus providing a higher piezoelectric field and energy conversion efficiency. Recently, there has been a report of InN nanowire nanogenerator showing a large output power voltage of up to 1 V that is ten times larger than the same design using ZnO nanowires. Since lower temperature is needed to prevent In segregation or desorption for InN nanowire growth, PA-MBE can uniquely achieve the development needs for InN based energy conversion devices. Although binary group-III-nitride nanowires, such as InN and GaN, have been studied for relevant applications, the potential of ternary group-III-nitride nanowires has yet to be fully exploited. In particular, the tunable-bandgap InGaN-GaN multi-segment nanowires can enhance the performance of piezotronics/piezo-phototronic applications due to its high piezoelectric coefficients, high n-type conductivity, and efficient spectral-slicing of the solar spectrum. The work discussed in this tutorial could shed light on possible further developments of piezo-phototronic for self-powered micro-devices and maintenance-free, semiconductor-based energy-nanogenerators where the coupling of solar energy and mechanical energy are utilized for producing electrical energy.

Furthermore, the combination of triboelectricity and piezoelectricity can enhance energy production more efficiently. The triboelectric effect is contact-induced electrification of a material after contacting a different material. Some of the reported hybrid nanogenerators were created by combining the piezoelectric material with dielectric materials, and operated in contact and separation modes. Application of the idea to group-III-nitride nanowires ensemble also seems promising.

C. PEC-based CO₂RR and NRR

This tutorial also discussed the setup and working mechanism of a PEC water-splitting system. For group-III-nitride nanowire-based photoelectrodes, PEC efficiency can be enhanced by optimizing the doping concentration, band alignment, surface passivation, co-catalysts loading, and so on. There are still many other methods to be adopted to boost PEC system performance. For instance, integrating the PEC set up as one tandem structure may overcome the circuit resistance and improve device compatibility. Combining or integrating photovoltaic structures along with nanowires can result in highly efficient photoelectrodes structures (photoanodes and photocathodes) with high solar absorption efficiency and rich catalyst loading area for effective reduction. In addition, the PEC cell design may influence the gas evolution in many ways, including light exposure, pressure, gas dissolve rates, and so on. Therefore, the PEC cell can be custom-designed to maximize system efficiency. Several prototypes can be found in literature.

Similarly, if the bandgap of group-III-nitride nanowires can straddle the redox potential of other reactions, the PEC idea may apply to different redox reactions in liquid/wet environments, such as in CO₂RR and NRR.

Solar-to-clean-fuel energy applications can be realized by group-III nitrides by bandgap tuning to maximize solar energy conversion into the desired electric energy, which can be further converted into chemical energy. Notably, PEC-assisted conversion of CO₂ into value-added hydrocarbon products, such as HCOOH, CH₄ and C₂H₆ has attracted broad research interest. The atmospheric CO₂ can be used as the source for hydrocarbon synthesis. This can potentially reduce the cost of hydrocarbon synthesis when considering alternative means of reducing CO₂ emission.

Similarly, solar-assisted nitrogen-reduction reaction applications have also received research attention for synthesizing ammonia (NH₃). At present, global ammonia demand is satisfied with the Haber-Bosch approach, which was established in the 19th century. PEC N₂ fixation can be an environmentally friendly strategy for sustained NH₃ synthesis that considers N₂ and water feedstock and renewable solar energy under ambient conditions. It has the potential for large-scale NRR applications and promises to harvest NH₃ with high Faradic efficiency, ultra-long durability, and high NH₃ selectivity under milder process conditions than their photocatalytic and electrocatalytic counterparts. Further, it offers a sustained ammonia production environment with zero carbon emissions, self-powered operation, storage, and transport of H₂ fuel. The portable NH₃ production can benefit the industrial and agricultural sectors. In PEC NRR, N₂ to NH₃ conversion can take place on the catalytic surface of the photoelectrode when it is illuminated with energy.
greater than the bandgap of material (see the reaction pathway of PEC NRR in equation 20) with the equilibrium potential required for the reaction vs. RHE. Together, the NRR performance in PEC forms a benchmark approach for stability and efficiency in deciding on the ideal photoelectrode material.

\[ N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3, \ \text{\(E_{N_2/NH_3}^0\)} = -0.148 \text{ \(V \ vs. \text{RHE}\)} \quad (20) \]

The challenges that lie ahead for efficient conversion of \(N_2\) into \(NH_3\) by solar \(N_2\) fixation include the band edge positions of photoelectrodes for NRR, the competition of \(H_2\) evolution through HER rather than NRR, and the high inertness of \(N_2\) molecules.

D. Summary

This tutorial paper provides an overview of PA-MBE InGaN nanowires growth mechanisms and characterization methods for optimizing the quality of nanowires ensemble as an application-inspired semiconductor platform for energy-related applications. A systematic approach to understanding the fundamentals of semiconductor-based piezoelectric-assisted energy conversion and PEC hydrogen generation is presented. InGaN semiconductors can support technological development for future energy harvesting and conversion, and the prospects for further development are promising.

Authors’ contributions

H.Z. and J.-W.M. contributed equally to this work.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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