III-nitride Nanowire Photoelectrodes: Design, Epitaxial

Growth, and Solar-to-Fuels Production

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To my family.

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Contribution of Authors

This dissertation work includes the contribution of the candidate and many other individuals. The candidate and his advisor Prof. Zetian Mi conceived the idea and worked together closely in designing the InGaN/Si tandem structure, optimizing the growth conditions of tunnel junction nanowires and InGaN nanowires, analyzing the photoelectrochemical experiments and in writing the manuscripts. The MBE growth was carried out by the candidate; Dr. H. P. T. Nguyen contributed by training the candidate closely for the operation of the GEN II MBE system at the initial stage of PhD study before any experiment was conducted in this thesis, and Dr. S. Zhao also contributed to the training during the same time. The fabrication of Si solar cell with or without tunnel junction was performed by the candidate, with some help from Srinivas Vanka and Yongjie Wang under the supervision of the candidate. The cleaning and loading of pristine Si substrates for MBE growth were performed by the candidate, with some help from Srinivas Vanka from time to time under the supervision of the candidate. The photoelectrochemical experiment for water splitting was conducted by the candidate independently, with some technical support from Bandar AlOtaibi during the work of InGaN tunnel junction nanowire/Si tandem photocathode. The STEM study was conducted by Dr. Steffi Y. Woo and Dr. Gianluigi A. Botton at McMaster University for the samples in PEC experiment as well as the candidate and David Liu at McGill University for the samples on nanowire coalescence and distribution of indium in spontaneous InGaNcore/GaN-shell structure. The SEM study was conducted by the candidate. The photoluminescence study was performed by the candidate, together with help from Dr. Kwai Hei Li, Junjie Kang, Xianhe Liu, Binh Le Huy and Songrui Zhao for training and tuning optical alignment. The XPS study was conducted by Josianne Lefebvre at École Polytechnique Montréal. The photocatalytic CO₂ reduction was conducted by the candidate together with Bandar AlOtaibi at McGill University, Dr. Shuxin Ouyang, Dr. Defa Wang and Dr. Jinhua Ye at National Institute of Material Science, Japan. The project on photocatalytic conversion of CH_4 to benzene was conceived by the candidate and Dr. Lu Li under the supervision of Prof. Zetian Mi and Prof. Chao-Jun Li, samples were prepared by the candidate, and the photocatalytic characterization was set up and conducted by Dr. Lu Li and the candidate.

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List of Acronyms

PEC	Photoelectrochemical
NHE	Normal hydrogen electrode
OER	Oxygen evolution reaction
HER	Hydrogen evolution reaction
STH	Solar-to-hydrogen
ABPE	Applied-bias-photon-to-current efficiency
LSV	Linear scanning voltammetry
CV	Cyclic voltammetry
IPCE	Incident-photon-to-current efficiency
MOCVD	Metal organic chemical vapor deposition
HVPE	Hydride vapor phase epitaxy
MBE	Molecular beam epitaxy
PA-MBE	Plasma-assisted molecular beam epitaxy
RHEED	Reflect high-energy electron diffraction
ALD	Atomic layer deposition
SEM	Scanning electron microscopy
(S)TEM	(Scanning) Transmission electron microscopy
EDX	Electron-dispersive X-ray
EELS	Electron energy loss spectroscopy
XPS	X-ray photoemission spectroscopy
PL	Photoluminescence
MDA	Methane dehydroaromatization

Abstract

The photoelectrochemical (PEC) approach of converting solar energy into fuels holds significant potential to establish a sustainable energy system. Tremendous effort has been devoted to metal oxide based PEC systems. However, it remains elusive to reach the calibre for application in terms of efficiency, stability and scalability, due to the intrinsic limits of metal oxide light absorbers. Herein, we demonstrate the versatility of indium gallium nitride (InGaN) alloys grown by plasma-assisted molecular beam epitaxy (PA-MBE) for the purpose of water splitting under sunlight. Using tunnel junction nanowires, we realize a monolithically integrated InGaNnanowire/Si tandem photocathode with dramatically improved efficiency and stability compared to other Si-based photocathodes. Besides, we establish a growth window to produce high quality InGaN alloy nanowires with indium content as high as 50%, which unprecedentedly extends the absorption edge to ~700 nm and leads to the highest photocurrent of InGaN photoelectrodes under AM1.5G one sun illumination. Based on such InGaN nanowires, we further construct an InGaNnanowire/Si tandem photoanode with an energy bandgap configuration approaching the ideal values of 1.75 eV (top cell) and 1.13 eV (bottom cell) for tandem photovoltaic devices. Such an innovation brings us one step closer to unassisted PEC water splitting with a solar-to-hydrogen (STH) efficiency above 20%. We have successfully coupled the tandem photoanode with NiFeO_x water oxidation co-catalyst, reaching a peak STH of 1.3% for water splitting in strong base electrolyte. In addition, we explore the photocatalytic properties of GaN nanowires for the formation and cleavage of C-H bond. Under UV illumination, photocatalytic CO₂ reduction towards CO and CH₄ is observed on GaN nanowires with Pt nanoparticles as co-catalyst. The difficulty of C-H bond formation on GaN nanowires inspires us to study the cleavage of C-H bond

on the surface of GaN nanowires under UV illumination, which leads to the photocatalytic conversion of CH₄ to benzene.

Abrégé

L'approche photoélectrochimique (PEC) de convertir l'énergie solaire en carburants détient un potentiel important d'établir un système d'énergie durable. De considérables efforts ont été consacrés à des systèmes PEC à base d'oxydes de métaux. Toutefois, il reste difficile d'atteindre un niveau de performance suffisant pour une application efficace, stable et grandissante, en raison des limites intrinsèques des absorbeurs de lumière en oxydes de métaux. Ici, nous démontrons la polyvalence des alliages en nitrure d'indium et de gallium (InGaN) formés par épitaxie par jets moléculaires (MBE) assistée par plasma à des fins de craquage de l'eau sous la lumière du soleil. Avec l'utilisation de jonctions tunnel de nanofils, nous réalisons une photocathode qui combine les nanofils en InGaN intégrés de façon monolithique au Si, avec une amélioration considérable de l'efficacité et la stabilité par rapport à d'autres photocathodes à base de Si. En outre, nous établissons les paramètres pour produire des nanofils en alliages d'InGaN de haute qualité avec un contenu d'indium aussi élevé que 50%, ce qui étend sans précédent la limite d'absorption à ~ 700 nm et mène au courant photoélectrique le plus élevé des photoélectrodes à base d'InGaN sous AM1.5G d'éclairage solaire. En nous basant sur ces nanofils d'InGaN, nous formons par la suite une photoanode en nanofils d'InGaN combinés au Si avec une configuration de la bande d'énergie interdite approchant les valeurs idéales de 1,7 eV (cellule supérieure) et 1,0 eV (cellulaire inférieure) pour les appareils photovoltaïques combinés. Une telle innovation nous rapproche au craquage de l'eau par PEC sans biais avec une efficacité solaire en hydrogène (SEH) au-delà de 20%. Nous avons couplé avec succès cette photoanode avec un cocatalyseur d'oxydation de l'eau en NiFeO_x, pour atteindre une efficacité SEH de 1,3% pour le craquage de l'eau dans un électrolyte de base forte. De plus, nous explorons les propriétés photocatalytiques de nanofils en GaN pour la formation et le clivage de liaisons C-H. Sous une illumination UV, la réduction photocatalytique

de CO_2 en CO et CH₄ est observée sur les nanofils en GaN avec des nanoparticules de platine en tant que cocatalyseur. La difficulté de la formation de liaisons C-H sur les nanofils en GaN nous incite à étudier la rupture de liaisons C-H sur la surface de nanofils en GaN sous une illumination UV, ce qui conduit à la conversion photocatalytique de CH₄ au benzène.

Chapter 1 Introduction

1.1 Broader context of the research on solar fuels

The main challenge facing human society in the 21st century is sustainable development. The rate of global energy consumption is predicted to increase by 67% in the next four decades.¹ As the global fossil fuel consumption has been increasing in the past half century,² the dwindling global fossil fuel resources are accelerating the arrival of a post-peak oil production era³, which could cause an increasing gap between energy supply and demand. It is expected that renewable energy would compensate the gap. However, the extraction of renewable energy based on stateof-art technologies could merely contribute 22.8% to the total amount of consumed energy in 2014⁴. Besides, the anthropogenic CO₂ emission due to the combustion of fossil fuels has exceeded one third of the total amount of CO₂ in the natural carbon cycle, leading to climate change and catastrophic environmental impact.⁵ Last but not least, the combustion of fossil fuels releases black carbon particles and pollutants including NO_x, SO₂ and other harmful chemicals, threatening human health and the global ecosystem. The worsening circumstance urges the replacement of fossil fuels by sustainable energy sources. Over 190 countries have reached an agreement on keeping global warming less than 2 °C above pre-industrial levels in the 2015 Paris Climate Conference.⁶

Among all the renewable energy sources, solar energy is the most promising candidate in terms of the projected amount of extractable energy, compared with wind, tides, biomass, and geothermal sources.⁷ Solar energy can be harnessed in two conventional means, solar thermal and photovoltaics, to generate electricity. Both the current levelized cost and the projected levelized cost of photovoltaics in 2040 are only about half as much as those of solar thermal.⁸ The intermittency and low power density of sunlight are two obstacles for the collection of solar energy.

The solar thermal approach generally requires concentrated solar power to achieve the high temperature to produce steam, which suits for regions of high solar irradiance like the Mojave Desert in United States. The intermittency of sunlight can be smoothed in a solar thermal plant, where steam turbines can keep generating electricity almost throughout the night, providing a reliable input for the electric grid. In comparison, the integration of photovoltaics with the electric grid is plagued by the intermittency of sunlight. Furthermore, the direct harnessing of the photon energy by semiconductor light absorbers promises a valuable way for energy storage—solar-to-fuel conversion. For example, hydrogen as one of the solar fuels can be the energy carrier of a sustainable energy system, because of its high energy density, high stability, and negligible environmental impact. Harvesting solar energy and its subsequent storage in the form of chemical fuels is a promising approach to meet the demand of global energy supply and meanwhile to mitigate environment pollution and the greenhouse effect. In this context, we have extensively studied the viability to harvest solar energy in photoelectrochemical (PEC) cells to produce H₂ and other chemical fuels such as CO and CH₄ under terrestrial sunlight illumination.

1.2 Artificial photosynthesis for solar hydrogen generation

Artificial photosynthesis by splitting water is a concept conceived by Giacomo Ciamician in 1912.⁹ The water splitting reaction requires input energy of 237 kJ/mol, shown by Eq. (1-1); in strong acidic solution (pH =0), the reaction can also be interpreted as two half reactions in Eqs. (1-2) and (1-3). To date, there is no comprehensive model which can settle the theoretical efficiency of solar-to-hydrogen (STH) conversion à *priori* considering the kinetic processes in these reactions, but in the next section, we will provide a semi-empirical limit of STH efficiency by taking each practical considerations into account. The proof-of-concept was first demonstrated in 1970s, when Fujishima and Honda ignited the enthusiasm to produce hydrogen in a PEC cell based on TiO₂.¹⁰

Meanwhile, the mimicry of the natural photosynthesis process in green plants has bred the design prototype of bioinspired solar fuel generation devices.¹¹ In addition, a straightforward way to form hydrogen is to split water by integrating photovoltaics and electrolyzers (represented by PV-electrolyzer system hereafter). A comparison of these approaches involves three figures-of-merit, including the projectable efficiency, the levelized cost and energy payback time.

$$H_2 O(l) \rightarrow H_2 \uparrow + \frac{1}{2} O_2 \uparrow, \Delta G = +237 \frac{kJ}{mol}$$
 Equation (1-1)
$$H_2 O \rightarrow 2H^+ + \frac{1}{2} O_2 \uparrow + 2e^-, E_o = +1.23 \text{ vs. NHE}$$
 Equation (1-2)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow, E_o = 0 \text{ vs. NHE}$$
 Equation (1-3)

1.2.1 The bioinspired solar-to-fuel approach

The mechanism of photosynthesis is the precise coordination between two photosystems. One of the photosystems called PSII (chlorophyll P680) can be activated by photons with energy above 1.83 eV, with the photoexcited electron transferred to a specific electron acceptor followed by a chain of electron transfers across an array of precisely ordered redox species, while the oxidized form of PSII obtains an electron from a specific electron donor.¹² In this way charge separation is realized across a membrane with a quantum efficiency close to unity at the cost of energy loss ~0.6 eV. The electron donor oxidized by PSII in turn scavenges electrons from a Manganese complex, which can undergo multiple-step transitions to the final oxidized state after losing 4 electrons and then oxidize water to release oxygen and protons with an overpotential of ~300 mV, as shown by Eq. (1-3).¹³

Meanwhile, the electron transfer along the array of redox species ends with another chlorophyll called PSI, which absorbs photons with energy above 1.77 eV to further excite the electron to a higher energy state, followed by electron transfer along another precisely ordered

redox chain.¹⁴ The two times of subsequent photoexcitation make the electron energetic enough to drive the reaction between 1) the protons generated by water splitting and 2) atmospheric CO₂ to form carbohydrate. In this sophisticated approach, plants can trap solar energy into chemical bonds with a peak efficiency of ~2%.¹⁵

Current research to mimic such an intriguing process is still in the early stage of arranging molecular structures to achieve efficient separation of photoexcited charges.¹⁶ The main challenge of bio-solar water splitting is the effective coupling of charge-transfer chromophores with molecular hydrogenase and water oxidizing catalysts. Efforts to combine chromophores with hydrogenase to generate hydrogen generally failed after some turn over number, because molecular chromophores degrade rapidly under illumination. However, chlorophylls in green plants maintain a self-repairing mechanism under sunlight illumination,¹³ which is lost when they are extracted from the organism.¹⁷ In comparison, only solid state semiconductor light absorbers can reach the pragmatic level of stability for application. Besides, chromophores have very low light absorption cross section compared with solid state semiconductors; it is formidable to arrange artificial biomolecular systems into structures resembling the "light-harvesting antenna" in leaves of green plants, which can capture over 50% of photons of suitable energy. Therefore, the biomolecular approach for solar fuels is still in its infancy stage.

1.2.2 PEC cells and PV-electrolyzer systems for solar-to-hydrogen production



Figure 1-1. The schematics of (a) a PEC cell and (b) a PV-electrolyzer system.

A PEC cell resembles a PV-electrolyzer system in that photoexcited carriers are generated in the light absorption layer and transferred to catalysts to drive the chemical reactions on electrodes, as shown by the schematics in Fig. 1-1. As shown in Equations (1-2) and (1-3), based on the change of Gibbs free energy, water splitting can in principle occur at an electrical bias of 1.23 V. Hereafter, external electrical bias exceeding 1.23 V required for water splitting is defined as overpotential, which can be attributed to resistances due to kinetic barriers for hydrogen evolution and oxygen evolution, hydrogen/oxygen gas bubbling, and mass transport of reactants such as H⁺ and OH⁻. Overpotential originated from gas bubbling and mass transportation becomes dominate as the electrode current density increases to 50 mA/cm².¹⁸ Therefore, to ensure the overpotential is used for driving the hydrogen evolution and oxygen evolution kinetic processes, it is favorable to keep the current densities on the electrodes in the range of few 10s' mA/cm². This constraint on current

density makes it a viable way to design solar-to-hydrogen devices functioning under terrestrial sunlight illumination, and also eliminates the necessity to use solar concentrators for PEC cells. In an electrolyzer, using Pt as hydrogen evolution reaction (HER) catalyst (overpotential of 50-100 mV at an electrode current density of 20 mA/cm²) and state-of-art water-oxidizing catalysts¹⁹ which require an overpotential of 300-400 mV to drive a current density of 10-20 mA/cm² on the electrodes, hydrogen can be produced at an input voltage of 1.6-1.7 V with a Faradaic efficiency (η_{FE}) of unity; though lower current density on the electrodes requires less overpotential and therefore lower input voltage, a minimum electrode current density of 10-20 mA/cm² has to be maintained for practical applications. At such an optimal applicable working point of the electrolyzer with an electrode current density of J_{WP} and an input voltage of V_{WP}, the electricity-to-hydrogen efficiency ($\eta_{electrolysis}$) defined by Eq. (1-4) is 72%-77%, which renders water splitting by a stand-alone electrolyzer uneconomic both financially and environmentally, since electricity in the grid is mainly produced by burning fossil fuel.

$$\eta_{electrolyzer} = \frac{1.23[V]}{V_{WP}[V]} \times \eta_{FE} \times 100\% \qquad \text{Equation (1-4)}$$

where η_{FE} and $\eta_{electrolyzer}$ represent the Faradaic efficiency and the electricity-to-hydrogen efficiency of the electrolyzer.

The practical application of both PEC cells and electrolyzers requires the separation of evolved hydrogen and oxygen gases while maintaining high ionic conductivity between the cathode and anode chambers. Besides, the water splitting reaction also favors strong acidic or alkaline conditions. Though neutral water splitting has attracted a lot of attentions,^{19h} the commercially available separator to allow selective ion transport at low resistivity, which is the proton exchange membrane, favors strong acidic electrolyte.²⁰

1.2.2.1 The anatomy of PV-electrolyzer systems

To assemble the electrolyzer with a solar cell, the maximum output power point (MMP) of the solar cell has to match the optimal hydrogen generation voltage of 1.6-1.7 V, because to introduce a power optimizer (DC-DC power converter) for impedance matching entails formidable cost in the foreseeable future. The maximum output power density of the solar cell (P_{MMP}) corresponds to a photocurrent density of J_{MMP} and photovoltage of V_{MMP}, described by Eq. (1-5); the deviation of the working point of the electrolyzer from the MMP of the solar cell can be defined as the matching efficiency (η_{match}) of the PV-electrolyzer system in Eq. (1-6), which represents the extra loss to convert solar electric energy to chemical energy in solar hydrogen. Nevertheless, such an electrolyzer can be integrated with an ideal tandem photovoltaic device to reach a η_{match} close to unity, promoting water splitting at a theoretical solar-to-hydrogen (STH) efficiency of $\sim 28\%$. In principle, to achieve current matching between the top cell and the bottom cell, the tandem solar cell can be constructed by a 1.75-eV/1.13-eV optimal tandem structure,²¹ with an open circuit potential (Voc) of ~1.9 V (assuming ideal bandgap-voltage offsets of 0.4-0.5 V for both top and bottom cells), a short circuit current (J_{sc}) of ~23 mA/cm², a fill factor (FF) of ~0.88 and a power conversion efficiency (η_{PV}) of ~38% under AM1.5G illumination ($P_{incident}$) of 100 mW/cm² (one sun).²² The aforementioned STH of 28% can be defined as the semi-empirical limit of STH, on the basis of a practical electrode current density of ~23 mA/cm² under AM1.5G one sun. It is beneficial to have PV-electrolyzer systems under concentrated sunlight to push Voc closer to the limit of bandgap-voltage offset. However, the semi-empirical STH could hardly be marginally increased under concentrated sunlight since the J_{sc} of ~23 mA/cm² already assumes the external quantum efficiency of the ideal tandem solar cell to be unity and the V_{oc} of 1.9 V already assumes ideal bandgap-voltage offsets. Further increase of the semi-empirical limit of STH becomes elusive, as

the catalytic overpotential of the proton-coupled-four-electron-transfer process in the oxygen evolution reaction (OER) can hardly be further reduced.

$$P_{MPP} = J_{MPP} \times V_{MPP} = J_{sc} \times V_{oc} \times FF$$
 Equation (1-5)

$$\eta_{match} = \frac{J_{WP} \times V_{WP}}{P_{MPP}} \times 100\%$$
 Equation (1-6)

$$\eta_{PV} = \frac{P_{MPP}}{P_{incident}} \times 100\%$$
 Equation (1-7)

$$STH = \eta_{electrolyzer} \times \eta_{match} \times \eta_{PV}$$
 Equation (1-8)

where η_{match} represents the matching efficiency of a PV-electrolyzer system; in the electrolyzer, V_{WP} and J_{WP} represent the input voltage and the current density on the electrodes, respectively; in the solar cell, J_{sc} , V_{oc} , FF and $P_{incident}$ represent the short circuit current density, the open circuit potential, the fill factor and the power density of the incident light, respectively, while P_{MPP} , J_{MPP} and V_{MPP} represent the output power density, the photocurrent density and the photovoltage at the MMP of the solar cell, respectively; STH represents the solar-to-hydrogen efficiency of the PV-electrolyzer system.

In practice, although tandem solar cells based on such a design has much inferior performance²³ mainly due to the non-ideal V_{oc} and η_{match} , a prototype PV-electrolyzer system (Device#1) demonstrated a STH of 22.4% by using an electrolyzer based on Ni foam and a GaInP/GaAs/Ge tri-junction solar cell under concentrated solar power (CSP) (100 suns).²⁴ (The STH value, however, may have some uncertainties because the J_{MPP} of the GaInP/GaAs/Ge tri-junction solar cell was measured as 1.77 A/cm² at V_{MPP}=2.05 V in ref. [22]; the theoretical-limited J_{ph} of GaAs is 3.17 A/cm², therefore, the J_{MPP} should be less than 1.585 A/cm² under 100 sun.) A second PV-electrolyzer system (Device#2) using a AlGaAs/Si tandem solar cell ($\eta_{PV} = 21.2\%$)

under the illumination close to one sun obtained a STH of 18.3% by sustaining an impractically low J_{WP} of 0.44 mA/cm² to reduce overpotential loss as well as to match the MMP of the solar cell.²⁵ To truly simulate the scenario of a solar plant, a third system utilized an array of GaInP/GaInAs tandem solar cells ($\eta_{PV} = 21\%$) under illumination of 500 suns to integrate with a polymer electrolyte membrane (PEM) electrolyzer working at a practical current density of ~30 mA/cm^{2,26} (The PV photocurrent density of 4.99 A/cm² from a PV area of 0.1884 cm² under 413.8 suns dissipated into an electrode area of 30 cm^2 , leading to an electrode current density of ~30 mA/cm².) In contrast, another PV-electrolyzer system (Device#4) of GaInP/GaAs tandem solar cell ($\eta_{PV} = 27.4\%$) only reached a STH of 16.5% under one sun with significantly mismatched V_{MMP} (= 2.10V) and V_{WP} (= 1.75V).²⁷ Other PV-electrolyzer systems (*e.g.*, Device#5) using solar cells in series^{19b, 28} to approximately coordinate the V_{MMP} and the V_{WP}; in such scenarios, marginal incentive can be gained for water splitting since the STH is fundamentally limited by the thermalization loss in the solar cells. The performance of the aforementioned five systems are summarized in Tab. 1-1, with the performance of solar cells separately presented in Tab. 1-2. Overall, it is beneficial to have PV-electrolyzer systems under CSP since the area of the electrodes in the electrolyzer can be adjusted based on the photocurrent.

Table 1-1. The comparison of five PV-electrolyzer systems with high STHs. where η_{match} represents the matching efficiency of a PV-electrolyzer system; in the electrolyzer, V_{WP} and J_{WP} represent the input voltage and the current density on the electrodes, respectively; in the solar cell, J_{sc} , V_{oc} , FF and $P_{incident}$ represent the short circuit current density, the open circuit potential, the fill factor and the power density of the incident light, respectively, while P_{MPP} , J_{MPP} and V_{MPP} represent the output power density, the photocurrent density and the photovoltage at the MMP of the solar cell, respectively; *STH* represents the solar-to-hydrogen efficiency of the PV-electrolyzer system.

Device	STH	$\eta_{electrolyzer}$	η_{match}	η_{PV}	V _{MMP}	V_{WP}	J _{WP}
#1	22.4%	57.5%	99.1%	38.6%	2.18	2.14	16.3
#2	18.3%	89.1%	96.8%	21.2%	1.30	1.38	0.44
#3	15.0%	76.9%	93.2%	21.0%	2.0	1.6	27.8
	16 50/	70.20		07.40/	2 10	1.75	12.4
#4	16.5%	70.3%	85.6%	27.4%	2.10	1.75	13.4
#5	12 304	70 404	08 7%	15 704	1.63	1 55	0.64
#5	12.3%	17.4%	<i>70.1%</i>	13.7%	1.05	1.33	0.04

Note: The STH of Device#3 was properly recalculated based on the low heating value of hydrogen gas for comparison.

Device	Solar cell structure	η_{PV}	V _{oc}	J _{sc}	FF	V _{MMP}	J _{mmp}
#1	GaInP/GaAs/Ge (1.83eV/1.42eV/0.67eV)	38.6%	2.55	18.2	0.84	2.18	17.8
#2	AlGaAs/Si (1.6eV/1.12eV)	21.2%	1.57	17.5	0.772	1.30	16.3
#3	GaInP/GaInAs (1.7eV/1.2eV)	21.0%	2.2	14.5	0.658	2.0	10.5
#4	GaInP/GaAs (1.83eV/1.42eV)	27.4%	2.32	13.4	0.88	2.13	12.8
#5	CH ₃ NH ₃ PbI ₃ in series (1.55eV)	15.7%	2	10	0.76	1.63	9.61

Table 1-2. The performance of the solar cells in the five PV-electrolyzer systems.

Note: For all the current densities and voltages in Tabs. (1-1) and (1-2), the units are mA/cm^2 and V, respectively; the J_{sc} and J_{MMP} of the PV cells in Device#1 and Device#3 were normalized photocurrent densities equivalent to photocurrent densities under one sun illumination for comparison.

1.2.2.2 The introduction to PEC cells

In the same principle as a PV-electrolyzer system, a PEC cell can be readily constructed by coating hydrogen/oxygen evolution (HER/OER) catalysts directly on the surfaces of a solar cell, which has been coined as a wireless PEC cell with both HER catalyst deposited on the cathode of the solar cell and OER catalyst deposited on the anode of the solar cell,²⁹ or a partially integrated PEC cell with only one type of catalyst coated on one side of the solar cell as the working photoelectrode and using a counter electrode^{28a, 30}. These PEC systems can sustain STHs of 4-14% under AM1.5G one sun illumination, mainly determined by the performance of the buried solar cell.

However, the distinction between a PEC cell and a PV-electrolyzer system is more fundamental than the difference in their configurations. In a PEC cell, both the light absorbing material and the catalyst are immersed in electrolyte, which imposes stringent requirement over the stability of the light absorbing materials. In dark condition, the Fermi level of the semiconductor aligned with the electrochemical potential of redox species in the electrolyte when the equilibrium state is reached, which induces surface band bending. The transfer of photoexcited carriers from the bulk of semiconductor electrode to the surface is determined by the Schottky junction at the solid-liquid interface³¹, as shown by the simplified energy band diagrams in Fig. 1-2. The coupling between the energy bands of the semiconductor and the electrochemical potential of the solution significantly affects the reaction energetics and kinetics. The electrochemical potential of the solution is determined by the standard potential of the charge exchange process, *i.e.*, the chemical reaction at the semiconductor-electrolyte interface, which can be probed by measuring the dark open circuit potential of the semiconductor electrode under equilibrium. For a stable semiconductor photoelectrode, the charge exchange process is determined by one of the half reactions of water splitting. At the semiconductor-electrolyte interface, a space charge layer is formed on the semiconductor side, with a thickness of 10's to 100's of nanometers depending on the doping level of the semiconductor. On the electrolyte side, a layer of charges called Helmholtz layer was formed by adsorbed ions or molecules, or by oriented dipoles or chemical bonding between chemical species in solution and surface states of the semiconductor. Ideally, the energy band edges of the semiconductor are pinned at the semiconductor-electrolyte interface in the absence of net charges. However, at a real semiconductor-liquid interface, the presence of surface states within the bandgap on the semiconductor side as well as the adsorption of chemical species on the surface of the semiconductor can harbor charges to shift the energy band edges relative to their original positions. The thickness of the Helmholtz layer is within few nanometers, with a capacitance hundreds of times larger than that of the space charge layer. Upon an external voltage

bias on the electrode, the band bending in the space charge layer is compensated first. The external bias required to eliminate the space charge region is the flat-band potential (E_{FB}). Further increase of the external bias can strongly tune the potential across the Helmholtz layer. Studies shown that the voltage drop across the Helmholtz layer can induce a high kinetic overpotential for water splitting reactions, represented by the equilibrium potential of the photoelectrode under dark and the onset potential of the photocurrent under illumination.³²



Figure 1-2. Surface band bending for *p*-type and *n*-type semiconductors at the interface with electrolyte. E_c , E_v and E_F represent conduction band edge, valence band edge and Fermi level, respectively; e^- and h^+ represent photoexcited electron and hole, respectively; D_{ox} and D_{red} represent the Gaussian distribution of the redox states versus electron energy, respectively, and the shadowed region represents energy states occupied by electrons. ΔG represents the change of Gibbs free energy in the electrochemical reaction.

Water splitting reaction favors strong acidic or strong base solutions. As for water splitting in strong base solution (pH = 14), the half reactions of water splitting are shown in Eqs. (1-9) and (1-10).

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow, E_o = -0.82 \ vs. \ NHE$$
 Equation (1-9)
 $2OH^- \rightarrow H_2O + \frac{1}{2}O_2\uparrow + 2e^-, E_o = +0.41 \ vs. \ NHE$ Equation (1-10)

The electrochemical potential of the electrolyte is close to the standard potential of OER $(E(O_2/OH^-))$.³² The energy band structure of an *n*-type semiconductor photoanode relative to the electrochemical potential of the electrolyte and the Fermi level of the Pt counter electrode is illustrated in Fig. 1-3. HER can occur without external bias only if the flat-band potential is above $E(H_2O/H_2)$. In other words, the conduction band minimum (CBM) and valence band maximum (VBM) need to straddle $E(H_2O/H_2)$ and $E(O_2/OH^-)$ and the photovoltage ΔV_{ph} needs to be higher than 1.23 V determined by the change of Gibbs free energy ΔG of water splitting. In this scenario, the semiconductor photoelectrode has a CBM below ($E(H_2O/H_2)$); therefore, an external bias ΔV_{bias} is required to split water, as shown in Fig. 1-3b.






Figure 1-3. A PEC cell with an *n*-type semiconductor as photoanode, Pt wire as counter electrode and 1 M KOH as electrolyte. The energy band structure of the photoanode relative to the electrochemical potential of the electrolyte and the Fermi level of the Pt counter electrode is illustrated under (a) dark and (b) illumination. $E(H_2O/H_2)$ and $E(O_2/OH^-)$ represent the equilibrium potential for hydrogen evolution and oxygen evolution half reactions in strong basic solution, respectively. η_{OER} represents the difference between the valence band edge of the semiconductor light absorber and $E(O_2/OH^-)$, while η_{HER} represents the hydrogen evolution overpotential provided by external bias.

In the PEC cell shown in Fig. 1-3b, the overpotential for HER (η_{HER}) is provided by external electrical bias, while the overpotential for OER (η_{OER}) is intrinsic to the semiconductor-electrolyte interface, which can in principle facilitate OER providing that the Fermi level of the counter electrode is tuned above E(H₂O/H₂). The intrinsic η_{OER} of a PEC system, compared with the electrically applied overpotential of a PV-electrolyzer system, could have more direct influence on the kinetics of charge transfer in OER. In a PV-electrolyzer system, two types of energy loss are inevitable, the loss in the solar cell due to voltage-bandgap offset (*e.g.*, loss for Si: $\frac{1.12V-0.74V}{1.12V} \approx$ 34%) and the loss in the electrolyzer due to HER/OER overpotential (*e.g.*, loss for optimal HER/OER at 20 mA/cm²: $\frac{0.4V}{1.23V+0.4V} \approx 25\%$). In a photoelectrode, the surface band bending which can generate photovoltage is induced by the offset between the Fermi level of the semiconductor and the equilibrium potential of the redox species; in *n*-type semiconductor, the Fermi level is close to the conduction band; hence it is the offset between the conduction band edge and the

equilibrium potential of OER that determines the photovoltage if we neglect the offset between conduction band edge and Fermi level ($\Delta_1 < 100 \text{ meV}$), while the offset between the valence band edge and the equilibrium potential of electrolyte is the intrinsic overpotential of OER η_{OER} , if we neglect the offset between the equilibrium potential of OER and the equilibrium of electrolyte(Δ_2 can be tuned to be <100 meV in electrolyte) as well as the potential drop across the Helmholtz layer, as shown in Fig. 1-4. Whether the intrinsic η_{OER} can lead to less energy loss is still unknown. The coupling between the semiconductor energy band structures and the electrochemical potentials of the electrolyte opens more avenues to the engineering of the photoelectrochemical properties for water splitting.



Figure 1-4. Illustration of the relation between photovoltage and intrinsic overpotential of OER at the semiconductorliquid interface. ΔV_{ph} and η_{OER} represent the photovoltage and the intrinsic overpotential of OER, respectively; Δ_1 and Δ_2 represent the offset between conduction band edge and Fermi level in the *n*-type semiconductor and the offset between the equilibrium potential of the electrolyte and the equilibrium potential of the OER, respectively.

Furthermore, for direct-bandgap materials, the generation of photoexcited charge carriers and their subsequent transport towards the catalytic active sites for HER/OER can be realized within few 100's of nanometers, promising higher quantum efficiency and lower overpotential loss

compared with PV-electrolyzer systems where the photoexcited charge carriers and electrochemical reactions are isolated. Therefore, semiconductor nanostructures including nanowires³³, nanofleaks³⁴, and nanoporous networks³⁵ demonstrated superior activities compared with planar structures. Solid state junctions can be buried inside the photoelectrodes to generate higher photovoltage. Lewis' group demonstrated that the performance of *p*-Si coated with Pt as photocathode can be improved if a buried *p*-*n*⁺ Si junction is used beneath the solid-liquid interface to promote photoexcited charge separation.³⁶ Monolithically integrated photoelectrodes demonstrated STHs comparable to the state-of-art PV-electrolyzer systems while offered more flexibility for system design and optimization and reduced cost.

Metal oxides have been widely studied in the past four decades as photoanodes due to the scalability of their solution-based synthetic methods,³⁷ low cost and high stability. Wide bandgap metal oxides such as TiO₂ (rutile 3.03 eV and anatase 3.2 eV)^{10, 38} and SrTiO₃ (3.2 eV)³⁹ can sustain stable photocurrent under UV illumination. Research on shrinking the energy bandgap of TiO₂ by introducing defects or doping for visible light absorption made very limited improvement on its water splitting performance.⁴⁰ Recently, study on nanostructured WO₃ (2.5-2.8 eV indirect band gap)³⁴, α -Fe₂O₃ (2.2 eV direct band gap)^{33, 41} and BiVO₄ (2.4 eV direct band gap)^{35, 42} as photoanodes witnessed tremendous progress. WO₃ nanowire/nanoleaf structure can significantly enhance the light absorption capability of the indirect band gap material and reach an incident-photon-to-current efficiency (IPCE) of 60% at 1.23 V vs. NHE.³⁴ The most abundant and stable (in alkaline solutions) photocatalytic semiconductor α -Fe₂O₃ has very short hole diffusion length (few nanometers), high defect density and poor conductivity, which makes it elusive to approach the theoretical limit of applied-bias-photon-to-current efficiency (ABPE) of 16% for α -Fe₂O₃. Nevertheless, α -Fe₂O₃ can sustain photocurrent density as high as 4.32 mA/cm² at 1.23 V vs. NHE

with an onset potential of 0.7 V vs. NHE after transformed into Pt-doped nanostructures with Co-Pi as OER catalyst;³³ another independent study showed that by reducing the surface defects of α -Fe₂O₃, its onset potential can be cathodic-shifted to 0.45 V vs. NHE.⁴³ As for BiVO₄, though very unstable compared to α -Fe₂O₃,⁴⁴ the hole diffusion length is ~100 nm³⁵ and the conductivity can be tuned by tungsten doping.⁴² Therefore, BiVO₄ photoanodes with OER catalysts have an onset potential in the range of 0.2-0.3 V *vs.* NHE, with a photocurrent density in the range of 3-5 mA/cm², while their stability for few 10's of hours can be realized with OER catalysts and protective layers.⁴⁴⁻⁴⁵ We have used the onset potential of photocurrent in different metal oxide photoanodes up to now. Generally, the onset potential is noted as the applied bias at which photocurrent becomes substantially higher than the dark current (~10-100 μ A/cm² depending on the saturated photocurrent density of the photoelectrode); Le Formal *et. al.* has defined the onset potential rigorously as the potential at which the first-derivative of the photocurrent density exceeds 0.2 mA/(cm²·V).⁴⁶

One of the major challenges facing metal oxides is the misalignment of their energy band structures with the equilibrium potential of HER/OER. The VBMs of transition metal oxides are configured by the 2p orbital of oxygen atoms, which is about 2.94 eV vs. NHE⁴⁷, and the CBMs are mainly configured by the 3d orbital of metal atoms, which is generally positive vs. NHE. The large built-in overpotentials (~ 1.5 V) of metal oxide photoanodes as the driving force for the transfer of photoexcited holes from the light absorber to the electrolyte may benefit the OER process but also represent unnecessary loss of photon energy. To overcome this issue, metal nitrides and oxynitrides with more suitable band alignment with equilibrium potentials of HER/OER have attracted much research interest.⁴⁸ Though not as stable as metal oxides, independent studies showed that metal (oxy)nitrides can be protected kinetically by OER

catalysts.⁴⁹ Kazunarai Domen's group discovered that GaN:ZnO solid solution powders with RhCrO_x nanoparticles as photocatalyst can split pure water under visible light.⁵⁰ Later, their separate work on TaON or Ta₃N₅ photoanodes showed the viability to construct high efficiency solar-to-hydrogen devices based on metal (oxy)nitrides.⁵¹ The energy bandgaps of the aforementioned metal (oxy)nitrides are relatively fixed; another material system, the III-nitrides or InGaN alloys, is more promising for solar hydrogen generation, because the energy bandgap of InGaN can be varied from 0.65 eV (InN) to 3.4 eV (GaN) to cover the whole solar spectrum and the CBM/VBM aligns well for water splitting, as shown in Fig. 1-5.⁵² Kibria M. *et al.* demonstrated that GaN nanowire can split pure water with high quantum efficiency.⁵³ Alotaibi B. *et al.* showed the PEC performance of InGaN/GaN nanowires in HBr solution.⁵⁴ Based on these initial demonstrations, we have achieved more significant progress to be elaborated in next few chapters.



Figure 1-5. The electronic energy band structures of InGaN alloy and other semiconductors. Bottom x-axis represents the theoretical maximal photocurrent density of the semiconductor under AM1.5G one sun; top x-axis represents the absorption edge of the semiconductor; and the y-axis on the right side represents the band position of the semiconductor.

In parallel with the development of photoelectrodes, the research on photocatalysts has brought up a lot of innovations. The photocatalytic powders suspended in electrolytes or photocatalytic nanostructures deposited on substrates are essentially micro-photoelectrodes wherein photoexcited charge separation is driven mainly by diffusion and HER/OER occurs at spatially separated active sites on the photocatalytic nanostructures. Some photocatalytic systems can only generate hydrogen with sacrificing reagents. In the case of water splitting, photocatalytic system generates a mixture of hydrogen and oxygen, which could be explosive given high activity or large scale application. Photocatalytic system cannot compete with PEC cells in terms of light absorption cross section, quantum efficiency of photoexcited carrier separation and scalability. However, the research on photocatalysts has significantly propelled the advance of photoelectrodes by developing novel nanostructure synthetic methods, assembling suitable HER/OER with semiconductor nanostructures and inquiring fundamental photochemical properties.

1.2.3 Hydrogen/Oxygen evolution catalysts

Ever since Brattain and Garrett's investigation on Ge/electrolyte interfaces as photovoltaic cells in 1955, the application of PEC devices is limited by their lifetime.⁵⁵ An efficient and stable photoelectrode requires nanostructured semiconductors to generate photoexcited charge carriers and catalysts to facilitate HER/OER. Semiconductor photoanodes such as Si, BiVO4⁴² and $Ta_3N_5^{51a}$, and photocathodes such as Si⁵⁶ and InP⁵⁷, can provide photovoltage under illumination, but the OER/HER processes are so sluggish that barely any photocurrent can be observed if the applied bias is lower than 1.23 V. Electrochemical HER/OER catalysts play a crucial role to extract photoexcited charge carriers from the semiconductors and to facilitate proton-coupled electron transfer processes to form hydrogen and oxygen. The effects of OER catalysts can be elucidated by the work of two independent groups. Kim T. et. al. demonstrated that by promoting nanoporous BiVO₄ photoanodes with only FeOOH, only NiOOH, NiOOH on top of FeOOH and or FeOOH on top of NiOOH, the photoexcited charge separation efficiencies were significantly improved when using Na₂SO₃ as hole scavenger, and the carrier extraction for each OER catalyst is evidently different with the BiVO₄/FeOOH/NiOOH (NiOOH on top of FeOOH) photoanode as the optimal combination.³⁵ Another effect of OER is to reduce the kinetic overpotential of the oxidation reaction; Du C. et. al. demonstrated that using NiFeO_x as OER catalyst, the equilibrium potential of the α -Fe₂O₃ photoanode under dark can be shifted positively from +0.85 V vs. NHE to +1.19 V *vs.* NHE, approaching $E_0(O_2/OH^2)$ of +1.23 V *vs.* NHE in strong alkaline solution (*p*H=14);³² in

other words, the potential drop in the Helmholtz layer was significantly reduced by using the NiFeO_x OER catalyst.

The catalytic activity of HER/OER catalysts can be evaluated based on the performance of the electrode formed by coating the HER on a degenerately *n*-doped semiconductor substrate or coating the OER on a degenerately *p*-doped semiconductor substrate; in both cases, Ohmic contact on the back side of the degenerately doped semiconductor electrode is required. The change of current density *vs*. overpotential (*J*- η characteristic) obeys the Butler-Volmer model, as shown in Eq. (1-11).⁵⁸

$$J = J_O \cdot \left[\frac{C_O}{C_O^*} \cdot \exp\left(-\alpha \frac{nF}{RT}\eta\right) - \frac{C_R}{C_R^*} \cdot \exp\left((1-\alpha) \frac{nF}{RT}\eta\right)\right] \text{ Equation (1-11)}$$

where *n* is the number of electrons involved in the electrode reaction, which is 2 for HER and 4 for OER; *F* is the Faraday constant, 96485 C/mol; *R* is the gas constant, 8.3145 J/(mol·K); T is the absolute temperature in Kelvin, 300 K at room temperature (RT); α is the transfer coefficient (0 < α < 1); η is the overpotential with respect to the equilibrium potential of the electrode reaction, which is E(H⁺/H₂) for HER (0 vs. NHE) and E(O₂/H₂O) for OER (1.23 V vs. NHE) in strong acidic condition (*p*H =0); *J* is the current density under an overpotential of η , and *J*₀ is the exchange current density at the equilibrium potential of the electrode reaction; *C*₀ and *C*_R are the concentrations of oxidized and reduced species at the electrode surface, while *C*^{*}₀ and *C*^{*}_R are the concentrations of oxidized and reduced species in the bulk of electrolyte. Under sufficient stirring, the electrode reaction is under kinetic transfer controlled regime, therefore *C*₀ = *C*^{*}₀ and *C*_R = *C*^{*}_R.

Note: In Eq. (1-11), the cathodic current is defined as the positive current of the electrode reaction to be consistent with Allen Bard and Larry Faulkner's definition in Ref [55],⁵⁸ but in the following discussion of photoelectrodes, cathodic current is defined as negative current while anodic current is defined as positive current.

$$J_0 = nFk_o \cdot C_0^{*(1-\alpha)} \cdot C_R^{*-\alpha} \qquad \text{Equation (1-12)}$$

where k_o is the standard rate constant of the electrode reaction.

The exchange current density (J_0) is represented in Eq. (12). For HER driven by an overpotential of η ($\eta \gg \frac{nF}{RT}$), the second term of the Butler-Volmer equation is negligible; so is the first term for OER. Therefore, Eq. (1-11) can be organized in the form of Tafel equation, as shown by Eq. (1-13).

$$\eta = a + b \cdot lg(J)$$
 Equation (1-13)

where the Tafel slope is defined in Eqs. (1-14) and (1-15).

$$b_{HER} = \frac{2.3}{\alpha_{HER}} \cdot \frac{RT}{nF}$$
 Equation (1-14)
$$b_{OER} = \frac{2.3}{(1 - \alpha_{OER})} \cdot \frac{RT}{nF}$$
 Equation (1-15)

Ideally, the transfer coefficient α_{HER} approaches unity, corresponding to a Tafel slope of HER close to 30 mV/dec at RT; α_{OER} approaches zero, corresponding to a Tafel slope of OER close to 15 mV/dec at RT. In reality, Pt as HER catalyst exhibits an exchange current density as high as few mA/cm² and a Tafel slope close to 30 mV/dec at RT. However, for OER catalysts, multiple steps of electron transfers are involved with significant molecular rearrangement in each step, leading to an exchange current density over five orders lower than that of Pt as HER. Therefore, the onset overpotential (for few 10's of μ A/cm²) instead of the exchange current density is used to calibrate OER, which is over 200 mV for state-of-art OERs. Up to now, the optimal Tafel slopes of OER are in the range of 30-80 mV/dec, much inferior to the theoretical limit of 15 mV/dec.^{19d} One reason could be that the transfer coefficient α_{OER} is generally much larger than zero.

Hypothetically, a more plausible explanation is that the applied voltage on OER catalyst dissipates into a sequence of elemental reaction steps to reduce the reaction barrier in each step instead of being applied on the only rate-determining elemental step.

Electrochemical HER/OER catalysts can be generally categorized as noble metal/metal oxides, earth-abundant metal/metal oxides and molecular catalysts. Noble metals including Pt, Ir and Ru have been widely studied as HER/OER. As for HER catalyst, Pt exhibits the highest activity in terms of Tafel slope and onset overpotential, which is explained by the close-to-zero atomic hydrogen binding free energy with respect to the adsorption free energy of gaseous hydrogen.⁵⁹ Alternative HER catalysts including MoS_x,⁶⁰ Ni-Mo,⁶¹ Co-Ni,⁶² NiO/Ni heterostructure,⁶³ NiFe layered double hydroxide (LDH)^{19b} and NiMoZn,^{29a} generally have exchange current densities one to several orders (<0.2 mA/cm²) lower than that of Pt (~1 mA/cm²),^{59a} and Tafel slopes in the range of 40 mV/dec to 100s' of mV/dec⁶³, as shown in Tab. (1-3). As for most semiconductors in photocathodes, including Si,^{36, 56a, 64} InGaP,⁶⁵ InP⁶⁶ and InGaN⁶⁷, Pt can synergistically function with the semiconductor light absorbers to sustain HER under illumination. Usually Pt was coated on the pristine semiconductor surface by physical vapor deposition under high vacuum. Photocathodes based on planar $p \cdot n^+$ Si at Pt loading of 3-15 μ g/cm² have optimal performance, with an onset potential of 0.4-0.5 V vs. NHE, an photocurrent density of 22-27 mA/cm² at ~0.3 V vs. NHE under AM1.5 illumination of 100 mW/cm².^{36, 56a, 64} The fill factor of the J-V curve degrades significantly if Pt loading is reduced to less than 100 ng/cm².⁶⁸ Since the world's annual Pt production is less than 200 ton, the feasibility and the scalability of PEC water splitting demands efficient photocathodes at Pt loading of $< 100 \text{ ng/cm}^2$.

Table 1-3. The comparison of HER catalysts.

HER Catalyst	Loading (mg/cm ²)	Tafel Slope (mV/dec)	η_{HER} (mV) @J (mA/ cm ²)	Electrolyte	Synergetic Light Absorbers
Pt ⁶⁹	N/A	30	25 mV@20 mA/cm ²	0.5M H ₂ SO ₄	InP, ⁷⁰ <i>c</i> -Si, ³⁶ <i>a</i> - Si, ^{43, 71} InGaN ⁷²
MoS _x ⁷³	0.28	41	150 mV@10 mA/cm ²	0.5M H ₂ SO ₄	<i>c</i> -Si, ^{59b, 60} InP ⁵⁷
Ni-Mo ⁶¹	1.0	N/A	70 mV@20 mA/cm ²	2М КОН	<i>a</i> -Si, ⁷¹ <i>c</i> -Si ⁷⁴
Co-Ni ⁷⁵	N/A	97.2	70 mV@10 mA/cm ²	6М КОН	N/A
Co-P ⁶⁹	2.0	50	85 mV@20 mA/cm ²	0.5M H ₂ SO ₄	N/A
NiO/Ni ⁶³	0.28	51	80 mV@10 mA/cm ²	1M KOH	N/A
NiFe LDH ^{19b}	N/A	N/A	210 mV@10 mA/cm ²	1M NaOH	N/A
NiMoZn ^{29a}	N/A	300	280 mV@10 mA/cm ²	1M KBi (pH=9.2)	N/A

As for OER catalysts, their stability and activity strongly rely on the *p*H value of electrolytes. Noble metals and their oxides including Ir,⁷⁶ IrO_x and RuO_2^{77} exhibit the highest activity in strong acids. In contrast, Ni- and Co- based non-precious metal oxides are only stable in base solution; nanostructured non-precious metal oxides can reach comparable performance as noble metal and their oxides.^{19a-d, 19f} For OER catalysts working specifically in neutral *p*H solutions, Nocera's group discovered the Co-Pi catalyst;^{19h} its synergistic effect with many semiconductors has been validated in phosphate buffered solution, such as BiVO₄,⁴² α -Fe₂O₃,³³ Ta₃N₅^{51a} and Si.⁷⁸ The practical application of neutral solution PEC systems, however, is hindered by the absence of proper ion exchange membranes.²⁰ In Chapter 6, we will discuss the coupling of NiFeO_x with InGaN nanowires as photoanode for water oxidation. State-of-art OER catalysts are compared in Tab. (1-4).

	Tafel Slope	η_{HER} (mV)		Synergetic Light
OER Catalyst	(mV/dec)	@J (mA/ cm ²)	Electrolyte	Absorbers
IrO _x ^{19a}	47	340 mV@10 mA/cm ²	1M KOH	<i>c</i> -Si, ^{76,79}
IrO_x^{19e}	N/A	300 mV@10 mA/cm ²	0.5M H ₂ SO ₄	α -Fe ₂ O ₃ ⁸⁰
$\begin{array}{l} [Ir(pyalc)(H_2 \\ O)_2(m-O)]_2^{2+} \\ Molecular \\ Catalyst^{81} \end{array}$	118	240 mV@1 mA/cm ²	0.1M KNO ₃ pH=2.6 (adjusted)	α-Fe ₂ O ₃ ⁸²
NiOx ⁸³	33.6	330 mV@10 mA/cm ²	1M KOH	<i>c-</i> Si, ⁸³⁻⁸⁴ BiVO4 ⁸⁵
Co-Pi ^{19h}	N/A	410 mV@1 mA/cm ²	0.1 M KPi (pH=7)	BiVO ₄ , ⁴²
Co-Pi ^{19e}	N/A	420 mV@10 mA/cm ²	1M NaOH	α -Fe ₂ O ₃ , ^{33, 86} WO ₃ , ⁸⁷ <i>c</i> -Si ⁷⁸
CoO _x ^{19e}	N/A	390 mV@10 mA/cm ²	1M NaOH	Fe ₂ TiO ₅ , TiO ₂ , ⁸⁸ BiVO4 ⁸⁵ , <i>c</i> -Si ⁸⁹
FeOOH/ NiOOH(on top) ³⁵	N/A	600 mV@1 mA/cm ²	0.5M KPi (pH=7)	BiVO4 ^{35, 45} BiVO4, ⁹¹
NiFeO _x ⁹⁰	N/A	280 mV@10 mA/cm ²	0.1M KOH	α-Fe ₂ O ₃ , ⁴³ InGaN
NiFe LDH ^{19a}	40	$302 \text{ mV}@10 \text{ mA/cm}^2$	1M KOH	N/A

Table 1-4. The comparison of OER catalysts.

The mechanism and reaction pathways of HER/OER involve the chemisorption and desorption of several reaction intermediates. The catalytic activity in terms of the exchange current density is correlated with the binding energy of the reaction intermediates, while the Tafel slope

is determined by the rate determining step, which could be an electrochemical process or the adsorption/desorption process with no charge transfer.⁷³ For HER, the key reaction intermediate is the chemisorbed hydrogen atom, *H, where * represents the reaction site. The plot of exchange current density versus the free energy of adsorbed hydrogen atom (with respect to the adsorption free energy of gaseous hydrogen) leads to a volcano relationship.⁹² For OER, the key reaction intermediates include *OH and *OOH. Depending upon the *p*H of the electrolyte, elemental reactions of these intermediates may involve H^+ , H_2O , and OH^- .

The HER mechanism in acidic solutions and basic solutions was proposed in Eqs. (1-16)-(1-18) and in Equations (19-21), respectively. The OER mechanism in acidic solutions and basic solutions was proposed in Equations (1-22)-(1-26) and in Equations (1-27)-(1-31).^{59a}

HER in acidic solutions:

Volmer reaction

$$H^+ + e^- \to H \tag{1-16}$$

Heyrovsky reaction (electrochemical desorption)

$$H^+ + * H + e^- \to H_2$$
 (1-17)

Tafel reaction (recombination desorption)

$$*H + *H \to H_2 \tag{1-18}$$

HER in basic solutions:

Volmer reaction

$$H_2 0 + e^- \to H + 0H^- \tag{1-19}$$

Heyrovsky reaction (electrochemical desorption)

$$H_2 O + e^- + H \to H_2 + O H^-$$
 (1-20)

Tafel reaction (recombination desorption)

$$*H + *H \to H_2 \tag{1-21}$$

OER in acidic solutions:

$$* + H_2 0 \to * 0H + H^+ + e^-$$
 (1-22)

$$* OH \to * O + H^+ + e^-$$
 (1-23)

$$* 0 + H_2 0 \to 00H * + H^+ + e^-$$
 (1-24)

$$* 00H \rightarrow * 0_2 + H^+ + e^-$$
 (1-25)

$$* 0_2 \to * + 0_2 \tag{1-26}$$

OER in basic solutions:

- $* + OH^- \to * OH + e^- \tag{1-27}$
- $* OH + OH^- \rightarrow * O + H_2O + e^-$ (1-28)
- $* 0 + 0H^{-} \rightarrow 00H * + e^{-}$ (1-29)
- $* 00H + 0H^{-} \rightarrow * 0_{2} + e^{-}$ (1-30)
- $* \ 0_2 \rightarrow * + 0_2 \tag{1-31}$

1.2.4 On the stability of photoelectrodes

Semiconductor light absorbers may undergo photo-induced corrosion in aqueous solutions. The first scenario is that the thermodynamic equilibrium potential of oxidation (reduction) of the

semiconductor is more negative (positive) than the thermodynamic equilibrium potential of OER (HER) so that the oxidation (reduction) of the light absorber is in competition with OER (HER) for photoexcited holes (electrons). Another scenario is that the semiconductor light absorber may be dissolved or be oxidized by the electrolyte, such as the oxidation of Si by strong base solutions and the dissolution of metal oxides in strong acids shown in Eqs. (1-32) and (1-34). The commercially available light absorbing materials, including c-/a-Si, GaAs, InP, CdZnTe and perovskites including CH₃NH₃PbI₃ and CH₃NH₃PbI_{3-x}Cl_x,⁹³ generally suffer from rapid photoinduced decomposition as photoanodes where the photoexcited holes can oxide the light absorbers instead of driving the sluggish OER. In comparison, the oxidation of metal nitrides are generally sluggish; simultaneous oxygen and nitrogen evolution was observed when (In)GaN thin films or nanostructures were on Sapphire substrate, and the photocurrent became negligible in 2-4 hours compared to the initial photocurrent.⁹⁴ For (In)GaN nanostructures on Si substrate as photoanodes, the etching of Si is catastrophic compared to the etching of (In)GaN, and nitrogen evolution was also detected.⁶⁷ In addition, the polarity of (In)GaN affects the stability of (In)GaN in strong base solution; it has been recognized that GaN surface terminated with N-atoms is attacked by strong base solutions while Ga-atom terminated GaN surface is stable in absence of UV illumination and anodic electric bias.95

$$Si + 20H^{-} + 4H_20 \rightarrow Si(0H)_2^{2+} + 2H_2 \uparrow + 40H^{-}$$
 Equation (1-32)

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$$
 Equation (1-33)

 $2(In, Ga)N + 6h^+ \rightarrow 2(In, Ga)^{3+} + N_2 \uparrow \qquad \text{Equation (1-34)}$

Highly-active catalysts can kinetically protect the light absorbing materials by efficiently extracting the photoexcited charge carriers in a time scale much shorter compared to the time scale

of photoinduced decomposition reaction of the light absorber. This approach has been applied for nitride materials including GaN:ZnO photocatalyst,^{48, 96} Ta₅N₃ photoanode,^{51a} and GaN photoanode^{49b, 49c, 94a} as well as Si photoanodes.⁸³ Another approach to protect light absorbers is to employ a protective layer which also functions as electron/hole transfer layer (ETL/HTL) between the light absorber and the catalyst. Chen *et. al.* demonstrated that photoexcited holes from the valence band of *n*-Si can tunnel through a thin layer of 2 nm ALD-deposited TiO₂ to reach the Ir catalyst layer.⁷⁶ Later, Hu *et. al.* discovered that 44 nm of ALD amorphous TiO₂ can function as a leaky protective layer for Si, GaAs and GaP photoanodes to transfer holes to the Ni catalytic layer on top of TiO₂.⁹⁷ Kenny *et. al.* demonstrated stable O₂ evolution in 1M KOH for 12 h on a *n*-Si with native oxide and 2 nm Ni deposited by sputtering.⁹⁸ Deli Wang's group used ITO layer to protect Si and to transfer holes to assure the OER catalyst NiO_x.⁹⁹ With proper surface functionalization, photoelectrodes can sustain stable hydrogen production for hundreds of hours.⁹⁷

1.2.5 The levelized cost and energy payback time

To compete with major energy sources, the projected hydrogen cost is 2-4 \$/kg.¹⁰⁰ To produce hydrogen in a PEM electrolyzer, the cost is 4-5.8 \$/kg with the $\eta_{electrolysis}$ of 60%-70% by 2014.¹⁰¹ In comparison, the cost of single junction *c*-Si solar panels is ~0.5 \$/Watt, with an efficiency of 16%-20%.¹⁰² (1 \$/Watt = 47 h·\$/kg, assuming $\eta_{electrolyzer}$ =70%) Solar inverters cost ~0.2 \$/Watt to stream electricity into the grid. The cost of current *c*-Si solar panels can breakdown into three aspects, Si/ingot (40%), cell fabrication (~20%) and module assembling (~40%).¹⁰³ Instead of connecting *c*-Si solar panels in series with an electrolyzer, ideally tandem solar cells with sunlight concentrator are more favorable for the PV-electrolyzer approach in terms of efficiency, which makes the cost to skyrocket. The projected cost of PV modules and solar inverters is declining at a faster rate than the cost of electrolyzers. Therefore, the increasing discrepancy between the cost of solar PV and the cost of solar hydrogen from PV-electrolyzer reduces the latter to an inferior position for hydrogen production. In contrast, PEC cells are economically more competitive; the estimated cost of the photoelectrode makes up over 30% of the cost of the whole module, which should include the PEC chamber, gas/liquid piping and the compression/storage of hydrogen gas. Once scaled up, the projected cost of nanostructured semiconductors such as metal oxides and (oxy)nitrides is much lower than that of bulk crystalline semiconductors used for solar PV. Besides, the fabrication of photoelectrodes could be less demanding than the fabrication of PV cells; in the case of a tandem photoelectrode, a whole PV cell without surface passivation to reduce surface recombination and screen printing of metal contacts can be used as the light-absorbing bottom cell of the photoelectrode.

The energy payback time for *c*-Si solar panels is 1.5-3 years depending on the region of installation, while the lifetime is over 20 years.^{102, 104} The fabrication of Si solar cells is energy intensive considering the high temperature processes to get crystalline Si and to make the *p-n* junction; the deposition of a passivation layer or *a*-Si in the case of HIT (*c*-Si/a-Si heterointerface with an intrinsic *a*-Si thin layer) Si solar cells requires high vacuum facilities like chemical vapor deposition chambers. As for PEC cells, fabrication can generally be processed under low temperature, and ideally the surface treatment and catalyst promotion should be conducted electrochemically *in situ* in the PEC chamber. With STH efficiency at ~10%, the energy payback time should be 6-8 years.¹⁰⁵ Extensive study on the stability of photoelectrodes is required to conclude the projected lifetime of photoelectrodes based on each material system (including both light absorbers and catalysts). However, the stability of PEC cells should be guaranteed for a lifetime over 20 years with proper catalysts regeneration *in situ* at night time.

1.3 Organization of this thesis

This thesis is a comprehensive summary and analysis of my thoughts, experiments and conclusions throughout my PhD research. Following up the introduction to PEC solar-to-fuel research in Chapter 1, the content is organized as below.

Chapter 2 focuses on the characteristic technologies for PEC water splitting and general synthetic methods of nanostructured semiconductors as photoelectrodes. A rigorous treatment of several crucial efficiencies is discussed. Besides, the essential parts to construct a practical PEC cell, structural and optical characterization techniques and an objective comparison between vapor-based and solution-based synthetic methods are elaborated in each section.

Chapter 3 discusses the growth of GaN/InGaN nanowire structures by molecular beam epitaxy (MBE). The study on MBE growth of (In)GaN nanowires includes three parts, i) coalescenceinduced defects and GaN layer based on coalescence of nanowires; ii) InGaN ternary nanowires; and iii) design and growth of tunnel junction in nanowires. This part establishes the foundation of growth conditions and the design of structures within nanowires for the following Chapters.

In Chapter 4, a tandem photocathode with InGaN nanowires as the top cell and Si solar cell as the bottom cell is demonstrated. The tunnel junction structure within nanowire discussed in Chapter 3 is used to connect the two cells. The purpose of the tandem photocathode is to facilitate HER in strong acidic condition.

The most distinctive advantage of III-nitrides is that the tunable bandgap of the alloy can cover the full solar spectrum. Therefore, it is crucial to enable the high In-content InGaN alloys as photoelectrodes. In Chapter 5, by probing the challenges facing the growth of high In-content InGaN alloys, we demonstrate an InGaN nanowire photoanode which can absorb deep visible light and sustain a high photocurrent density.

Our discussion on the ideal tandem device to reach a semi-empirical STH of ~28% in section 1.2.2.1 is further extended in Chapter 6. An InGaN-nanowire/Si tandem photoanode with a nearly ideal energy bandgap configuration of 1.75 eV/1.13 eV for tandem devices is realized. The tandem photoanode is also coupled with NiFeO_x cocatalyst for water splitting in strong base electrolyte.

Chapter 7 includes miscellaneous research on photocatalytic CO_2 reduction and CH_4 conversion. The reaction mechanism involving the formation and cleavage of C-H bond is discussed.

Chapter 8 summarizes the work demonstrated in Chapter 2-7 and provides an outlook of the future work to achieve unassisted water splitting in strong alkaline and acidic conditions with a STH of over 20%.

Chapter 2 Critical technologies for PEC devices

2.1 Basic metrics of PEC devices

An ideal PEC device for hydrogen generation requires no external electric bias. Therefore, solar-to-hydrogen (STH) efficiency is the most important metrics of PEC devices. PEC devices buried with multijunction solar cells and catalysts as photoelectrodes can sustain hydrogen generation at zero bias but cannot reveal the fundamental thermodynamic and kinetic properties of the semiconductor-liquid interface. Besides, such PEC devices generally entail formidable high cost and a STH much inferior to the semi-empirical limit of STH (28%) shown in <u>Section 1.2.2</u>. A single semiconductor-liquid interface without buried solid state junctions generally cannot drive hydrogen generation at zero electric bias; its properties can be reflected by other critical metrics such as applied-bias-photon-to-current efficiency (ABPE) and incident-photon-to-current efficiency (IPCE).

2.1.1 Solar-to-hydrogen efficiency

In Chapter 1, we introduced STH for PV-electrolyzer systems by multiplying the solar cell efficiency, the electrolyzer efficiency and the matching efficiency in Eq. (1-8); the STH efficiency can be expressed more succinctly as the ratio of chemical energy in evolved hydrogen to the incident sunlight energy, as shown by Eq. (2-1). Generally, researchers use Xe- or Hg- lamps in the lab as light source; however, caution should be taken that the light source should exactly match AM1.5G sunlight for the zero-bias hydrogen generation efficiency to be STH. In other words, the light intensity should be 100 mW/cm² and the light source should match the AM1.5G solar spectrum, which is defined as the terrestrial solar spectral irradiance at a 37° tilted surface towards the sun according to ISO 9845-1, 1992.

$$STH = \frac{\Delta G_0 \cdot n(H_2)}{P_{incident} \cdot A \cdot T} \times 100\%$$
 Equation (2-1)

where ΔG_o is the change of Gibbs free energy in the water splitting reaction, 237 kJ/mol; $n(H_2)$ is the evolved amount of hydrogen in a duration of time *T*; $P_{incident}$ is the incident light intensity and *A* is the area of the sample under illumination.

In a PEC cell, side reactions including oxygen reduction reaction, the dissolve of materials or contaminates on the photoelectrode and the oxidation-reduction reactions of traces metal ions in water could accompany the water oxidation/reduction half reaction, so it is essential to define the Faradaic efficiency for water splitting, which is the fraction of electrode current facilitating water splitting reaction over the total electrode current. A stable photoelectrode well separated from the counter electrode has a Faradaic efficiency of unity, so its STH efficiency can also be represented by the photocurrent density (J_{ph}) and the incident light intensity ($P_{incident}$) in Eq. (2-2).

$$STH = \frac{1.23[V] \times J_{ph}[^{mA}/_{cm^2}]}{P_{incident}[^{mW}/_{cm^2}]} \times 100\%$$
 Equation (2-2)

STH defined by Eqs. (2-1)-(2-2) is specifically used for solar water splitting. Solar hydrogen generation from chemicals other than water also has the potential to scale up or fits for certain niche applications, but the STH in Eq. (2-1) has to be modified by using the change of Gibbs free energy of the corresponding PEC reactions. The TI solar energy system based on HBr splitting and HBr fuel cell demonstrated a successful prototype for residential application in 1980s.¹⁰⁶ Independent studies using *n*-WSe₂ photoanodes to split HI without external bias reached a stable STH of 5%.¹⁰⁷ Another example is the use of photoanodes for seawater splitting, which produces hydrogen, oxygen and chlorine.¹⁰⁸

2.1.2 Applied-bias-photon-to-current efficiency

The applied-bias-photon-to-current efficiency (ABPE) is a criterion to characterize photoelectrodes which require external electric bias to drive hydrogen generation.

$$ABPE = \frac{(1.23[V] - |V_{bias}|) \times J_{ph}[^{mA}/_{cm^2}]}{P_{incident}[^{mW}/_{cm^2}]} \times 100\%$$
 Equation (2-3)

If the required bias vs. the counter electrode is more than 1.23 V to achieve an appreciable photocurrent, the photoelectrode is categorized as a photo-switch, which is no longer a PEC device for hydrogen generation. Caution should be exerted on against what electrode the bias is applied. In a 3-electrode configuration shown in Fig. 2-1, the electric bias can be applied vs. reference electrode, and the ABPE can be calculated by converting the bias vs. reference electrode to a bias versus NHE, which assumes a hypothetically ideal counter electrode.^{36, 57, 66, 72, 74a, 83, 109} In this case, the overpotential loss on the counter electrode is excluded; the ABPE represents the true power conversion capability of the semiconductor-liquid interface but not that of the whole PEC device. As for research focusing on the design of a single photoelectrode, it is a rigorous approach to evaluate ABPE vs. reference electrode, since a highly efficient photoelectrode with a highly catalytic counter electrode can form a practical PEC cell for hydrogen generation. The ABPE vs. NHE values of state-of-art photoanodes and photocathodes are summarized in Tab. 2-1 and Tab. 2-2, respectively. We noted that the ABPE vs. NHE values of state-of-art photocathodes were generally about 10%, much higher compared to those of photoanodes shown in Tab 2-1. The main reason is that the photoanodes incur an OER overpotential of 300-500 mV, while the HER overpotential is generally in the range of 20-100 mV.



Figure 2-1. The PEC device with 3-electrode configuration.

Table 2-1.	Summary of	of ABPE	vs. NHE	values of	f state-of-art	photoanodes.
	~					1

Photoanode	ABPE vs.NHE	Vonset vs.NHE	$J_{ph}@E_0(O_2/H_2O)$	Electrolyte
p^+ - n Si/75 nm NiO _x ⁸³	2.1%	1.05	30.9	1M KOH
<i>a</i> -Si/ <i>c</i> -Si HIT structure w. sol-gel NiOx ⁸⁴	1.5%	0.96	21.64	1M NaOH
<i>p</i> ⁺ - <i>n</i> GaAs/118 nm TiO ₂ /2 nm Ni ⁹⁷	4.77%	0.634	14.25	1M KOH
Pt-doped Fe ₂ O ₃ /Co-Pi ³³	0.6%	0.5	4.32	1M NaOH
BiVO ₄ /FeOOH/NiOOH ³⁵	1.75%	0.2	4.6	0.5M KPi (pH=7)
TiO ₂ /Fe ₂ TiO ₅ w. CoO _x ⁸⁸	2.7%	0.18	4.1	1M KOH
Ta ₃ N ₅ /TiO ₂ /				
Fh/Ni(OH)x ¹¹⁰	2.5%	0.6	12.1	1M NaOH

Photocathode	ABPE vs.NHE	V _{onset} vs.NHE	$J_{ph}@E_0(H^+/H_2)$	Electrolyte
n^+ -p Si/1.5 nm Pt ³⁶	9.6%	0.56	-28	0.5M H ₂ SO ₄
<i>a</i> -Si/ <i>c</i> -Si HIT structure w. 2nm Pt ⁸⁴	13.26%	0.64	-33.49	1M H ₂ SO ₄
<i>p-i-n a-</i> Si/80 nm TiO ₂ /2 nm Pt ⁷¹	6.0%	0.93	-11.6	0.5M KPi (<i>p</i> H=4.0)
<i>p</i> -InP/TiO ₂ /2 nm Ru ⁶⁶	14.5%	0.73	-37*	1M HClO ₄
<i>p</i> -GaP/5 nm Ga ₂ O ₃ /Pt ¹¹¹	2.9%	0.76	-9.8	1M HClO ₄
<i>p</i> -WSe ₂ /Pt-Ru ¹¹²	7.2%	0.63	-24.5	0.5M K ₂ SO ₄ + 0.2M KPi (<i>p</i> H=4.2)
Cu ₂ O/16 nm Al:ZnO/97 nm TiO ₂ /40 nm RuO _x ¹¹³	1.1%	0.55	-5	0.5M Na ₂ SO ₄ + 0.1M KPi (<i>p</i> H=5)

Table 2-2. Summary of ABPE vs. NHE values of state-of-art photocathodes.

*The photocurrent density of 37 mA/cm² exceeds the theoretical limit of InP, which is 35 mA/cm². Therefore, the ABPE is debatable.

The *J-V* curve of a hypothetical PEC device consisting of a photocathode and an electrocatalytic anode in a 3-electrode configuration is shown in Fig. 2-2a and the *J-V* curve of the same photocathode in a 2-electrode configuration is shown in Fig. 2-2b. The red curves represent the photocurrent density *vs.* applied bias. As for the electrolytic performance of the HER catalyst on the photocathode, the current density *vs.* applied bias against reference electrode is shown by the blue curve on the left side of Fig. 2-2a. As we elaborated in *Section 1.2.3*, the electrocatalytic cathode is made by coating the HER catalyst (the same HER catalyst coupled with the photocathode) onto the degenerately *n*-doped semiconductor (the same type of semiconductor used

in the photocathode). The blue curve on the right side of Fig. 2-2a is the current density *vs.* applied bias of the electrocatalytic anode *vs.* NHE. The ABPE based on bias *vs.* NHE is represented by the shaded region in Fig. 2-2a. In a 2-electrode configuration, the HER and OER overpotentials are indistinguishable; by replacing the photocathode with the aforementioned electrocatalytic cathode we can obtain an electrolyzer; the current density *vs.* applied bias against the anode of the electrolyzer is the blue curve in Fig. 2-2b. The ABPE based on applied bias *vs.* anode is represented by the shaded region in Fig. 2-2b.



Figure 2-2. The characteristics of a hypothetical PEC system measured in (a) a 3-electrode system and (b) a 2-electrode system.

2.1.3 Incident-photon-to-current efficiency

The incident-photon-to-current efficiency (IPCE) is used to identify the external quantum efficiency of photoelectrodes under monochromatic incident light of various wavelengths. Systematic study on a PEC device should demonstrate IPCE at zero bias or essential applied bias

values for universal comparison (*e.g.*, 0 vs. NHE, 1.23 vs. NHE or at MMP) over the interested range of solar spectrum.

$$IPCE = \frac{(J_{ph} - J_{dark})[^{mA}/_{cm^2}]}{P_{incident}[^{mW}/_{cm^2}]} \cdot \frac{1240[V \cdot nm]}{\lambda[nm]} \times 100\% \qquad \text{Equation (2-4)}$$

Though the dark current density is subtracted in Eq. (2-4), negligible dark current density is expected from a stable photoelectrode in the thermodynamic regime of water splitting. External factors like light blocking due to catalyst on the surface of light absorber can shrink IPCE value over the whole spectrum. Ideally, a highly efficient photoelectrode should exhibit rapid increase of IPCE as the incident photon energy exceeds the bandgap and reach a 'spectral plateau' as the incident photon energy increases. In the same principle as solar cells, photoelectrodes with multiple solid state junctions and tunnel junctions cannot be characterized by IPCE. The spectral photo-response of multijunction photoelectrodes can only be probed by measuring each single cell as a PV device separately. Ideally, the convolution of the IPCE spectrum with solar spectrum should be equivalent to the photocurrent density observed at the same applied bias. Nevertheless, it is well known at high incident light intensities, recombination centers in the photoelectrode can be saturated so that the fraction of carrier recombination can be reduced. Therefore, it is not uncommon that the convolution of the IPCE obtained at low light intensity is slightly lower than the photocurrent density obtained at a higher light intensity. The IPCE values and cut-off wavelengths of state-of-art photoanodes (at 1.23 V vs. NHE) and photocathodes (at 0 vs. NHE) are summarized in Tab. 2-3 and Tab. 2-4, respectively.

Photoanode	Peak IPCE@V vs.NHE@λ(nm)	Eg (eV)	λcut-off (nm) of IPCE
p^+ - n Si/75 nm NiO _x ⁸³	>90%@1.93V@500-750nm	1.12	N/A
Pt-doped Fe ₂ O ₃ /Co-Pi ³³	55%-80%@1.23V@300-400nm	2.1	550
WO ₃ /(W, M) /BiVO ₄ /FeOOH/NiOOH ⁴⁵	>90%@1.23V@340-440nm	2.5	500
TiO ₂ /Fe ₂ TiO ₅ w. CoO _x ⁸⁸	>20% @0.4V @350-580nm	2.2	700
WO ₃ ¹¹⁴	50%-70% @0.5V vs. Pt CE @350-420nm	2.6 (indirect)	475
Ta ₃ N ₅ /TiO ₂ /Fh/Ni(OH) _x ¹¹⁰	>90%@1.23V@390-550nm	2.06	625

Table 2-3. Summary of IPCE values and cut-off wavelengths of state-of-art photoanodes.

Table 2-4. Summary of IPCE values and cut-off wavelengths of state-of-art photocathodes.

Photoanode	Peak IPCE@V vs. NHE@λ(nm)	Eg (eV)	λcut-off (nm) of IPCE
<i>n</i> ⁺ - <i>p</i> Si/1.5 nm Pt ³⁶	65%@0V@600-850 nm	1.12	N/A
<i>a</i> -Si/ <i>c</i> -Si HIT structure w. 2nm Pt ⁸⁴	>90%@0V@600-900 nm	1.12	N/A
<i>p-i-n a</i> -Si/80 nm TiO ₂ /2 nm Pt ⁷¹	75%@0.4V@400-500 nm	~1.7	730 nm
<i>p</i> -WSe ₂ /Pt-Ru ¹¹²	>60%@0V@480-580 nm	1.4	920 nm
Cu ₂ O/16 nm Al:ZnO/97 nm TiO ₂ /40 nm RuO _x ¹¹³	>60%@0V@420-470 nm	2.0	610 nm

The IPCE of a photoelectrode reflects the loss of incident photons due to insufficient light absorption and the loss of photoexcited carriers due to recombination. Recombination of photoexcited electrons and holes could occur in the bulk of the light absorber or at the interface

between the light absorber and the HER/OER electrocatalyst. The fundamental advantages of nanostructured semiconductor light absorbers include 1) to decouple the light penetration path from the charge separation path so that light absorption can be significantly enhanced; and 2) to optimize the size of the nanostructure so that the charge diffusion length and the width of the surface space charge region are comparable to facilitate charge separation in the bulk. The light penetration depth is determined by the absorption coefficient, which is $\sim 10^5$ cm⁻¹ for directbandgap materials (InGaN, InP, GaAs) and 10³-10⁴ cm⁻¹ for indirect-bandgap materials (c-Si, GaP, WO₃). The electron/hole diffusion length is an intrinsic property of the light absorbing semiconductor, which is also affected by the crystalline quality and dopant concentrations. Generally the electron/hole diffusion length is in the range of 10-100 nm; while α -Fe₂O₃ is intrinsically limited by the hole diffusion length of 2-4 nm¹¹⁵ and the minority carrier diffusion length in undoped Czochralski c-Si can reach 100's of um and even millimeters. As for the width of space charge region, as shown in Eq. (2-5), is generally in the range of 10's nanometers. Besides reducing light reflection, the aim of semiconductor nanostructures is to reduce the loss due to the drastic discrepancy of light penetration depth, charge diffusion length and the width of the space charge region.

$$W = \sqrt{\frac{2\varepsilon_0 \varepsilon_r \Delta V}{eN_D}}$$
 Equation (2-5)

where $\varepsilon_o = 8.85 \times 10^{-12} C^2 / (m^2 \cdot N)$, $e = 1.6 \times 10^{-19} C$, ε_r : dielectric constant and ΔV : the voltage across the interface.

2.1.4 Charge separation efficiency and catalytic efficiency

As we elaborated in the previous section, one type of energy loss in photoelectrodes is related to the recombination of photoexcited carriers in the bulk of the light absorber, which is referred to as charge separation efficiency; the other loss is related to the recombination of photoexcited carriers at the coupling interface between the light absorber and the HER/OER electrocatalyst; which is referred to as catalytic efficiency.¹¹⁶ By introducing a hypothetical current density, which is light-absorption current density (J_{abs}) defined as the theoretical current density corresponding to the absorbed photons by the light absorber, the relation between the photocurrent density (J_{ph}), charge separation efficiency (η_{sep}) and catalytic efficiency (η_{cat}) can be illustrated by Eq. (2-6).

$$J_{ph} = J_{abs} \cdot \eta_{sep} \cdot \eta_{cat} \qquad \text{Equation (2-6)}$$

Generally, procedures such as electrochemical cycling and thermal annealing are used to promote the formation of chemical bonds between the catalyst and the light absorber, based on which mechanical and electronic properties of the interface between catalyst and light absorber can be tailored; and the interface properties further determine the efficiency and stability of the PEC device. Charge separation efficiency is employed to identify the reaction kinetics of the catalyst-semiconductor interface in the context of electrolyte. As we elaborated in *Section 1.2.3*, sufficient Pt loading can generally facilitate HER to reveal the ultimate performance of light absorbing materials in photocathodes, which equivalents to $\eta_{cat} \sim 1$ for Pt. By replacing the HER catalyst of the photocathode with Pt or directly loading optimal amount of Pt on the photocathode, the charge separation efficiency of the photocathode can be defined as the ratio of the photocurrent density over the light-absorption current density shown in Eq. (2-6), and the catalytic efficiency of a photocathode with the photocurrent after promoted with Pt at essential bias values for universal comparison (*e.g.*, 0 vs. NHE, 1.23 vs. NHE or at MMP) as shown in Eq. (2-7).^{74a}

$$\eta_{sep} = \frac{J_{ph}^{Pt}}{J_{abs}}$$
 Equation (2-6)

$$\eta_{cat} = \frac{J_{ph}}{J_{ph}^{Pt}} \qquad \qquad \text{Equation (2-7)}$$

As for photoanodes, highly reactive hole scavengers are generally used to expedite the oxidation reaction kinetics to achieve the ultimate PEC performance. Therefore, the OER reaction kinetics can be assessed by comparing the photocurrent of the light absorber in the presence of hole scavengers and the photocurrent of the light absorber coupled with the catalyst in the absence of hole scavengers at essential bias values for universal comparison (*e.g.*, 0 vs. NHE, 1.23 V vs. NHE or at MMP), as shown in Eqs. (2-8)-(2-10).

$$J_{ph}^{hole \, scavenger} = J_{abs} \cdot \eta_{sep} \qquad \qquad \text{Equation (2-8)}$$

$$\eta_{cat} = \frac{J_{ph}^{hole \, scavenger}}{J_{abs}}$$
 Equation (2-9)

$$\eta_{cat} = \frac{J_{ph}}{J_{ph}^{hole \, scavenger}} \qquad \qquad \text{Equation (2-10)}$$

The oxidation reactions of hole scavengers such as H_2O_2 ,^{42, 117} Na₂SO₃³⁵ and CH₃OH,¹¹⁸ as shown in Eqs. (2-11)-(2-14), are kinetically more facile and thermodynamically much easier compared with the oxidation of OH⁻ in base solutions or H₂O in acidic/neutral solutions. The charge separation efficiency is defined as the ratio of the stable photocurrent at identical bias without the hole scavenger over that with the hole scavenger. Caution should be exerted that "photocurrent-doubling effect" could occur if the hole scavenger is a strong reducing agent which can inject electrons into the conduction band of the semiconductor as well as consume photoexcited holes from the valence band of the semiconductor under illumination.¹¹⁸⁻¹¹⁹

$$H_2O_2 \rightarrow 2H^+ + O_2 \uparrow + 2e^-, E_o = +0.695 V vs. NHE$$
 Equation (2-11)

$$H_2SO_3 + H_2O \rightarrow 4H^+ + SO_4^{2-} + 2e^-, E_o = +0.172 V vs. NHE$$
 Equation (2-12)

$$SO_3^{2-} + 2OH^- \rightarrow H_2O + SO_4^{2-} + 2e^-, E_o = -0.930 V vs. NHE$$
 Equation (2-13)

$$CH_3OH + H_2O \rightarrow CO_2 \uparrow + 6H^+ + 6e^-, E_o = +0.044 V vs. NHE$$
 Equation (2-14)

2.2 Experimental setup and practical concerns

2.2.1 The PEC chamber

A PEC chamber should have the following functionalities: 1) allowing incident light reach the working electrode with unity light transmission; 2) sealed for analyzing the evolved gases; 3) having suitable ports for the arrangement of working electrode, reference electrode and counter electrode with magnetic stirrer for the study of single photoelectrodes in 3-electrode configuration; and 4) effectively separating working electrode from counter electrode to avoid the oxygen reduction reaction on the cathode side.

The photoelectrode could also be designed for backside illumination to avoid the light blocking issue related to catalyst at the cost that photoexcited carriers are not generated in the vicinity of the semiconductor/catalyst-liquid interface. In this way, the PEC chamber can be designed to expose the backside of the photoelectrode towards the light source.

2.2.2 Equipment for PEC characterization

Equipment required for PEC characterization includes 1) a solar simulator as light source; 2) long/short pass optical filters; 3) a spectrometer for rigid IPCE measurement; 4) an electrochemical potentiostat for cyclic voltammetry (CV), chronoamperometry (CA); chronopotentiometry (CP); open circuit potential (OCP), Mott-Schottky measurement (MS) and electrochemical impedance spectroscopy (EIS); 5) Gas chromatograph for the detection of hydrogen; and 6) reference electrodes.

For a practical prototype, other essential elements of a PEC system include 1) plumbing for the circulation of electrolyte and gas flow; 2) facilities for hydrogen gas collection and compression.

2.3 The fabrication of photoelectrodes

Currently most of photoelectrodes are prepared following these steps: 1) make Ohmic contact on the backside of the photoelectrode sample; 2) connect the back contact with a copper wire by silver paste; 3) cover the backside and edge of the sample with insulating epoxy or tape, with only the photocatalytic front side exposed to the electrolyte. The photoelectrodes for backside illumination requires the fabrication of back contact in the same manner as the deposition of the front contact of solar cells.

2.4 An overview of material synthesis

The material synthesis of photoelectrodes involves the deposition of light absorbing materials, HER/OER catalysts, and protective layers or charge transfer layers at the interface between light absorbers and catalysts. Generally synthetic approaches can be categorized into vapor-based and solution-based processes. As for vapor-based processes, it is inevitable to have sophisticated reaction chambers to control the precursor flow/flux and the substrate temperature during the whole deposition process.

One type of vapor-based processes is physical vapor deposition, which requires high vacuum during the whole deposition process, such as molecular beam epitaxy process, plasma-induced sputtering, electron-beam induced evaporation and laser pulsed deposition. Physical deposition processes are fundamentally dictated by kinetics; however, at elevated deposition temperatures, thermodynamic relaxation could affect the growth process as well. With physical vapor deposition,

highly precise control of hetero-interfaces can be realized; however, the growth rate is slow, generally in the range of 1~10 nm/min. The other type of vapor-based deposition is thermodynamically driven by chemical reactions on the substrate, such as metal organic chemical vapor deposition (MOCVD), plasma-enhanced chemical vapor deposition (PECVD) and atomic layer deposition (ALD). Another technique similar to CVD is spray pyrolysis; in this process, precursor solution droplets are sprayed onto the substrate, followed by vaporization and chemical reaction. Other than ALD, CVD processes and chemical spray pyrolysis can produce high quality crystalline bulk materials at a rate in the range of 20 nm/min to few 100's nm/min depending on the materials. Nevertheless, the alternating purging/pumping cycles in ALD process makes it a suitable technique for high quality atomic coating at a rate much slower than those of physical vapor processes. Vapor-based processes are prevalent in the synthesis of high quality thin films or nanostructures and solid state homo-/hetero- junctions of III-V, II-V and Si, as well as ultrathin metal or metal oxide charge transfer layers/catalysts for PEC devices.

Metal oxides including TiO₂,³⁷ WO₃,³⁴ BiVO₄^{35, 44} and α -Fe₂O₃^{33, 43, 120} can be synthesized by solution-based processes, which include two steps; 1) electrochemical deposition or solution casting on conductive substrate at room temperature and 2) subsequent annealing at elevated temperature. Such simple and low cost processes can be readily scaled up compared with vacuum-based processes. Furthermore, solution-based synthesis has the versatility to incorporate dopant by adding precursors in the solution,^{33, 35, 121} to control the morphology of the nanostructured semiconductors by changing precursors³⁵ or the concentrations and ratios of precursors,³⁴ as well as to change the crystalline status by varying the annealing condition³⁷ and regrowth cycles.⁴³ Our review over α -Fe₂O₃ photoanodes revealed that the champion α -Fe₂O₃ nanostructures in terms of either the onset potential or the photocurrent density at 1.23 V vs. NHE were synthesized by

solution-based processes^{33, 43} despite that tremendous research effort has been focused on the synthesis of α -Fe₂O₃ using ALD,^{41b} spray pyrolysis¹²² and vapor phase deposition^{41a, 123}. Solution-based BiVO₄ outperformed that made by spray pyrolysis as well, though the latter approach enables the formation of gradient *n*-doped BiVO₄ junction to facilitate charge separation.^{35, 42}

Recently, solution-based process witnessed revolutionary progress in perovskite solar cells and organic polymer solar cells. Even though monolithical integration of solution-based metal oxides with perovskite¹²⁴ or organic polymer solar cells^{23c} is prohibited by the annealing process at 450 °C-800 °C for few hours and the instability of perovskite solar cells in aqueous environment, a tandem photoelectrode solely by solution-based synthesis with a STH of 4.3% has emerged.¹²⁵

Given aforementioned advantages of solution-based processes, the importance of vapor-based synthesis for the development of PEC devices cannot be underestimated. Firstly, solution-based processes are limited to the synthesis of relatively homogenous anisotropic nanostructures. High-quality solid state junctions are required to form tandem structures for zero bias hydrogen generation with high efficiency. In the solar cell community, the growth of solid state junctions by vapor-based processes is commercially mature. Secondly, solution-based processes are limited to the synthesis of metal oxides. As discussed in *Section 1.2.3*, the energy bandgaps and band alignments of metal oxides are not optimal for water splitting. Si, III-V and II-V semiconductors with proper surface protective layer and catalysts deposited by ALD or sputtering demonstrated significantly superior PEC performance to metal oxides.^{76, 97-98} Besides, metal nitride alloys whose energy bandgap can cover solar spectrum and with suitable band alignment for water splitting require vapor-based processes.^{51a, 72}

As for the deposition of HER/OER catalysts, solution-based synthesis is the dominant approach, which also promises *in situ* regeneration of catalysts for long-term stability. Solution-

based catalysts can be formed by casting precursor solution and subsequently annealing,^{49b, 49c, 50,} ¹²⁰ *in situ* electrochemical/PEC deposition^{19h, 35, 45, 88} and photodeposition.^{43, 72, 96} In photochemical or PEC deposition, the reduction/oxidation of the catalyst precursors is driven by photocurrent; therefore the nucleation sites of the catalyst particles are determined by the optimal pass of photoexcited charges to the interface, which promises the optimal coupling between the light absorber and catalyst particles.

Vapor-based processes are still required to improve the charge transfer at the interface between light absorber and catalysts and the stability of the light absorbers, such as the deposition of ultrathin conductive charge carrier transfer layer and compact catalytic protective layer, since solution-based processes generally produce dispersed nanostructures but not compact layers.^{64, 97-98} Catalysts such as precious metal or metal oxides formed by vapor-based processes generally requires a substantial amount of loading, as analyzed in <u>Section 1.2.4</u>, which will be further discussed in Chapter 4.

2.5 The characterization of material properties for photoelectrodes

The optical properties of the light absorber in photoelectrode include the absorption spectrum, photoluminescence emission spectrum and photoexcited carrier lifetime measurement. The optical bandgap and absorption coefficient can be obtained by linear-fitting of the absorption edge.¹²⁶ For semiconductors deposited on opaque substrates such as Si and metal foils, the optical bandgap can also be estimated by the photoluminescence (PL) peak. Besides, the crystalline quality can be revealed by the PL peak intensity and the full-width-half-maximum (FWHM) of the PL peak. Strong optical emission indicates low Shockley-Read-Hall (SRH) recombination rate, *i.e.*, low defect density within the energy bandgap and small FWHM indicates little energy bandgap
photoexcited carriers. Such information together with the turnover frequency of the catalyst, the surface density of active sites and the electrocatalytic active surface area enables the design of photoelectrodes on the atomic level.

Structural characterization is essential for nanostructured semiconductors/catalysts and the design of heterostructures. Scanning electron microscopy (SEM), (scanning) transmission electron microscopy ((S)TEM) and electron energy-loss spectroscopy (EELS) in STEM mode are the facilities used for the following research projects in this thesis, 1) the study on nanowire heterostructures and defects in Chapter 3; 2) the research on tunnel junction nanowires, Pt nanoparticle distribution and the amount of Pt loading in Chapter 4; 3) the optimization of InGaN nanowire thickness and the study on In distribution in InGaN nanowires in Chapter 5; and 4) the inquiry on catalytic activities of various crystal facets of GaN in Chapter 7. The corrosion of photoelectrodes can be identified under SEM as well.^{72, 94b}

Study on the X-ray photoemission spectrum (XPS) provides information on the chemical bonding between semiconductor and catalyst.³⁰ XPS results can also reveal elemental compositions of nanostructural surfaces as well as the possible mechanism of activity droop by comparing the sample before and after experiment, such as the analysis of InGaN nanowires in Chapter 5. The analysis on the chemical bonding of HER/OER catalysts also promotes understanding of the origin of catalytic activity.^{59b}

2.6 Summary on the critical technologies for PEC devices

In this chapter, we began with the discussion on the essential metrics to characterize a PEC device, including STH, ABPE, IPCE, charge separation efficiency and catalytic efficiency. Subsequently, experimental facilities and procedures were studied in <u>Sections 2.2 and 2.3</u>. The quality of a PEC device is fundamentally determined by the synthesis of light absorbing materials, HER/OER catalysts and the engineering of the interfaces. In <u>Section 2.4</u>, we identified the compensating features of vapor-based and solution-based synthetic processes in terms of the formation of solid-state junctions, the incorporation of dopants and the control of nanostructures. Critical optical, structural and chemical characterizations of photoelectrodes were discussed in <u>Section 2.5</u>.

Chapter 3 The growth of GaN/InGaN nanowire structures by molecular beam epitaxy

3.1 An overview of III-nitride growth techniques

Ever since the invention of GaN-based blue light emitting diode (LED) by Nakamura in the early 1990s, research on the growth of III-nitrides has been booming. Currently the commercial growth technique for III-nitride LEDs and LDs is metal organic chemical vapor phase (epitaxial) deposition (MOCVD or MOVPE). Other growth techniques include hydride vapor phase epitaxy (HVPE), ALD, MBE, reactive sputtering deposition and laser ablation deposition. Compared to MOCVD, HVPE uses the same nitrogen source by thermally decomposing NH₃ at temperatures above 1000 °C but with GaCl₃ as metal precursor at much higher flow rate. The deposition rate of GaN can reach 0.2-1 µm/min but with high defect densities which is generally not suitable for optoelectronic devices. ALD is a low temperature "self-terminating" CVD process which can produce highly uniform GaN films at extremely slow rates of 1-5 nm/hr. To our knowledge, IIInitrides formed by reactive sputtering deposition and laser ablation deposition have not brought about optoelectronic devices as well. MBE is the only mature technique other than MOCVD which can produce high quality GaN for optoelectronic devices; compared to MOCVD, it has much superior capabilities to control the deposition of multiple layer III-nitride nanostructures by the instantaneous open/close of shutters and provides in situ characterizations such as reflection highenergy electron diffraction (RHEED) and photoelectron spectroscopy. In this study, the growth rate of GaN in a GEN II MBE system is in the range of 2-5 nm/min, about one tenth of that in standard MOCVD systems. Furthermore, as we discussed in Chapter 2, MBE is a physical vapor deposition process dictated by kinetics, therefore the deposition rate of InGaN alloys in our MBE system is also in the range of 2-5 nm/min. Modern MBE system with more efficient N₂-plasma cell can significantly increase the growth rate. The indium composition is restricted to less than 25% in MOCVD due to thermodynamic limit to be discussed in the following context. Emerging growth techniques based on modification of MOCVD and MBE include low pressure remote plasma-enhanced MOCVD, migration-enhanced MBE and metal-modulation-enhanced MBE.¹²⁷ Solution-based synthesis of GaN requires formidable high nitrogen vapor pressure in the range of few GPa's;¹²⁸ even at such conditions, InGaN alloys can hardly form at the reaction temperature over 1000 °C because the In-N bond dissociates at much lower temperature of ~550 °C.

To date, GaN-based materials and devices are generally grown on foreign substrates, such as sapphire,¹²⁹ SiC,¹³⁰ ZnO and silicon.¹³¹ Due to the large lattice and thermal mismatches, the heterostructures typically exhibit very high densities of threading defects as well as rough surfaces,¹³² severely limiting the device performance and reliability. In commercial LED and LD devices, GaN films are grown on sapphire substrate, which exhibit defect densities in the range of 10^8 - 10^{10} cm⁻³ due to the lattice mismatch and low thermal conductivity of the sapphire substrate. Nevertheless, the one-dimensional nanowire structure can accommodate the strain and the thermal conducting issue related to foreign substrates. In this perspective, the growth of nanowire structures on large area foreign substrates like Si makes it viable to obtain high quality single crystalline III-nitrides. Furthermore, prior to the growth of InGaN nanowires, we can promote a buried *p*-*n* junction inside the epi-ready surface of the Si substrate as a bottom cell of tandem solar cells; the growth temperature of InGaN nanowires is lower than 800 °C, which can avoid thermal annihilation of the buried Si *p-n* junction. By growing high quality crystalline InGaN with an energy band gap of 1.75 eV or indium content ~50% as the top cell, the monolithic InGaN/Si heterostructure tandem cell approaches the optimal bandgap configuration of 1.13 eV (bottom cell)/ 1.75 eV (top cell) to reach a theoretical power conversion efficiency of over 38% under

AM1.5G one sun illumination,²² which would be the ideal tandem cell for solar-to-hydrogen conversion discussed in <u>Section 1.2.2.1</u>. To this point, we initiated the study on GaN nanowire coalescence on Si substrate for potential growth of high quality InGaN epilayers on GaN/Si template in Section 3.3. In parallel, we will demonstrate high quality crystalline InGaN nanowires grown on Si substrates with indium content of ~50% as photoanode in Chapter 5; we will further discuss the integration of InGaN nanowire structures as top cell on Si bottom cell as photoanode in Chapter 6.

The synthesis of high In-content InGaN alloys is challenging due to the following factors. Firstly, the lattice mismatch between GaN and InN is ~11%; the strain due to lattice mismatch is responsible for high density of defects during growth, leading to unintentional electron concentration of 10¹⁷ cm⁻³ in InGaN epilayers;¹³³ defects can become the nucleation sites to form In-rich clusters;¹³⁴ besides, the strain between GaN and InN leads to a miscibility gap between InN and GaN, which precludes the random distribution of In and Ga atoms in the lattice under thermal equilibrium. Secondly, the significantly higher vapor pressure of InN as compared to GaN causes facile In desorption from the growth front;¹³⁵ in MBE and MOCVD the growth temperature is tuned in the range of 450-650 °C to reduce the desorption rate of indium, which fundamentally limits the incorporation of indium by conventional MOCVD due to the insufficient thermal dissociation of NH₃; independent research on InN growth by CVD process with high pressure of GPa's has been conducted to combat indium desorption as well.¹²⁸ Thirdly, the difference between the formation enthalpy of InN (ranges from -120 kJ/mol to -140 kJ/mol in literature) and that of GaN (ranges from -150 kJ/mol to -170 kJ/mol in literature) is another factor to drive phase separation thermodynamically.¹³⁶ Lastly and most importantly, the dissociation temperature of the In-N bond ~550 °C in low pressure CVD or vacuum environment necessities the use of N2 or NH3

plasma as nitrogen source to grow InGaN kinetically and to design processes which can compensate thermodynamic effects.

In-rich InGaN nanocrystals with the dimension of ~100 nm is sufficient for light absorption. Even though the scarcity of indium in the earth's crust increases the cost of PEC devices based on InGaN photoelectrodes, it could not preclude the development of In-rich InGaN nanocrystals. A comparison of rare-earth elements indicates that the abundance of indium in the earth crust is one order of magnitude larger than that of tellurium and two orders of magnitude larger than that of platinum,¹³⁷ while cadmium telluride photovoltaics becomes one of the leading thin film technology and Pt-based fuel cells have been developing towards a full-fledged technology.

3.2 The growth of GaN nanowires and InGaN ternary nanowires on Si substrates

We started with the growth of catalyst-free GaN nanowires in a Veeco Gen II MBE system, which consists of six thermal effusion cells for Ga, In, Al, Si, Ge and Mg; a radio-frequency plasma cell for ultrahigh purity nitrogen gas; a substrate heater which is suitable for 3-inch substrates and is equipped with motor for rotation; and an electron gun for *in situ* observation of RHEED patterns, which provides electron beam of ~15 keV. Using a Cryo-Torr Cryopump at 11 K and an ion pump at ~100 μ A, the background pressure is maintained at 3×10⁻¹⁰ Torr in idle condition without liquid N₂ cooling.

Consisted with the growth window identified previously for GaN nanowire growth on Si substrate,¹³⁸ we used a growth temperature of 740 °C, a Ga beam equivalent pressure (BEP) of 8×10^{-8} Torr, a N₂ flow rate of 1 standard cubic centimeter per minute (sccm), and a plasma power of 350 W; the growth duration is 4 hours. As shown in the 45° tilted SEM image of Fig. 3-1a, the GaN nanowires arrays are vertically aligned on the Si substrate, with lengths ~1 µm; top-view

SEM images in Fig. 3-1b-c shows the nanowire diameters in the range of 55-130 nm, and a nanowire density of $\sim 4.0 \times 10^9$ /cm². Subsequently, we grew InGaN nanowires for 3 hours at 590 °C, a Ga BEP of 8×10^{-8} Torr, an In BEP of 8×10^{-8} Torr, a N₂ flow rate of 1 sccm, and a plasma power of 350 W. The 45° tilted SEM image of the InGaN nanowires in Fig. 3-2 shows that the morphology of the InGaN nanowires are irregular compared to GaN nanowires with visible steps on sidewalls. We compared the room temperature (RT) PL spectra of the GaN nanowires and InGaN nanowires as well, using a 325 nm He-Cd laser as the excitation source and the PL emission was spectrally resolved by a high resolution spectrometer and detected using a photomultiplier tube. As shown in Fig. 3-3, the emission peak of the GaN nanowires is at 365 nm, with a FWHM of 7 nm, corresponding to an optical bandgap of 3.4 eV. The emission peak from the InGaN nanowires is of a much lower intensity and the FWHM is much broader. Shown in the inset of Fig. 3-3, the peak from InGaN nanowires is at 560 nm, with a FWHM of 90 nm, corresponding to an optical bandgap of 2.2 eV. The broadening of PL peak indicates that there could be high density of defects or inhomogeneous distribution of indium in the nanowires. By using the bandgap variation equation at room temperature as shown in Eq. (3-1),¹³⁹ the highest local indium content based on the PL emission peak is estimated to $\sim 35\%$.

$$E_q = 3.42(1-x) + 0.77x - 1.43x(1-x)$$
 Equation (3-1)

Note: for the energy bandgap of InN, though 0.77 eV deviates from the well-established value of 0.65 eV, taking the bowing factor into account, this equation holds a reasonable empirical approximation of the energy bandgap of InGaN.



Figure 3-1. SEM images of GaN nanowires. (a) 45° tilted view, (b) top view and (c) high-magnification top view of GaN nanowires.



Figure 3-2. 45° tilted view SEM image of InGaN nanowires.



Figure 3-3. The RT PL spectra of GaN nanowires (red curve) and InGaN nanowires. Inset: the PL peak and FWHM of the InGaN nanowires.

We further characterized the InGaN nanowires by STEM with Energy-dispersive X-ray spectroscopy (EDX) analysis. A FEI Tecnai G² F20 STEM with an accelerating voltage of 200 kV was used to study the distribution of indium within the InGaN nanowire. The STEM image in Fig. 3-4a shows an InGaN nanowire of length ~550 nm. At 50 nm from the top of the nanowire, we chose the orange line across the lateral direction of the nanowire in Fig. 3-4b for EDX line-scan and the distribution of EDX signal intensities from Ga and In is presented in Fig. 3-4d. It is evident that the nanowire has a shell with a thickness of 5 nm with prominent X-ray signals from Ga but negligible signals from In, which confirms that the InGaN nanowire actually has a GaN shell of 5 nm in thickness. To check whether the distribution of indium is uniform inside the InGaN nanowire core, we proceed to fit the experimental EDX distribution of indium and gallium with the hexagonal InGaN-core/GaN-shell nanowire structure shown in Fig3-4c, which is essential because the EDX signal intensities from both indium and gallium vary with 1) the composition of InGaN at the particular position and 2) with the thickness of the nanowire at the same particular position. Our fitting of uniform indium distribution inside the InGaN core leads to the dashed green curve for indium and dashed blue curve for gallium shown in Fig. 3-4d, respectively. It is seen that the experimental data of EDX signal from indium correlates quite well with the fitting, indicating that the actual indium distribution is quite uniform inside the InGaN core, which should preserve a hexagonal cross section. The experimental data of EDX signal from gallium, however is evidently higher towards the edge of nanowires compared to the fitting data, which is consistent with the observed irregular nanowire sidewalls with visible steps shown in the SEM image in Fig. 3-3. Therefore, the GaN sheath is non-uniform in thickness. Furthermore, EDX elemental mapping in Fig. 3-5 further confirms that the indium distribution is relatively uniform within the top 75 nm section of the InGaN nanowire as a high In-content region. For the next 75 nm section beneath

the high In-content region, which is approximately 75-150 nm from the top of InGaN nanowire, the indium composition is dramatically low. We chose another orange line along the growth direction of the nanowire in Fig. 3-5a for EDX line-scan from top to bottom. As shown in Fig. 3-5d, the EDX analysis further validated the boundary of high In-content region at 75 nm from the top of the nanowire. The presence of two InGaN sections with high and low In-content is consistent with the asymmetric broad PL emission peak. More EDX analysis has evidenced that virtually no indium at the bottom of the InGaN nanowire. In conclusion, InGaN-core/GaN-shell structure is spontaneously formed under the specific MBE growth condition, and In-rich region is formed close to top of nanowire.



Figure 3-4. (a) STEM image of one InGaN nanowire; (b) EDX line scans across the lateral direction at 50 nm from the top of nanowire, indicated by the orange line; the yellow box is for drift correction during line scanning; (c) the hexagonal InGaN-core/GaN-shell nanowire structure with uniform indium distribution inside the InGaN core and uniform thickness of the GaN shell for fitting the experimental data of EDX signal intensities from indium and gallium in (d); (d) EDX line scan spatial spectra of the orange line in (b); the black and red curves are X-ray signal counts from indium and gallium, respectively. The green and blue dash lines are fitting spectra based on the InGaN-core/GaN-shell nanowire structure shown in (c).



Figure 3-5. The top 150 nm segment of the InGaN nanowire shown in (a) for EDX elemental mapping of (b) indium and (c) gallium distribution. Line scanning EDX along the vertical direction of nanowire shown in (d); the line chosen for scanning is indicated as orange in (a), and the direction of scanning is opposite to the growth direction, indicated as black arrow in (a). The boundary between high/low indium composition segments in InGaN nanowire is approximately 75 nm from the top of nanowire.

Tourbot *et. al.* has reported similar observation of spontaneously formed InGaN-core/GaNshell structure¹⁴⁰ when InGaN was grown on top of a GaN nanowire basis, which was explained to be driven purely by the elastic relaxation of the strained InGaN. As pointed out by Tourbot¹⁴⁰, a pyramidal shape of In-rich region¹⁴¹ is expected as the Stranski-Krastanov growth of quantum dots, and similar trend is shown in the EDX elemental mapping in Fig. 3-5. To sum up, the spontaneous formation of InGaN-core/GaN-shell structure in the radial direction, and high/low composition InGaN gradient heterostructures along the axial direction is governed by the competitive kinetic incorporation of In and Ga adatoms and *in situ* thermodynamic redistribution of indium inside the nanowire. We will further discuss the PEC performance of such InGaNcore/GaN-shell nanowires, improve the indium distribution uniformity in Chapter 4 and identify the growth conditions for high In-content nanowires without GaN shell in Chapter 5.

3.3 Controlling the coalescence of GaN nanowires

The coalescence of GaN nanowires during MBE growth is a common phenomenon. The nanowire coalescence, accompanying the formation of defects, is usually treated as a detrimental process. Although there are observations that the degree of coalescence is reduced when the growth temperature is elevated, the correlation of coalescence with growth conditions is hardly established. It has been envisioned that such nanowires, through spontaneous coalescence, may lead to high quality, affordable GaN templates¹⁴² on low-cost large-area Si substrates. In this perspective, the propagation of defects during the nanowire coalescence process could impair the potential GaN template on the top.

In this regard, significant efforts have been devoted to coalescing nanowires grown on various substrates. Kazuhide *et al.* demonstrated the growth of GaN layers on nano-columns using sapphire substrates, and found that the overgrown GaN layer was strain-relaxed by X-ray diffraction (XRD)

analysis.¹⁴³ Many other studies also revealed that hexagonal GaN microcrystals^{131g} and GaN layers^{131d, 131f} could be obtained on Si substrates by lateral epitaxial overgrowth (LEO) of nanowires. It was further observed that dislocation densities of GaN films formed by LEO could be reduced by several orders of magnitude from typical dislocation density of ~ 10^9 /cm² to 10^4 - 10^5 in the lateral growth sidewalls.^{129d, 130} In addition, the surface polarity was suggested to be controllable from the coalesced GaN nanowires grown on *r*-plane sapphire.^{129e, 142} However, due to the crystallographic misalignment between coalesced nanowires, various types of defects can propagate and eventually terminate at the nanowire sidewalls during the growth process,¹⁴⁴ recent studies have revealed the presence of extended "zipper" arrays of defects in the coalesced nanowires.^{131b}

In our experiment, catalyst-free GaN nanowires with lengths of ~ 150 nm to 1 μ m were grown on Si(111) and SiO_x by MBE under nitrogen rich conditions. The 2-inch Si(111) wafers were cleaned by standard solvents and subsequently dipped in buffered oxide etch solution (BOE with a 6:1 volume ratio of 40% NH₄F to 49% HF in aqueous solution) for 2 mins to remove the native oxide layer prior to loading into the MBE system. The growth conditions include a substrate temperature of ~ 545 to 740 °C, a Ga BEP of ~ 7×10⁻⁸ to 1.5×10^{-7} Torr, and a plasma power of 350W. Prior to the growth initiation, a thin Ga seeding layer was deposited *in situ* to promote the formation of GaN nanowires. The growth duration was varied from 40 mins to 4 hours to study the evolution of coalescence at different growth stages. In addition to the growth on Si substrates, the low growth temperature of GaN in MBE (500-800 °C) may promise the integration of GaN into Si CMOS; therefore, we also explored the growth of GaN on Si substrate with 100 nm of SiO_x deposited by PECVD. The growth mechanism of GaN nanowires on SiO_x is similar to that on Si substrate.¹⁴⁵ SEM and TEM studies were conducted using a LASEM Hitachi S-4700 system and a FEI Tecnai G² F20 system with an accelerating voltage of 200 kV, respectively.

To realize high quality GaN epilayers, it is important to first develop closely packed and defect-free nanowires, and to control the subsequent coalescence process. It has been well established that the density of nanowires is largely determined in the nucleation stage.^{131a-c} In this study, we have first investigated the effect of growth temperature and N/Ga flux ratio on the nanowire size and density and the resulting impact on the spontaneous coalescence process. GaN nanowire arrays on Si(111) were grown for 4 hours under three different conditions, to tune the nanowire density. Figures 3-6a-c show the top view SEM images. It is seen from Fig. 3-6a-c that, most of the nanowire top surfaces vary from near-perfect hexagons to irregular shapes, due to the increased nanowire coalescence. Shown in Fig.3-6a, the nanowires were grown at 740 °C under 1 sccm nitrogen flux, referred to as Sample A. It has nanowires with diameters of 55-130 nm, lengths of ~0.96 μ m, and a wire density of 4.0×10^9 /cm², with ~30% of the nanowires formed by the coalescence of several nanowires. Shown in Fig.3-6b (Sample B), by gradually increasing the nitrogen flux from 0.3 to 1 sccm during the first 20 mins growth, the nanowires exhibit increased diameters of 100-250 nm, with >50% of nanowires having certain degree of coalescence. Sample C was grown by reducing the growth temperature to 700 °C with other conditions identical to Sample B. It is seen that these nanowires have diameters of 100-360 nm and a nanowire density of 2.6×10^9 /cm², shown in Fig.3-6c, with >95% of nanowires formed by coalescence. The average diameter of nanowires and the corresponding standard deviation are 90 nm and 30 nm for Sample A; 143 nm and 45 nm for Sample B; and 145 nm and 48 nm for Sample C. The increased coalescence (Sample B vs. Sample A) with reducing N/Ga flux ratio is due to the enhanced nanowire density at the nucleation stage, which agrees well with the previous reports that a higher Ga flux at the nucleation stage can induce a higher nanowire density^{131b}. The spacing between the nanowires is further reduced by decreasing the growth temperature, leading to a further enhanced coalescence (Sample C vs. Sample B).



Figure 3-6. Top-view SEM images of (a) Sample A, (b) Sample B, and (c) Sample C grown on Si(111) for 4 hours. Sample B was grown with the use of a low nitrogen flow rate ~0.3 sccm during the first 20 minutes, compared to the 1 sccm used for Sample A. The growth conditions of Sample C are identical to those of Sample B except that the growth temperature was reduced from 740 to 700 °C. It is seen that a lower growth temperature and reduced N/Ga flux ratio can significantly enhance the spontaneous coalescence of nanowire arrays.

TEM and SEM studies were performed subsequently to study the spontaneous coalescence process at different growth stages for Sample C. Figure 3-7a-c show the emergence of coalescence when the growth duration was varied from 40 mins to 4 hours. In Fig. 3-7a, the SEM image of nanowires grown in 40 mins, recognized as the nucleation stage^{131b}, shows nanowires of lengths

of ~150 nm and a density of ~ 3.75×10^{10} /cm², without any coalescence observed in our survey of the nanowire samples. The TEM image of a single nanowire is further shown in Fig. 3-8a, which has a uniform diameter of ~ 20 nm. From the SEM image in Fig. 3-7b, it is seen that the nanowires grown in 2 hours have diameters of ~70 nm, lengths of ~500 nm, and a density of ~ 7.3×10^9 /cm², with coalescence formed due to the tilting of nanowires with respect to the surface of substrates. For nanowires grown in 4 hours, the coalescence between near-parallel close-packed nanowires was also observed, shown in Fig. 3-7c. The average growth rate in the vertical direction is 180 nm/hr, while the nanowire diameters are in the range of 100-360 nm, with a density of 2.6×10^9 /cm². Various coalescence processes during the 4 hours' growth can be clearly identified by the TEM images, shown in Figs. 3-8b-d. It is seen that these coalescence processes, either due to the variation in the growth direction or the enhanced lateral growth, contribute significantly to the increased diameters and reduced densities observed in the SEM images, which are critical to form GaN epilayers.



Figure 3-7. 45° tilted view SEM images of GaN nanowires grown on Si(111) after (a) 40 minutes, (b) 2 hours, and (c) 4 hours growth duration.



Figure 3-8. (a) TEM image for nanowires grown after 40 minutes, showing the absence of any coalescence. (b)-(d) Representative TEM images for GaN nanowires grown after 4 hours, showing coalescence due to variations in the growth direction or enhanced lateral growth. Circles indicate the coalescence interface, and arrows indicate the growth direction of nanowires.

We have subsequently performed high-resolution TEM studies to examine the formation and propagation of dislocations during the coalescence process. Shown in Fig. 3-9a are two coalesced nanowires with a tilting angle of \sim 5°. Threading dislocations are formed at the interface. However, they are localized within ~10 nm above the boundary. The coalescence between two nanowires with a large tilting angle of ~25° is shown in Fig. 3-9b. It is seen that threading dislocations extend along the coalescence interface and are largely confined within the thinner nanowire branch. Twin boundaries can also be identified at the coalescence interface. With continued growth, however, the dislocations can bend toward and eventually terminate at the nanowire lateral surface, driven by the reduction of dislocation line energy. Moreover, the extended "zipper"-like arrays of defects were not observed under this growth condition. As a result, the coalescence interface.



Figure 3-9. High resolution TEM images for two coalesced nanowires with tilting angles of (a) \sim 5° and (b) \sim 25°. Dashed arrows indicate the growth direction of the two coalesced branches. The inset of (a) shows that threading dislocations are localized above the coalescence interface. The inset of (b) shows the propagation of threading dislocations along the coalescence interface (dashed oval) and the twin boundary (dotted oval). The lattice spacing along growth direction is 0.256 nm, labeled in the insets indicating that nanowire growth is along the *c*-axis and strain free.

With the coalescence process identified by the growth on Si substrate, we expect a similar coalescence process for the growth on SiO_x , due to the similar growth mechanism for the nanowire formation on both Si and SiO_x . The SEM images of GaN nanowires grown on Si(111) for 4 hours and SiO_x for 3 hours are shown in Figs. 3-10a-b, respectively. It is seen that, by changing the

substrate to SiO_x , the size and height uniformity of nanowires can be maintained. The alignment between the nanowire growth direction and the substrate, however, becomes more tilted for nanowires grown on SiO_x , due to surface roughness¹⁴⁵. This could provide an advantage for SiO_x in the nanowire coalescence process.



Figure 3-10. SEM images of GaN nanowires grown (a) on Si(111) substrate for 4 hours and (b) on SiO_x for 3 hours. The SiO_x layer is indicated by black arrow in (b). The tilting of nanowires is more pronounced for GaN nanowires grown on SiO_x, due to the surface roughness.

To achieve high quality GaN epilayers on SiO_x, we have developed a multi-stage growth process, which enables the separate optimization of the nanowire density, sizes, and coalescence process. During the initial nucleation and pre-coalescence stage, GaN nanowire arrays were first grown directly on SiO_x using the afore-described optimum growth conditions (for Sample C) for ~ 2 hrs at 700 °C. As we observed from Sample C, most of the coalescence occurs within the first 2 hrs; the lateral overgrowth in the next 2 hrs led to large-diameter nanowires. Herein, we tuned the Ga flux from ~7×10⁻⁸ to ~1.5×10⁻⁷ Torr, the nitrogen flow rate from 1 sccm to ~0.1 sccm, and the growth temperature from 700 °C to 575 °C to further enhance the lateral growth rate. Closely packed nanowires with diameters of ~ 0.3 µm was formed on the SiO_x template, illustrated in Fig. 3-11a. From the lateral view SEM image shown in Fig. 3-11b, the nanowire nucleation and the formation of GaN microcrystals can be clearly identified. To obtain GaN epilayers, we also

decreased the growth temperature~545 °C to further enhance the lateral growth rate after the first 2 hrs of nanowire coalescence. As such, crack-free GaN epilayers is formed directly on SiO_x with only 1 μ m growth thickness, illustrated in Fig. 3-11c. Further shown in Fig. 3.3.6d, the enhanced lateral growth of the microcrystals leads to the formation of GaN epilayers with relatively smooth surface. Detailed studies confirm that the bright spots on the top surface, shown in Fig. 3-11c, are related to the top facet of GaN microcrystals^{131c, 131g}. Such GaN microcrystals can be completely embedded in the GaN epilayers with increased growth duration, leading to superior quality, crack-free GaN epilayers grown directly on SiO_x. Detailed PL studies also showed that both the GaN nanowires and GaN epilayers formed on SiO_x exhibit nearly identical optical properties, further confirming the superior quality of GaN epilayers.



Figure 3-11. (a) Top view and (b) lateral view SEM images of GaN microcrystals grown on SiO_x with a growth temperature of 575 °C during the coalescence stage. (c) Top view and (d) lateral view of GaN epilayers grown on SiO_x with a growth temperature of ~545 °C during the coalescence stage. The SiO_x layer is indicated by the white arrow. The presence of GaN nanowires in the nucleation stage and the subsequent coalescence into microcrystals (a) and smooth epilayers (b) are indicated by dashed lines.

In summary, we have examined the coalescence process of catalyst-free GaN nanowire arrays grown on Si and on SiO_x. By tuning the metal/nitrogen ratio and growth temperature, highly-coalesced nanowire arrays with diameters in the range of 100-360 nm, a nanowire density of 2.6×10^9 /cm², and a growth rate of 180 nm/hr. It was further observed that defects formed at the coalescence interface were localized and terminated on the nanowire surfaces. As a consequence, the resulting GaN microcrystals are nearly free of dislocations. Moreover, by utilizing a two-stage growth process, including nanowire nucleation and coalescence and subsequent lateral overgrowth, we have demonstrated that relatively smooth, high quality GaN epilayers formed directly on SiO_x with an ultrathin (~1 µm) nanowire buffer layer. Further studies on the optimization of GaN

epilayers and their applications in various device applications will be conducted. This work provides a promising approach for the development of high performance GaN-based optoelectronic devices on a Si-platform.

3.4 The design of tunnel junction III-nitride nanowires

In the published literature, most studies on (In)GaN used hydrogen bromic acid (HBr) or hydrogen chlorine acid (HCl) as electrolyte while the focus was on the photoresponse from (In)GaN and its potential as photoanode in strong acidic condition.^{54, 146} (In)GaN photoanodes are stable in HBr solutions, as evidenced by previous publications^{54, 146c-e, 146h, 146j-l, 146o}. However, by changing the electrolyte from HBr/HCl to HClO₄/H₂SO₄/HNO₃ --both InGaN and Si substrate are unstable to perform water oxidation without being kinetically protected by oxygen-evolution catalysts;^{67, 94b, 147} though (In)GaN can be kinetically protected by NiO for water oxidation in strong base solution,49b, 49c, 148 the Si substrate needs to be capsulated to avoid photodecomposition.^{76, 83, 97-98} In contrast, p-(In)GaN could serve as stable photocathodes in strong acids such as HClO₄/H₂SO₄/HNO₃ for water splitting.^{67, 146d} Nevertheless, there is scarcely any study on p-(In)GaN photocathodes because unlike p-GaP and p-InP, it is challenging to realize pdoped (In)GaN and Ohmic contact with p-doped (In)GaN in the absence of native substrates. Currently Mg is used as p-dopant for (In)GaN with an activation energy for ionization in the range of 120-180 meV.¹⁴⁹ Besides, the non-doped GaN by MBE has an electron concentration close to 10¹⁷ cm⁻³, due to nitrogen vacancy defects,^{133b} which has to be compensated to achieve a reasonable hole concentration. Even if p-type (In)GaN with suitable hole concentration can be grown on Si substrate, the carrier transfer between p-doped (In)GaN and Si substrate becomes the bottleneck since neither n^+ -Si nor p^+ -Si can form Ohmic contact with p-doped (In)GaN, as illustrated in the schematics in Fig. 3-12.



Figure 3-12. Band diagram schematics of *n*-Si/*p*-GaN junction and *p*-Si/*p*-GaN junction.

The conduction band offset between *n*-Si (electron affinity: 4.05 eV)¹⁵⁰ and *n*-GaN (electron affinity: 3.5-4.1 eV)¹⁵¹ is small, as shown in Fig. 3-13. Previous studies confirmed the Ohmic contact at the *n*-GaN/*n*-Si heterointerface.¹⁵² Therefore, a tentative approach to address the carrier transport issue from *p*-type InGaN to the Si substrate is to grow n^+ -GaN on n^+ -Si for Ohmic contact with the Si substrate firstly, and to use a tunnel junction for carrier transfer between the *p*-type (In)GaN on top and the n^+ -GaN bottom segment.



Figure 3-13. Band diagram schematics of *n*-Si/*n*-GaN junction.

Tunnel junctions (TJ) are widely used in optoelectronic devices to get negative differential conductivity and in multijunction solar cells as interconnect between adjacent cells. Recently, tunnel junctions were applied for III-nitride based LEDs to achieve uniform hole injection into the highly resistive p-GaN layer.¹⁵³ Herein, we propose the use of tunnel junction in p-type (In)GaN nanowires for water splitting.

In tunnel junction, a space charge layer is formed at the interface between heavily n^+ -doped and p^+ -doped regions, with fixed positive and negative sheet charges on each side, respectively. The space charge dipole can induce a strong built-in electric field, which aligns the conduction band of the n^+ region with the valence band of the p^+ region. Under forward electric bias, the conduction band electron in the n^+ layer can tunnel into the valence band of p^+ layer through the space charge region and recombine with the majority carrier of holes in the *p*-region. The tunneling probability is determined by the space charge layer thickness, the energy band gap which forms the triangle energy barrier, and the alignment between conduction in the n^+ layer and valence band in the p^+ layer, which supplies electrons from one side and available energy states on the other side.¹⁵⁰

However, the p^+/n^+ tunnel junction discussed above has low tunneling efficiency in GaN based optoelectronic devices because of the large bandgap and difficulty to reach high hole concentration in p^+ -GaN. The depletion width for p^+/n^+ GaN junction can hardly be reduced to a thickness close to 6 nm¹⁵⁴. Significant extra forward voltage for LED is consumed by the tunnel junction¹⁵⁵. For efficient tunneling with low voltage consumption, a higher electric field within a thinner tunnel layer is required. One approach to induce high electric field is to use piezoelectric polarization charge at the *c*-plane in metal nitrides. Spontaneous and piezoelectric polarization are intrinsic properties of wurtzite III-nitrides because of the non-centrosymmetric crystalline structures as well as the ionic characteristic properties of III-nitride bonding, as shown in Fig. 3-14. As for a coherent thin InGaN layer formed on GaN, if the top surface of the InGaN/GaN structure is N-faced, *i.e.*, the growth direction is $[000\overline{1}]$, the compressive strain in the InGaN layer produces a piezoelectric field at the InGaN/GaN interface towards the top surface; if the structure is Ga-faced, the piezoelectric field is towards the substrate.¹⁵⁶ The piezoelectric field intensity is proportionally determined by the compressive strain, which in turn is proportionally determined by the indium composition in the InGaN layer. High compressive strain induced by high indium composition can smear the epitaxial relation between InGaN and GaN at the interface leading to defects and reducing the strength of piezoelectric polarization. Based on our previous study on the growth of InGaN dots in GaN nanowires, coherent In_xGa(*1-x*)N quantum dots can be obtained by MBE growth with *x* ~0.4.



Figure 3-14. A stick-and-ball schematic diagram of two types of polarity in wurtzite GaN.^{151c}

The growth direction of GaN nanowires under N-rich condition is along the *c*-axis, as shown in Fig. 3-9. It has been widely accepted that GaN nanowires grown on Si(111) substrate by MBE is N-faced. However, depending on the use of AlN buffer layer or not, and what technique is used

for measurement, Ga-faced^{129d} and mixed polarity¹⁵⁷ have been reported. Measurements based on several techniques can determine the polarity of III-nitride nanowires, including convergent beam electron diffraction (CBED), piezo-response force microscopy (PFM), and resonant X-ray diffraction. Another method to determine the nanowire polarity is to etch nanowires by KOH. The negatively charged OH⁻ ions can attack the N-faced facet, forming pyramidal etched structures or pencil-like tips. In contrast, the etch rate of Ga-faced facet by KOH is very slow and flat surface is formed after etching, because Ga-faced GaN is more stable than N-faced GaN considering the negatively charged triple dangling bonds at the surface of Ga-polar GaN. Herein, we used KOH of 45 w.t. % at 70 °C to etch pristine nanowires for 1 min. Fierce gas bubbles were observed upon dropping the sample into KOH solution, which could be N_2 produced by GaN etching. SEM images before and after etching was shown in Figs. 3-15a-b. Nanowires across the whole sample showed reduced size with pyramidal tips, indicating N-faced polarity. The compressive strain at the InGaN/GaN interface induce piezoelectric polarization towards the direction of $[000\overline{1}]$. Therefore, the piezoelectric polarization induced tunnel junction in nanowires can be designed by sandwiching an InGaN interlayer with n^+ -GaN segment (heavily Si doped) from the bottom and p^+ -GaN segment (heavily Mg doped) from the top.



Figure 3-15. Nanowires (a) before and (b) after KOH etching. Note: the black rods on top of the nanowire sample may be Si debris formed from the edge of the Si substrate and was scattered onto the front surface during the fierce etching process.

To optimize the performance of the tunnel junction, the indium composition in the InGaN interlayer and the thickness of the interlayer should be grown rationally. As for 40% indium, the required thickness of InGaN interlayer to align the conduction band of n^+ -GaN segment with the valence band of the p^+ -GaN is calculated as below. The relation between piezoelectric polarization and strain is expressed in Eq. (3-2).

$$P = e_{33}\varepsilon_z + e_{31}(\varepsilon_x + \varepsilon_y)$$
 Equation (3-2)

with piezoelectric constants e_{33} and e_{31} , the in-plane strain $\varepsilon_x = \varepsilon_y = (a - a_o)/a_o$, and the strain along *c*-axis $\varepsilon_z = (c - c_o)/c_o = -\frac{2C_{13}}{c_{33}}(a - a_o)/a_o$. C₁₃ and C₃₃ are the elastic constants; a_o and c_o are the equilibrium lattice constant of the tunnel layer. So the piezoelectric polarization along the *c*-axis can be determined by Eq. (3-3).

$$P = \frac{2(a-a_o)}{a_o} (e_{31} - e_{33} \frac{c_{13}}{c_{33}})$$
 Equation (3-3)

The piezoelectric polarization can be determined by linear interpolating of the physical properties of GaN and InN in Tab. 3-1. The polarization induced sheet charge density and electric field are determined by Eqs. (3-3) and (3-4).

Table 3-1. Piezoelectric, elastic constants, and spontaneous polarization of GaN and InN¹⁵⁸.

	$e_{31}(C/m^2)$	$e_{33}(C/m^2)$	C ₁₃ (GPa)	C ₃₃ (GPa)	P_{sp} (C/m ²)	$a_o(\text{\AA})$	ε _r
GaN	-0.49	0.73	106	398	-0.029	3.189	10.4
InN	-0.57	0.97	121	182	-0.032	3.533	13.1

$\sigma = P_{pz} - P_{sp}$	Equation (3-3)		
$E_{pz} = \sigma/(\epsilon_o \epsilon_r)$	Equation (3-4)		

where ϵ_o is the permittivity in vacuum, ϵ_r is dielectric constant of the tunnelling layer, and P_{pz} , P_{sp} are the piezoelectric polarization and spontaneous polarization, respectively.

The piezoelectric polarization is calculated to be $P_{pz} = 0.0707 \text{ C/cm}^2$. The difference in spontaneous polarization at the InGaN/GaN interface is $\Delta P_{sp} = 0.0012 \text{ C/cm}^2$ and is opposite to the piezoelectric polarization. Therefore, the total polarization is 0.0695 C/cm², corresponding to

a polarization induced sheet electron concentration of 4.34×10^{13} /cm² and an electric field of $E_{pz} = 6.84 \times 10^{6}$ V/cm. We also calculated the space charge induced electric field in tunnel junction without contribution from the InGaN interlayer based on Eq. (3-5) by taking the effective doping concentration $(\frac{N_A N_D}{N_A + N_D})$ as 5×10^{18} cm⁻³, the average space charge induced electric field is $E_{sc} = 1.24 \times 10^{6}$ V/cm, with the space charge layer width of 27.4 nm.

$$E_{sc} = \sqrt{\frac{E_g(GaN)}{2\epsilon_o\epsilon_r}} \frac{N_A N_D}{N_A + N_D}$$
 Equation (3-5)

The lateral surface of the nanowire could accommodate for the relaxation of a fraction of lateral strain. For a thin InGaN interlayer of 5 nm, assuming 50% of the strain can be retained in nanowires of 30 nm in diameter, the band tilting due to piezoelectric field is 1.71 eV. Including the space charge induced electric field, the tunneling barrier thickness is 8.8 nm in the polarization-enhanced n^+ -GaN/In_{0.4}Ga_{0.6}N/ p^+ -GaN tunnel junction. Besides reducing the tunneling thickness, the tunneling probability could be further increased by the accumulation of electron/hole inside the InGaN interlayer. The energy band diagram of the n^+ -GaN/In_{0.4}Ga_{0.6}N/ p^+ -GaN tunnel junction under equilibrium is shown in Fig. 3-16.



Figure 3-16. The energy band diagram of the n^+ -GaN/In_{0.4}Ga_{0.6}N/ p^+ -GaN tunnel junction under equilibrium.

3.5 Summary on the growth of GaN/InGaN nanowires by MBE

In this chapter, we reviewed the growth techniques for III-nitrides and specifically identified the predominant advantages of plasma-assisted MBE for the growth of InGaN alloys. We studied the structural and optical properties of GaN nanowires and InGaN nanowires grown on Si substrate in the GEN II MBE system. Consistent with our prediction of InGaN phase separation in *Section 3.1*, we observed the InGaN-core/GaN-shell structure spontaneously formed at the top region of nanowires when attempting to grow InGaN nanowires of pure alloy phase. The observation established the foundation for the growth of InGaN in Chapters 4-6. We also studied the growth of GaN epilayers on Si substrates to address the issue of no large-area III-nitride native substrates, which paved the way towards the integration of III-nitride with Si. In *Section 3.4*, we discussed the potential of *p*-type InGaN as photocathode, and proposed the use of an n^+ -GaN/In_{0.4}Ga_{0.6}N/ p^+ -GaN polarization-enhanced tunnel junction to facilitate charge transfer between *p*-type InGaN and the Si substrate. Such tunnel junction has been realized in Chapter 4 and is used in an InGaN-nanowire/Si tandem photocathode for water splitting.

Chapter 4 A monolithically integrated InGaN/GaN/Si adaptive tunnel junction photocathode

An essential component of a solar-hydrogen production system is a high efficiency and highly stable photocathode; wherein photo-excited electrons lead to H₂ generation. The energetic diagram at the semiconductor-electrolyte is illustrated in Fig. 4-1. Over the past decades, extensive studies have been performed to develop photocathodes that can absorb a large part of the solar spectrum and can lead to efficient charge carrier separation and proton reduction.¹⁵⁹ The semiconductor light absorber should have a conduction band minimum (CBM) more negative than that required for hydrogen evolution reaction (HER) (4.44 eV below the vacuum level in solutions of pH=0).¹⁶⁰ This requirement limits the choice of high efficiency semiconductor photocathodes mainly to Si and a few III-V materials, including GaP, InP, and their alloy.^{65, 161} ^{57, 66, 162} Various HER catalysts or protection layers integrated with Si^{59b, 60, 109, 163} exhibited improved performance compared to platinized *p*-Si photocathodes.³⁶ Some other materials have also been studied, but are often limited by either rapid degradation¹⁶⁴ or very poor absorption of visible light.¹⁶⁵ A summary of the ABPE values of state-of-art photocathodes were shown in Tab. 2-2.

To effectively utilize photons within a wide range of the solar spectrum, a dual light absorber with a narrow bandgap material like Si at the bottom and direct wide-bandgap materials on top can provide energetic electrons for H₂ production. However, the design and performance of such multijunction devices is limited by the current matching related issues between the two absorbers, because the carrier collection and extraction is only available on the front surfaces. For such photoelectrodes consisting of dual or multiple light absorbers, although the required external bias can be reduced, the photocurrent density is ultimately limited by the light absorber that provides the smaller maximum photocurrent density.^{41b, 166} Recently, the use of 1D nanostructures, such as

nanowires has been intensively studied, which can enable highly efficient carrier extraction and proton reduction on the large area lateral surfaces.^{36, 56a, 57, 66} To date, however, there have been no reports on such nanowire-based monolithically integrated multi-junction photoelectrodes.



Figure 4-1. The energy diagram at the semiconductor/electrolyte interface of a photocathode.

Note: E_C, E_V: conduction band minimum (CBM) and valence band maximum (VBM), respectively;

E_F: Fermi level across the semiconductor-electrolyte system;

 ΔG^{\ddagger} : kinetic energy barrier for electron transfer process;

 ΔG : Gibbs free energy input for water splitting;

 $E(H^+/H_2)$: standard electrochemical potential for hydrogen evolution half reaction at pH = 0;

 $E(O_2/H_2O)$: standard electrochemical potential for oxygen evolution half reaction at pH = 0;

D_{ox}, D_{red}: empty or occupied energy states corresponding to the oxidized or reduced species of the redox system, respectively;

 ΔV_{FB} : flat-band potential determined by the surface band bending at equilibrium, which is the upper limit of OCP observed in experiment.

Compared to other semiconductor photocatalysts, the band edges of InGaN can straddle water oxidation and hydrogen reduction potentials under deep visible light irradiation, as shown in Fig. 1-5.^{54, 67, 167} We have developed an adaptive double-junction photocathode by integrating InGaN nanowire arrays onto a planar Si solar cell wafer. Schematically shown in Fig. 4-2a, the device heterostructure consists of a planar n^+ -p Si solar cell wafer, 150 nm n^+ -GaN and 600 nm p-InGaN nanowire segments along the axial direction. The top InGaN nanowire arrays, with an indium composition of ~25%, is designed to absorb the ultraviolet and a large portion of the visible solar spectrum. The rest of the photons with wavelengths $< 1.1 \ \mu m$ are absorbed by the underlying planar Si p- n^+ junction. The n-GaN and p-InGaN are connected by an n^{++} -GaN/InGaN/ p^{++} -GaN polarization-enhanced tunnel junction,¹⁶⁸ which enables the transport of photo-excited holes from the p-InGaN to the n^+ -GaN within each single nanowire. The presented device differs from conventional tandem electrodes in that both the top InGaN and the bottom GaN/Si light absorbers can simultaneously drive proton reduction by taking advantage of the lateral carrier extraction scheme of nanowires. Schematically shown in Fig. 4-2b is the energy band diagram along the vertical direction of the heterostructure. Due to the relatively small offset between the Si and GaN conduction band edges and the heavy *n*-type doping, photo-excited electrons of the underlying Si solar cell can readily inject into the n^+ -GaN nanowire segment, as discussed in Section 3.4. A large portion of the injected electrons can drive proton reduction on GaN surfaces, with the rest recombining with holes from the p-InGaN in the tunnel junction. In addition, the large valence band offset of $\sim 2 \text{ eV}$ at the n^+ -GaN/ n^+ -Si heterointerface reflects the photoexcited holes from Si and resembles the back surface field in solar cells, which reduces the surface recombination of photoexcited charge carriers in Si. It is seen that such a unique design, with the use of GaNnanowire/Si as the bottom light absorber, can surpass the restriction of current matching in

conventional dual absorber devices and, at the same time, provide energetic photo-excited electrons to the HER catalyst. Compared to the conventional buried multi-junction light absorbers,^{29a, 42} such adaptive junction can reduce chemical loss by allowing charge carriers with different overpotentials to participate HER/OER simultaneously.¹⁶⁹



Figure 4-2. Design of integrated InGaN/Si photocathode. (a) The schematic of the photocathode formed by InGaN tunnel junction nanowires on n^+ -p Si solar cell substrate. (b) The energy band diagram of InGaN tunnel junction nanowires on n^+ -p Si substrate under illumination. Proton reduction on the lateral surfaces of GaN and InGaN nanowire segments is also illustrated.

4.1 The performance of Si solar cells and the properties of InGaN/GaN tunnel junction nanowires

The n^+ -p Si solar cell wafer was prepared using a standard thermal diffusion process. The front and back side of a double side polished p-doped Si(100) wafers (WRS Materials, thickness: $256 - 306 \mu$ m; resistivity: 1-10 Ω ·cm) was first covered with phosphorus and boron dopants by spin coating, respectively. Subsequently, the sample was baked at 950 °C for 20 mins under a N₂ flow rate of 200 *sccm* in a diffusion furnace. The thermal diffusion process leads to the formation of an n^+ emitter layer and a p^+ electron back reflection layer on the front side and back side of the Si wafer, respectively. The sheet resistivity of the n^+ emitter layer was in the range of 8-14 Ω /sq, corresponding to donor concentrations of $\sim 5 \times 10^{20}$ /cm³. For the p^+ back reflection layer, the sheet resistivity was in the range of 30-60 Ω /sq, corresponding to acceptor concentrations of $\sim 1.5 \times 10^{20}$

/cm³. Such solar cell wafers were used for the MBE growth of InGaN/GaN tunnel junction nanowire arrays. In parallel, Si solar cell devices were realized by depositing Ti/Au metal contact surrounding a window region for illumination on top of the n^+ emitter layer and Ni/Au metal contact on the whole p^+ backside, followed by rapid thermal annealing at 550 °C for 2 mins. The Si solar cell were tested using a LCS-100 Solar Simulator (Newport Oriel) as light source and the light intensity was calibrated to be 100 mW/cm². The *J-V* curves of a *p*-Si solar cell of 0.253 cm² under illumination and dark are shown in Fig. 4-3; the power conversion efficiency of the solar cell is 8.30%.



Figure 4-3. The *J*-*V* curve of the *p*-Si based solar cell under AM1.5G simulated one sun illumination (red curve) and dark (black curve).

InGaN/GaN tunnel junction nanowires were subsequently grown on the n^+ -Si surface of the Si solar cell substrate by the GEN II MBE system. Growth of identical nanowire structures on n^+ -Si substrates was also performed as a control experiment. We have utilized the p^{++} -GaN(20nm)/In_{0.4}Ga_{0.6}N/ n^{++} -GaN(20nm) polarization-enhanced tunnel junction structure designed in Section 3.4. On top of the tunnel junction, ~600 nm *p*-InGaN nanowire was grown. The surface oxide of Si was first removed using buffered hydrofluoric (HF) acid before loading into the MBE
chamber. The substrate was further degassed in situ at ~800 °C before growth initiation. Subsequently, InGaN/GaN nanowire structures were grown under nitrogen rich conditions with the following growth parameters: a nitrogen flow rate of 1.0 *sccm*, a forward plasma power of 350 W, and Ga and In flux in the ranges of 4.5×10^{-8} to 8×10^{-8} Torr and 4×10^{-8} to 8×10^{-8} Torr, respectively. Prior to the deposition of tunnel junction, heavily Si doped GaN nanowire template was grown at 780 °C, which was labeled as *n*⁺-GaN. Then the substrate temperature decreased to 650 °C to enhance the incorporation of indium in the tunnel junction. Si and Mg were used as the *n*- and *p*-type dopants, respectively. The doping concentration of Si was further increased by increasing the Si cell temperature for the *n*-doped layer of the tunnel junction, labeled as *n*⁺⁺-GaN. The tunnel junction consists of 20 nm *n*⁺⁺-GaN, 5 nm InGaN, and 20 nm *p*⁺⁺-GaN. Detailed schematic representations of the studied samples are shown in Fig. 4-4.



Figure 4-4. Schematic illustration of (a) the n^+ -p Si solar cell wafer, (b) the p-InGaN/tunnel junction/ n^+ -GaN nanowires on n^+ -p Si solar cell substrate. The p-InGaN/tunnel junction/ n^+ -GaN nanowires grown on n^+ -Si substrate and n^+ -p Si solar cell substrate have identical structures. The p-InGaN nanowires (red region) consist of six InGaN segments connected by ~15 nm p-type GaN/InGaN short period superlattices to minimize indium phase separation during the MBE growth process and also to facilitate hole transport along the vertical direction of nanowires. The tunnel junction (shaded gray region) consists of n^{++} -GaN (20 nm)/In_{0.4}Ga_{0.6}N (4 nm)/ p^{++} -GaN (20 nm).

The 45° tilted SEM image of nanowires is shown in Fig. 4-5a. It is seen that such nanowires are vertically aligned on the Si substrate, with relatively uniform lengths of ~800 nm and diameters

varying from 50~150 nm. Previous studies revealed that such nanowires were N-polar,¹⁷⁰ which was evidenced in Section 3.3 as well, with their sidewalls being the nonpolar *m*-plane.¹⁷¹ Shown in Fig. 4-5b is the PL emission spectrum measured at RT using a 325 nm He-Cd laser as excitation source, spectrally resolved by a high resolution spectrometer and detected using a photomultiplier tube. The peak wavelength is at 515 nm, corresponding to an average indium composition of ~25% and an energy bandgap of 2.4 eV. Therefore, photoexcited electrons in *p*-InGaN can in principle reduce protons without external bias.¹⁷² In comparison with the InGaN nanowires directly grown on Si substrate shown in Fig. 3-3 of *Section 3.2.*, which has a RT PL emission peak at 560 nm with FWHM of 90 nm, the blueshift of the emission peak from this sample is due to the reduced In flux (8×10⁻⁸ Torr for the sample of *Section 3.2*, and 4.5×10^{-8} Torr for this sample). Meanwhile, the FWHM of 35 nm was much narrower in this sample, which is because of the improved indium distribution uniformity by using the multiple-InGaN-segment growth scheme to combat the long-term diffusion of indium.

The downward surface band bending of *p*-InGaN facilitates the flow of electrons towards the electrolyte. In addition, the accumulation of photoexcited holes in *p*-InGaN and their transport across the tunnel junction can enhance the injection of photoexcited electrons from the n^+ -*p* Si substrate towards the n^+ -GaN beneath the tunnel junction. As a result, the total interfacial resistance at the n^+ -Si/ n^+ -GaN and the tunnel junction is expected to be lower in the presence of *p*-InGaN. In addition to absorbing the ultraviolet and a portion of the visible photons, such nanowire arrays can lead to highly efficient light trapping¹⁷³ and significantly enhance the light absorption of the underlying Si. In the subsequent experiments, the nanowire samples were cut into square shapes with sizes in the range 0.35 to 0.7 cm², and were platinized by a photodeposition process to be discussed in *Section 4.2*.



Figure 4-5. (a) 45° tilted SEM image of InGaN/GaN tunnel junction nanowire arrays. (b) Photoluminescence emission spectrum of the nanowires measured at room temperature; emission peak wavelength is 515 nm and the FWHM of the emission peak is 35 nm.

The structure of the polarization enhanced tunnel junction was evidenced by STEM images in Fig. 4-6. The STEM was performed using a double aberration-corrected FEI Titan Cubed 80-300 STEM operated at 200 kV. Atomic resolution, atomic-number sensitive (Z-contrast) STEMhigh-angle annular dark-field (HAADF) images were obtained using a detector angular range of 63.8-200 mrad. In Fig. 4-6a, the tunnel junction was clearly identified between the bottom n^+ -GaN and top p-InGaN nanowire segments. The atomic-resolution HAADF image in Fig. 4-6b demonstrated that the InGaN interlayer is coherently buried in the n^{++} -GaN and p^{++} -GaN segments on both sides. We further conducted geometric phase analysis (GPA) on the HAADF image in Fig. 4-6b to reveal the strain in the tunnel junction structure. Figure 4-6c shows the distribution of inplane compressive strain within the InGaN interlayer and at the InGaN/GaN interfaces. The epitaxial InGaN interlayer, corresponding to the yellow region, endures an in-plane compressive strain up to 5%, while the white box at the bottom indicates strain relaxation towards the sidewall of the nanowire.



Figure 4-6. (a) STEM image of a *p*-InGaN/tunnel junction/ n^+ -GaN nanowire; (b) High resolution STEM image of the polarization enhanced tunnel junction structure; (c) geometric phase analysis (GPA) of the image in (b).

4.2 Photodeposition of Pt nanoparticles on InGaN/GaN tunnel junction nanowires with structural characterization

We have developed a photodeposition recipe to form Pt nanoparticles on the surface of InGaN/GaN tunnel junction nanowires. The solution-based deposition process was conducted in a sealed glass reactor with a quartz lid. The sample was immersed in a mixed solution of methanol (12 mL) and deionized water (50 mL). 20 μ L of 1mM chloroplatinic acid hydrate (H₂PtCl₆·*x*H₂O, 99.9%, Sigma Aldrich) was used as Pt precursor. A UV-enhanced 300 W Xenon lamp (Bulbelectronics, USA) was used to shine light from the top quartz lid. Under illumination, photo-

excited holes from nanowires were consumed by methanol while the Pt precursor was reduced to form Pt nanoparticles on the surface of nanowires.

The distribution of Pt nanoparticles on the surface of *p*-InGaN tunnel junction nanowires were further characterized using STEM. Elemental mapping by electron energy-loss spectroscopy (EELS) in STEM mode was done with the N K, In $M_{4,5}$, Ga $L_{2,3}$, and Pt $M_{4,5}$ -edges and the spectrum imaging technique. Weighted-principal component analysis (PCA) was applied to the spectrum images for noise-reduction of the Ga-, and Pt-signals in their respective elemental maps using the MSA plugin implemented within DigitalMicrograph by HREM Research Inc. A fairly uniform distribution of Pt nanoparticles on the InGaN/GaN nanowire surfaces can be clearly seen in Fig. 4-7a. Detailed STEM analysis, shown in Fig. 4-7b-c, reveals that the crystalline Pt nanoparticles have diameters of 2 to 3 nm. The tunnel junction is identified in Fig. 4-7c. It is seen that nearly identical Pt nanoparticles were deposited on both sides of the tunnel junction, *i.e.* the p-(In)GaN and n^+ -GaN nanowire segments. Therefore, HER can occur on both sides of the tunnel junction provided there are photo-excited electrons. The even distribution of Pt nanoparticles along the nanowire is most evident in the Pt elemental map in Fig. 4-7d. Pt nanoparticles both on the nanowire side surfaces and on surfaces viewed in projection are visible, with direct correspondence to the brightest features in Fig. 4-7a confirming them as Pt nanoparticles. Based on STEM survey, we can estimate the Pt loading amount is $\sim 3 \,\mu g/cm^2$.



Figure 4-7. (a) STEM image of an InGaN tunnel junction nanowire with Pt nanoparticles. The white arrow indicates the growth direction. (b) High resolution STEM image showing Pt nanoparticles uniformly distributed on the *p*-InGaN segment of the nanowire. (c) High-resolution STEM image showing Pt nanoparticles were formed on both sides of the tunnel junction. The red arrow indicates the tunnel junction. (d) Composite elemental map of Pt and Ga from the selected area (purple square frame) in (a), showing an even surface coverage with Pt nanoparticles along the nanowire that corresponds with the bright features in (a); scale bar, 100 nm; green, Pt; red, Ga.

The solution-based photodeposition of Pt nanoparticle has several advantages over physical vapor deposition processes generally used in literature, such as electron beam evaporation or sputtering. Firstly, photodeposition can facilitate relatively dispersed and uniform Pt nanoparticles of 2-3 nm on the lateral surface of nanowires; in contrast, other solution-based depositions

generally form Pt of 5-10 nm;^{56a, 174} even sputtering system with dedicated mass-selective nanoparticle deposition facilities can only reduce Pt nanoparticle size to 5nm.⁶⁸ Secondly, other than the photodeposition method, Pt nanoparticles can only formed on the tip of nanowire structures. Lastly, the matrix solution for photodeposition can be recycled for continuous deposition process by adding proper amount of H_2PtCl_6 periodically, which can be easily scaled up.

The photodeposition process is not applicable for Si since photoexcited charge carriers in Si is not energetic enough for the reduction of the precursor H₂PtCl₆ to Pt nanoparticles. To test the PEC performance of n^+ -p Si with Pt as photocathode, the n^+ -p Si substrate was rinsed by buffered HF solution for 2 mins to remove the surface oxide layer, and was subsequently loaded into an electron beam evaporation chamber to deposit Pt of ~5 µg/cm². We also deposited ~5 µg/cm² Pt on ITO substrate (12 Ω ·cm from Sigma Aldrich) by electron beam evaporation as well.

4.3 The PEC performance of the InGaN/GaN/Si adaptive tunnel junction photocathode

The photoelectrochemical (PEC) reaction was conducted in 1M HBr solution, with InGaN/GaN nanowires, silver chloride electrode (Ag/AgCl) and Pt as the working, reference, and counter electrode, respectively (Supp. Info. S8). A 300 W Xenon lamp with an AM1.5G filter was used as the light source, with incident light intensity ~130 mW/cm². Linear sweep voltammogram (LSV) of platinized InGaN tunnel junction nanowires on n^+ -Si substrate were conducted, shown in Fig. 4-8a. For InGaN tunnel junction nanowires grown on n^+ -Si substrate, the onset potential, corresponding to a photocurrent density of -2 mA/cm² is at $V_{NHE} = -0.08$ V. With more negatively applied potential, the current density increased with or without illumination. In this regime the platinized nanowires behave as a HER catalyst. The very small onset potential and high resistance

is largely due to the nanowire surface depletion effect¹⁷⁵ and the resulting poor current conduction, schematically shown in the inset of Fig. 4-8a. In Fig. 4-8b, the Tafel plot for the InGaN tunnel junction nanowires with Pt nanoparticles in dark shows an onset potential of -75 mV vs. NHE and a Tafel slope of 100 mV/dec; the Tafel plot of the ITO with 5 μ g/cm² Pt shows an exchange current density of 0.2 mA/cm² and a Tafel slope of 50 mV/dec. The relatively inferior performance of the nanowire sample compared to the platinized ITO indicates the presence interfacial resistance in dark.



Figure 4-8. (a) The change of current density with applied voltage versus NHE for InGaN tunnel junction nanowires grown on n^+ -Si substrate in 1 M HBr solution under dark (fully filled black squares) and 1.3 sun of AM1.5G illumination (fully filled red circles). ITO substrate (12 $\Omega \cdot \text{cm}$) with 5 μ g/cm² Pt deposited by electron beam evaporation was tested under identical conditions as a reference, represented by the curve with half-filled green circles. The inset shows the lateral band diagram of *n*-GaN. (b) The Tafel plots for InGaN tunnel junction nanowires grown on n^+ -Si substrate in 1 M HBr solution under dark (fully filled black squares) and platinized ITO electrode (half-filled green circles).

The LSV of platinized InGaN tunnel junction nanowires on n^+ -p Si substrate and platinized n^+ -p Si solar cell wafer are shown in Fig. 4-9a. The platinized n^+ -GaN nanowires on n^+ -p Si substrate is also shown for comparison. Drastically improved performance, however, was measured when InGaN tunnel junction nanowire arrays were integrated on the n^+ -p Si solar cell

wafer. Illustrated by the red curve in Fig. 4-9a, under illumination, the onset potential of InGaN tunnel junction nanowires on n^+ -p Si substrate is at $V_{NHE} = 0.5$ V (for the same current density of -2 mA/cm^2). The significantly enhanced onset potential of photocurrent confirms the additional photo-voltage provided by the underlying Si solar cell. A saturated photocurrent density of -40.6 mA/cm^2 is reached at $V_{NHE} = 0.26$ V and remained constant with more negative bias. The photocathode requires an external bias $|V_b|$ versus counter electrode to drive the overall water splitting. Therefore, the ABPE was calculated using the following equation,

$$ABPE = \frac{|J[mA/cm^2]| \times (1.23V - |V_b|)}{130 \ [mW/cm^2]} \times 100\%$$
(1)

where V_b is the applied potential versus an ideal counter electrode.¹⁷⁶

Illustrated in Fig. 4-9b, a maximum ABPE of 8.7% was obtained at $V_{NHE} = 0.33$ V. The maximum ABPE was also verified to be the same in a 2-electrode PEC system with Pt wire as the counter electrode. It is worthwhile mentioning that, among the many samples we investigated, variations of the saturated photocurrent density were within 2 mA/cm², and the maximum ABPE was obtained at V_{NHE} between 0.25 V and 0.35 V. These variations are likely related to the sample surface preparation conditions and other factors. In this experiment, the total photon flux that can be possibly absorbed by GaN/InGaN and Si is 3.51×10^{17} photon/(s·cm²). Therefore, the saturated photocurrent density of -40.6 mA/cm² corresponds to an average IPCE of 72.3% over the solar spectrum from 280 nm to 1100 nm. In a 3-electrode PEC system, the polarization curves of photocathodes in 1 M HNO₃ were found to be nearly identical to those obtained in 1 M HBr. In addition, under concentrated solar illumination, we observed a drop in the ABPE, which is likely caused by bubbling resistance¹⁸ and limited mass diffusion of protons at the semiconductor-liquid interface.



Figure 4-9. (a) The change of current density with applied voltage versus NHE for InGaN tunnel junction nanowires grown on n^+-p Si substrate in 1 M HBr solution under dark (fully filled black squares) and 1.3 sun of AM1.5G illumination (fully filled red circles). ITO substrate (12 Ω -cm) with 5 µg/cm² Pt as a reference, represented by the curve with half-filled green circles. The changes of current density with applied bias for n^+ -GaN nanowires grown on n^+-p Si substrate (fully filled blue diamonds) and for platinized n^+-p Si solar cell wafer (fully filled purple triangles) are also shown for comparison. The inset shows the lateral band diagram of n^+ -GaN under the electron current from the Si solar cell substrate. (b) ABPE of the photocathode formed by InGaN tunnel junction nanowires on n^+-p Si substrate.

In the presented double-band photocathode, the photocurrent density generated by the top *p*-InGaN nanowire absorber is estimated to be ~ -5 mA/cm². The equivalent circuit diagram of the double-band photocathode is shown in Fig. 4-10. To verify the effect of top *p*-InGaN nanowire segments, we tested platinized n^+ -*p* Si and *n*-GaN nanowires grown on identical n^+ -*p* Si substrate to compare with the *p*-InGaN tunnel junction nanowires, as shown by the polarization curves in Fig. 4-9a. The saturated photocurrent density of *n*-GaN nanowires on n^+ -*p* Si substrate is 35 mA/cm², higher than the current density of 23 mA/cm² from platinized n^+ -*p* Si, but lower than the current density of 40.6 mA/cm² obtained from *p*-InGaN tunnel junction nanowires on n^+ -*p* Si substrate. With the incorporation of nanowires, the measured saturated photocurrent density can greatly surpass that of the platinized n^+ -*p* Si. The underlying reason has been investigated. The electron current from the Si solar cell substrate can be injected directly to the n^+ -GaN nanowire

segment, schematically shown in Fig. 4-2b, due to the small conduction band offset between Si and GaN. The significantly increased electron concentration in GaN nanowires can reduce the depletion region width and thereby the resistance,¹⁷⁵ illustrated in the inset of Fig. 4-9a. Moreover, electrons can readily migrate to the surface of GaN nanowires for proton reduction, due to the reduced surface band bending and the highly uniform Pt nanoparticle coverage on the nanowire surfaces (see Fig. 4-7). Therefore, the superior performance of n^+ -GaN nanowires on n^+ -p Si substrate compared with platinized n^+ -p Si can be attributed to the anti-reflection effect, enhanced carrier extraction of n-GaN nanowires, and improved semiconductor/Pt/electrolyte interface (GaN/Pt/electrolyte versus Si/Pt/electrolyte). The performance of the photocathode was further improved with the incorporation of p-InGaN nanowire segments on top of n^+ -GaN with the assistance of the polarization-enhanced tunnel junction, which is due to the reduced HER resistance and interfacial series resistance when p-InGaN is activated under visible light. Evidently, the unique lateral carrier extraction of 1D nanowires can significantly enhance proton reduction and, in doing so, also surpass the limitations of current matching required by conventional multijunction planar photoelectrodes.^{42, 177} Moreover, the InGaN tunnel junction nanowire arrays play a critical role in enhancing the performance of the underlying Si solar cell, due to the enhanced light absorption, efficient carrier extraction and reduced surface recombination.



Equivalent circuit diagram of the photocathode

We have further studied the stability of the integrated InGaN/Si photocathode. InGaN nanowire photocathode can exhibit a relatively high level of stability at a bias close to the equivalent HER potential. Shown in Fig. 4-11a, the current remains nearly constant and no significant degradation was measured for the duration of 3 hours. The chemical stability of defect-free III-nitride nanowire photocatalyst has been previously reported and has been explained by the strong ionic bonding characteristics, compared to other III-V semiconductors, which can lead to the absence of surface states in the fundamental energy bandgap.^{54, 178} In this experiment, we have also observed rapid degradation of some InGaN/Si photocathodes. It is further noticed that in these samples the performance degradation is related to the shift of the onset potential, rather than the reduction of the saturated photo-current density. During the epitaxial growth of GaN nanowires on Si, a thin (~2 nm) SiN_x layer may form.^{131e, 179} The formation of such an amorphous layer, however, highly depends on the surface preparation conditions of the Si substrate, which may contribute to the observed variations in the device stability.

Figure 4-10. The equivalent circuit diagram of the double-band photocathode under illumination. The photodiodes, n^+/p Si and *p*-InGaN/electrolyte, represent the photovoltages from the buried n^+-p Si junction and the *p*-InGaN/electrolyte semiconductor-liquid junction. The current sources, $J_{ph,1}$ and $J_{ph,2}$, represent the photocurrent densities generated from Si and InGaN respectively.

Finally, to evaluate the Faradic efficiency, we have analyzed the H₂ generation from the monolithically integrated photocathode using a gas chromatograph (Shimadzu-8AI) equipped with a thermal conductivity detector. Shown in Fig. 4-11b, the photocurrent density and the H₂ evolution was measured simultaneously at $V_{NHE} = 0.26$ V. The slight difference in the operation voltage compared to the maximum efficiency shown in Fig. 4-9b is related to sample variations. The Faraday efficiency was calculated using the following equation.

$$\eta_{Faraday} = \frac{2 \times n_{H_2}(t=T_0)[\mu m ol] \times 10^6 \times F}{\int_0^{T_0[s]} I[mA] \cdot dt \times 10^3} \times 100\%$$
(2)

where *F* represents the Faraday constant (96485 *C/mol*), *I* is the measured current, T_0 is the time duration, and n_{H2} is the total amount of H₂ produced. By correlating the measured current with H₂ production, the Faraday efficiency was derived to be in the range of 97% to 105% during the measurements (~1.5 hr). Considering the error bar (~10%) of H₂ sampling and analysis, it is concluded that near-unity Faraday efficiency can be achieved.



Figure 4-11. (a) Stable photocurrent for 3 h at an applied bias of 0.06 V versus NHE under 1.3 sun of AM1.5G illumination. (b) H_2 generation at an applied voltage of 0.26 V versus NHE under 1.3 sun of AM1.5G illumination. Red dots represent the amount of H_2 evolved at different times, the black curve represents photocurrent and the blue curve is the theoretical amount of H_2 versus time based on the photocurrent, by assuming a 100% Faradaic efficiency.

In conclusion, we have shown that, by exploiting the lateral carrier extraction scheme of 1D nanowire structures, the generation of equal numbers of charge carriers in the bottom and top junctions is no longer required, thereby providing tremendous flexibility in optimizing the design and efficiency of multi-junction photoelectrodes. Such an adaptive tandem cell can also be designed as a photoanode to perform water oxidation.

4.4 Summary on the monolithically integrated InGaN/GaN/Si adaptive tunnel junction photocathode

In this chapter, we demonstrated a monolithically integrated InGaN/Si photocathode with an ABPE of 8.7%. Though the use of n^+ -GaN/InGaN/ p^+ -GaN polarization-enhanced tunnel junction in nanowire could surpass the restriction of current matching, the onset potential of the photocathode is 0.53 V vs. NHE at -1 mA/cm², mainly determined by the n^+ -p Si, which exhibited a V_{oc} of 0.525 V in a solar cell. The contribution from the InGaN nanowires was to significantly reduce the HER resistance, to enhance the charge separation efficiency and to increase the light absorption. Besides, the photodeposition of Pt nanoparticles provided a solution-based process of high scalability.

Compared to state-of-art photocathodes summarized in Tab. 2-2, the main disadvantage of the InGaN/Si photocathode is the relatively small onset potential. One approach to improve the onset potential of the InGaN photocathode is to capsulate the n^+ -GaN base and the tunnel junction by stable insulating materials to obstruct the path of photoexcited electrons from the n^+ -p Si to the electrolyte for HER reaction, which will build up the photovoltage from both the n^+ -p Si and the p-InGaN nanowires/electrolyte junction. Besides, the insulating layer can protect the underlying Si and the GaN/Si interface, making the photocathode more stable. In such a scenario, current matching between Si and InGaN is required, and the photocurrent density would be restricted by

InGaN. Another alternative is to eliminate the bottom n^+ -GaN base and to deposit a semitransparent metal layer of <5 nm as tunnel junction at the interface between the n^+ -Si and p-InGaN nanowires, as shown in Figs. 4-12a-b. Ultrathin thin metal layers including Au, Ag, and Al were widely used as tunnelling layer between the top cell and the bottom cell of tandem organic solar cells. Hiramoto¹⁸⁰ and Yahimov¹⁸¹ demonstrated that with an ultrathin Au or Ag layer (thickness of 5 to 10 A) between two stacking cells in series, the open circuit voltage can almost double those of the single cells. Our attempt of using a semi-transparent Ti layer of 3 nm as tunnel junction between the n^+ -p Si and p-InGaN nanowires (without the n^+ -GaN base) revealed that the photovoltage can be improved to 0.77 V vs. NHE at -1 mA/cm² at the sacrifice of J_{ph}, which is -14.8 mA/cm² at 0 V vs. NHE, as shown in Fig. 4-12c. The ABPE is 6.6% at the MPP of 0.51 V vs. NHE. However, the onset potential of the tandem photocathode with the Ti (3 nm) tunnel junction is much inferior to the expected total photovoltage from InGaN and Si, which should be over 1.5 V. One reason could be the recombination of photoexcited carriers at the p-InGaN/Ti junction, which necessities the use of an AlGaN electron blocking nanowire base. The J_{ph} of -14.8 mA/cm² is much lower than the theoretical limiting J_{ph} of ~22 mA/cm² from an InGaN (1.75 eV)/Si (1.12 eV) structure, because 1) the light reflection and absorption of the Ti metal layer and 2) the low indium content in the InGaN nanowires (high energy bandgap of $\sim 2 \text{ eV}$). The development of high In-content InGaN nanowires will be discussed in Chapter 5, and the design of tunnel junction at the interface of Si and InGaN will be discussed in Chapter 6 for tandem photoanode.



Figure 4-12. Schematic illustration of the proposed InGaN-nanowire/Si photocathode with a semi-transparent metal layer as the tunnel junction. (a) A schematic of the device structure and illustration of the photon management enabled by the metal reflector. (b) The energy band diagram of the tandem photocathode. (c) The LSV of an InGaN-nanowire/Si photocathode with 3 nm Ti as the tunnel junction.

Chapter 5 High In-content InGaN nanowire photoanodes

5.1 The current status of photoanodes

Since the pioneer work of Fujishima and Honda using a TiO₂ photoelectrode to produce H₂ under ultraviolet (UV) illumination,¹⁰ metal oxide semiconductors have been extensively studied for solar-to-hydrogen generation in the past four decades. To date, however, the realization of highly efficient photoelectrodes using metal oxide semiconductors has remained elusive, due to several fundamental limiting factors. Stable metal oxides such as TiO_2 and $SrTiO_3^{182}$ have energy bandgaps >3 eV; therefore only the UV photons (<4% of the solar illumination) can be harnessed to drive the water splitting reaction. Although some metal oxides including $BiVO_4^{44a}$ and Cu_2O^{164} have bandgap energies of 2.1-2.4 eV, they are not stable in strong acids or base solutions required for PEC water splitting. In addition, some other visible light responsive metal oxides are limited either by the very poor conductivity and the presence of high defect densities (*e.g.*, $Fe_2O_3^{183}$) or by the poor light absorption capability (*e.g.*, WO_3^{184} and NiO_x^{185}). For most metal oxide photoanodes, the photo-response cuts off at ~550 nm; $^{34-35, 186}$ cuprous oxide (Cu₂O) is the only metal oxide which can provide photocurrent under deep visible light up to 600 nm,¹¹³ but it has not been studied as photoanode, mainly due to the unsuitable band alignment for water oxidation and poor stability. To date, the reported photocurrent densities of metal oxide photoanodes, even with various hole scavenging agents, ^{35, 42, 117-118} are limited to 4.6 mA/cm² under AM1.5G one sun illumination.^{33, 35,} ¹⁸³ Albeit other semiconductors, including Si, GaAs, InP, InGaP₂ and perovskites have been designed as photoanodes, their practical applications have been often limited by the stability issue and, in some cases, the unsuitable electronic energy band structures.^{19b, 97, 187} State-of-art photoanodes based on a-(c-)Si, GaAs, and metal oxides are summarized in Tab. 2-2.

5.2 Potentials and Challenges of InGaN photoanodes

Recently III-nitride semiconductors have been intensively studied for PEC water splitting. Compared to conventional metal-oxides, they offer several unique advantages: 1) The direct bandgap of InGaN can be tuned from 0.65 eV to 3.4 eV by simply varying the indium incorporation, which, together with their superior light absorption capability and excellent charge carrier transport properties, promise a theoretical solar-to-electricity conversion efficiency up to 62% for multijunction solar cells;¹⁸⁸ 2) the conduction band minimum (CBM) and valence band maximum (VBM) of InGaN are suitable for water splitting with an indium composition up to 50%, which correspond to an energy bandgap of ~1.7 eV;¹⁶⁷ 3) the strong ionic bonding of In-N and Ga-N makes InGaN a stable photoelectrode in electrolytes.^{54, 72, 94a, 146k, 172} To date, however, the best reported InGaN photoelectrodes only produced photocurrent densities (J_{ph}) less than 3 mA/cm² under AM1.5G one sun illumination.^{146k, 146n, 189} Efforts in enhancing the indium incorporation lead to the formation of extensive defects and dislocations, due to the large difference (~11%) in lattice constants between InN and GaN.¹⁹⁰ Recently, significantly enhanced photocatalytic activities have been reported for InGaN nanowires, ^{54, 72, 94a, 172} due to the drastically reduced defect densities and the efficient charge carrier separation. The performance of such nanowire devices, however, still suffers severely from the formation of indium-rich nanoclusters, due to the solid phase miscibility gap between InN and GaN, which not only limits the absorption wavelength but also enhances carrier recombination loss.^{146b, 191} Moreover, under typical epitaxial growth conditions, such nanowires generally form InGaN-core/GaN-shell structures with a GaN shell thickness of 5–20 nm irrespective of indium-composition,^{54, 140, 192} due to the higher surface desorption rate of In than that of Ga.¹⁹³ As a consequence, the extraction of minority carriers is

severely limited by the presence of a large bandgap GaN shell. To date, only a J_{ph} of sub-mA/cm² was observed under AM1.5G one sun illumination.¹⁹⁴

For water splitting on photoanodes, the promotion of water oxidizing catalysts is essential to facilitate the oxygen evolution half reaction as well as to stabilize the semiconductor anodes. Meanwhile, sacrificing agents were used to probe the light absorption and charge separation properties of photoanodes.^{35, 42} Independent studies demonstrated that bare GaN suffers from photodecomposition in 1 M KOH or 0.5 M H₂SO₄ solutions,^{67, 94b, 147} while GaN can be stabilized by NiO nanoparticles in 1 M KOH solution for water splitting.^{49b, 49c, 94a, 148} In this study, 1 M HBr solution was used and bromide ions were oxidized on the InGaN photoanode, as shown by the schematic representation in Fig. 5-1. One of the fundamental challenges facing the application of III-nitrides for solar-to-hydrogen conversion is the synthesis of InGaN nanostructures for high photocurrent.^{146c, 194} We focus on the design of InGaN nanowire photoanode to achieve effective absorption of deep visible light photons and efficient separation of photoexcited charge carriers.



Figure 5-1. The schematic representation of the PEC device.

5.3 The growth and characterization of high In-content InGaN nanowires

We have performed a detailed investigation of the growth and characterization of indium-rich InGaN nanowires with significantly suppressed phase separation. The absence of GaN-like shell structures is confirmed by structural and optical characterization. Such nearly homogeneous indium-rich InGaN nanowires were grown directly on degenerately *n*-doped 3" Si(111) substrates (0.001-0.005 Ω ·cm) by a Veeco GEN II PA-MBE system. The Si substrates were cleaned using buffered hydrofluoric (HF) acid and rinsed by deionized water before loading into the MBE chamber. Prior to growth, the Si substrates were degassed *in situ* at ~800 °C. The growth conditions include the substrate temperature of 500-690 °C, a Ga BEP of 2-8×10⁻⁸ Torr, an In BEP of 3.5-7.5×10⁻⁸ Torr, a Ge dopant cell temperature of 1000-1050 °C, a N₂ flow rate of 0.3-1 *sccm* and a plasma power of 350-400 W. The use of radio-frequency plasma nitrogen source can efficiently produce atomic nitrogen species independent of the substrate temperature; the flux of atomic nitrogen species is precisely controlled by the nitrogen flow rate and plasma power.

Schematically shown in Fig. 5-2a, a degenerately *n*-doped GaN nanowire template (with height ~100 nm) was first grown on Si substrate, which can promote the formation of *n*-doped InGaN nanowires with controlled structural and optical properties. Subsequently, multiple cycles of InGaN (~150 nm)/GaN (~20 nm) were grown, shown as a single InGaN segment in the schematic of Fig. 5-2a. Germanium was used as the *n*-type dopant considering that the similar atomic radii of Ge compared to those of Ga or In facilitates substitutional doping. Previously reported catalyst-free InGaN nanowires were generally synthesized under nitrogen-rich conditions, with the formation of InGaN/GaN core-shell like structures.^{54, 140, 192} In this work, in order to achieve homogeneous indium-rich InGaN nanowire structures, we have utilized a multiple cycle

growth scheme for the InGaN, with thin GaN domains introduced as diffusion barriers to prevent strain-induced segregation effects cumulating along the growth front. We have also optimized the growth parameters and their impact on the structural, optical and photoelectrochemical properties of InGaN nanowire photoanodes.

In contrast to the conventional nitrogen-rich growth conditions used to promote nanowire growth, we have demonstrated that the use of nearly unity metal/nitrogen flux ratio, together with a low substrate temperature, can significantly suppress the formation of indium-rich nanoclusters. The epitaxial growth conditions for three representative InGaN nanowire samples, labelled A, B, and C, are shown in Tab. I. Both Sample A and Sample B have three cycles of InGaN/GaN while Sample C has seven cycles. Sample A was grown at a relatively high substrate temperature of 660 $^{\circ}$ C with a N₂ flow rate of 1 standard cubic centimeter per minute (sccm). The corresponding SEM image is shown in Fig. 5-2c. It is seen that the nanowires are vertically aligned on the substrate, with the lateral sizes in the range of 70 to 100 nm. Room temperature photoluminescence spectrum from the nanowire samples were obtained using a 405 nm diode laser as the excitation source, a high-resolution spectrometer to resolve the emission light spectrally, and a photomultiplier tube to detect the emitted light. Shown by the red curve in Fig. 5-2b, the photoluminescence emission is centered at 525 nm, with an estimated average indium composition of 28% using Eqn. (3-1). In order to enhance the indium incorporation, Sample B was grown at a relatively lower substrate temperature of 595 °C and with increased indium flux and reduced Ga flux. This leads to increased nanowire coalescence and increased diameters (in the range of 120-250 nm), shown in Fig. 5-2d. A clear redshift in the photoluminescence emission was measured, shown by the green curve in Fig. 5-2b, which spans from ~500 to 600 nm. The relatively broad spectral linewidth (FWHM ~90 nm) is due to the formation of extensive indium-rich nanoclusters, resulting in large inhomogeneous broadening. Such nanoclusters can lead to significant carrier confinement, thereby reducing the photocurrent density of the nanowire photoelectrodes.¹⁹⁵

	InGaN growth			N ₂ flow rate
Sample	temperature ($^{\circ}C$)	$\begin{array}{c} BEP_{In} \\ (\times 10^{-8} \ Torr) \end{array}$	$\begin{array}{c} BEP_{Ga} \\ (\times 10^{-8} \ Torr) \end{array}$	(sccm)
А	660	3.5	6.0	1
В	595	7.5	2.0	0.5
С	520	7.5	2.0	0.5

Table 5-1. Growth conditions of InGaN nanowire array samples.



Figure 5-2. Optical and structural properties of InGaN nanowire arrays. (a) Schematic of the InGaN on GaN nanowire structure grown on Si substrate. (b) Room temperature photoluminescence spectra of InGaN nanowire arrays in Sample A (red curve), Sample B (green curve) and Sample C (blue curve) under the excitation of a 405 nm diode laser. The 45° tilted SEM images of InGaN nanowire arrays in (c) Sample A, (d) Sample B, and (e) Sample C.

Through extensive studies of the effect of growth temperature and N₂ flow rate, we have observed that indium phase separation can be significantly suppressed by growing InGaN

nanowires at a low substrate temperature (~520 °C) and by using nearly unity metal/N₂ flux ratio. Shown by the blue curve in Fig. 5-2b, the photoluminescence emission peak of Sample C is centered at ~670 nm, corresponding to an average indium composition of ~50%. The spectral linewidth is ~70 nm, which is narrower than that of sample B and the previously reported InGaN multiple quantum well structures (λ ~640 nm, and FWHM > 100 nm).¹⁹⁶ The SEM image of Sample C is shown in Fig. 5-2e. The nanowire diameter is increased to ~300 nm. The prevalence of surface texturing on the side wall of InGaN nanowires increases the effective surface area.

As mentioned above, we have grown multiple cycles of InGaN (~150 nm)/GaN (~20 nm) to form InGaN nanowires. The incorporation of In is a kinetic process under a growth temperature below the thermodynamic equilibrium critical temperature for miscibility of GaN and InN.¹⁹⁷ The incorporated In undergoes long-range diffusion, forming high In-content clusters towards the front growth surface.¹⁹⁸ In nanowire structure, the long-range In diffusion leads to the strain-induced segregation of In at the growth front of nanowires, as described by composition pulling effect, and we have observed that when continuous InGaN growth was conducted, In-rich cluster formed at the top of nanowires, and the bottom part of nanowires had very low In-content. Generally GaN/InGaN/GaN double heterostructures were used to get high In content and to improve the uniformity of In distribution.^{190b} The purpose of the GaN domains in the growth process is to compensate the long-range diffusion of incorporated In and to trap the In species.¹⁹⁹ Here we optimized the growth duration of very thin GaN domains (~20 nm in thickness) to prevent the diffusion of incorporated In towards the top of the nanowire as well as to compensate the In diffusion inside the GaN domains to form relatively uniform InGaN along the growth direction of nanowires. Structural properties of the InGaN nanowires of Sample C were studied by aberrationcorrected scanning transmission electron microscopy (STEM), elemental analysis using energy

dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS). Our TEM survey of nanowires revealed the nanowires have one majority phase with relatively uniform In along the growth direction without the presence of pure GaN domains above the bottom n^+ -GaN template, as shown in Fig. 5-3.



Figure 5-3. STEM-HAADF image and EDX map of several nanowires from Sample C, overlaying the Ga (red) and In (green) distributions from their respective La peaks, also showing the absence of pure GaN domains.

Furthermore, the STEM high-angle annular dark-field (STEM-HAADF) image of an InGaN nanowire is shown in Fig. 5-4a. Elemental mapping over the nanowire by EELS was further performed and the In composition was quantified according to the methods described elsewhere.²⁰⁰ The indium-content map (normalized to thickness in projection) displayed in pseudocolor in Fig. 5-4b shows similar variations as the STEM-HAADF image in Fig. 5-4a, indicating the absence of

an InGaN/GaN core-shell structure. Also from Fig. 5-4b, the average In composition is estimated as ~50% within the bulk of the nanowire. While there are some deviations towards the nanowire surface, the In composition locally remains high at ~30% close to the surface. Some instances of composition fluctuations are evident in Sample C, such as the atomic ordering (alternating indiumrich/gallium-rich *c*-planes) prominent on one side of the InGaN nanowire in Fig. 5-4c, or resemblance of phase segregation at the top sidewall in Fig. 5-4a. The coexistence of such nanoscale phase separation processes in a single nanowire, while remaining spatially isolated, suggests that the driving force promoting atomic ordering indeed simultaneously suppresses phase separation.²⁰¹ It is also noteworthy to mention that the nanowire presented in Fig. 5-4a has a growth axis along < $10\overline{11}$ >, as shown in the image FFT in the inset of Fig. 5-4c. A majority of other nanowires examined in STEM also exhibit a non-*c*-plane growth axis (such as < $10\overline{12}$ > or < $10\overline{10}$ >). Additional EDX point analysis from various lateral positions on a separate InGaN nanowire revealed only small variations of In compositions, shown in Fig. 5-5.



Figure 5-4. STEM study on InGaN nanowires in Sample C. (a) STEM-HAADF image of an InGaN nanowire viewed along { $1\overline{210}$ } zone-axis, showing evidence of contrast at sidewalls due to the strong surface texturing. (b) The thickness-projected indium-content map derived using STEM-EELS spectrum imaging, displayed in pseudocolor, indicative of relatively uniform distribution of indium in the nanowire (~50% in the bulk, ~30% at the near-surface region). (c) High-magnification image of the region in the red dashed box in (a) highlighting the presence of atomic ordering along *c*-axis direction. Additional inset shows the image's Fast-Fourier Transform (FFT) confirming various crystallographic directions.



Figure 5-5. EDX analysis of the near-surface and bulk region composition of a representative InGaN nanowire from Sample C. The locations where spot spectra were collected and quantified based on the ratios of the In L_{α} and Ga K_{α} peaks are labeled as red, blue and yellow squares, and the indium composition of each spot was shown in identical color, respectively.

The mechanism to form the relatively homogeneous InGaN alloy nanowires in PA-MBE is correlated with the particular growth conditions. The incorporation of In into nanowires is a subtle result of the dynamic equilibrium between In-N bond dissociation, facile In desorption and the exchange reaction of In with Ga during the deposition. The growth temperature of 520 °C is lower than the dissociation temperature of In-N bond (~550 °C), leading to relatively low In volatility. With a III/V ratio close to unity, the thermodynamics favor the growth of nanowires while the low In volatility eliminates the formation of GaN shell in nanowires due to decreased surface desorption. Further decreasing the N₂ flow rate or increasing the In flux suppresses the formation of nanowires and also leads to the presence of In droplets.

To further confirm the absence of GaN-like shell structure surrounding the InGaN nanowire, we have quantified the elemental composition of the top few nm's of InGaN nanowire surfaces by X-ray photoelectron spectroscopy (XPS). A VG-ESCALAB3 MKII XPS system equipped with a Mg K_{α} X-ray source of the beam size of 2-3 mm was used to obtain the XPS spectra of Sample C before any PEC experiment. The survey scan in Fig. 5-6a confirmed the presence of both In and Ga on the surface of InGaN nanowires. High resolution XPS spectra in Figs. 5-6b-d revealed that the In composition of the top few nm's of the nanowires is > 40%, which is consistent with the In composition of 50% determined by the room temperature photoluminescence spectra. It is therefore evident that the In_{0.5}Ga_{0.5}N nanowires exhibit nearly homogeneous indium distribution, and contrary to previous findings,¹⁹ the high In-content nanowires do not exhibit a pure GaN shell.



Figure 5-6. XPS spectra of as grown InGaN nanowire arrays in Sample C. (a) The survey scan confirmed the presence of both Ga and In on the surface of the nanowires, energy step size: 1 eV. High-resolution scans of the spectra of (b) In 3d, (c) Ga 2p, (d) Ga 3d / In 4d and (e) N 1s. In (b) the fitting curves include two satellite peaks related to In $3d_{5/2}$, shown by the blue and purple curves, energy step size: 0.05 eV. In (d) contributions of the Ga 3d and In 4d spectra were deconvolved in the fitting. Quantification of the In-to-Ga ratio based on the XPS spectra confirmed the indium composition on the top few nm's of InGaN nanowires is >40%.

5.4 PEC properties of In_{0.5}Ga_{0.5}N nanowire photoanode

The PEC cell consists of the nanowire working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode inside a sealed quartz reactor. The Ag/AgCl reference electrode has a double-junction configuration to minimize chloride ion contamination in the electrolyte. Saturated KCl solution was used for the Ag/AgCl reference electrode in the inner junction. The outer junction protects the reference electrode with an intermediate solution of 10% KNO₃ while the inner tube contains saturated KCl solution. The equilibrium potential of the reference electrode

constantly stayed at +0.197 V *vs.* NHE during the experiment. An Interface 1000 electrochemical station (Northern Materials) was used throughout this study. The backside of the Si substrate was covered with an alloy of Ga-In eutectic (Sigma-Aldrich) and subsequently connected with a copper wire by silver paste to form Ohmic contact. After drying in air, the backside and edge of the sample were covered with insulating epoxy, with only nanowires on the growth front exposed for PEC reaction in solution. A solar simulator (Newport Oriel) was used as light source and the light intensity was calibrated to be 100 mW/cm² at the position of the InGaN nanowire photoelectrode for all linear sweep voltammogram (LSV) and chronoamperometric experiments in this study. A 375 nm long pass filter was used to confirm the contribution to photocurrent from InGaN, whose transmission spectrum was shown in Fig. 5-7.



Figure 5-7. The normalized transmission spectrum of the 375 nm long pass filter.

PEC properties of the InGaN nanowire samples were subsequently investigated in 1 M HBr solution under the three-electrode configuration. The applied bias *vs*. Ag/AgCl has been converted to applied bias *vs*. NHE in this study. Hydrogen evolution occurred at the Pt counter electrode and bromide ions were oxidized at the photoanode; the half reactions on each electrode was shown by

Eqs. (5-2) and (5-3). The PEC performance of Samples A, B, C and a pure GaN nanowire sample was compared in Fig. 5-8. In Fig. 5-8b, the dark current density from the photoanode made from Sample A was 3.5 μ A/cm² at 1.2 V vs. NHE. Under illumination, the photocurrent density (J_{ph}) took off at -0.2 V vs. NHE and reached a saturated value of 0.4 mA/cm² at 0.35 V vs. NHE, which increased by ~30% compared to a pure GaN nanowire photoanode shown in Fig. 5-8a. The photocurrent dropped to 0.2 mA/ cm^2 after adding the 375 nm long pass filter, confirming that the InGaN nanowire segments only contributed ~50% of the photocurrent, with the rest being produced by GaN. For Sample B, the J_{ph} increased to 1.33 mA/cm^2 at 1.2 V vs. NHE and the contribution from InGaN increased to ~87% in Fig 5-8c, which is attributed to the reduced GaN potential barrier in Sample B. Shown in Fig. 5-8d, the J_{ph} of Sample C reached 7.3 mA/cm² at 1.2 V vs. NHE, with the contribution from InGaN of 88%. The J_{ph} of Sample C measured at 1.2 V vs. NHE is nearly a factor of twenty times higher than that measured for Sample A. Such an unprecedentedly high photocurrent for an InGaN photoanode is attributed to the significantly enhanced carrier extraction due to the elimination of a GaN-like shell structure and more efficient absorption of deep visible light due to the relatively high (~50%) indium composition in Sample C.

$$2Br^- \rightarrow Br_2 + 2e^-, E_0 = +1.09 V vs. NHE$$
 Equation (5-2)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow, E_o = 0 \text{ vs. NHE}$$
 Equation (5-3)



Figure 5-8. The change of current density with applied voltage *vs.* NHE for (a) non-doped GaN nanowire photoanode. Figures b-d) are the change of current density with applied voltage *vs.* NHE for InGaN nanowire photoanodes made from Sample A, Sample B, and Sample C in 1 M HBr solution under AM1.5 illumination of 100 mW/cm² (red solid curve), with 375 nm long pass filter (dashed curve) and dark (black solid curve), respectively. The scan was performed at a rate of 20 mV/s.

We have also studied the wavelength dependent photo-response of InGaN nanowire photoanodes (Sample C) in 1 M HBr solution. Shown in Fig. 5-9, Sample A can only utilize UV photons and visible photons up to 450 nm; Sample B has photo-response up to the 550 nm but the IPCE is only ~10% in the visible range, which might be because of high defect density, consistent to the low photoluminescence emission and broad FWHM. In contrast, the IPCE spectrum of Sample C exhibits a plateau of ~40% from 380 nm to 442 nm, and then begins to drop when the excitation wavelength is redshifted. At 650 nm, close to the band-to-band room temperature photoluminescence emission peak, the IPCE is 12.8%. At 750 nm, the IPCE is 2.2%, and the photo-response becomes negligible at wavelengths >750 nm. For comparison, the IPCE of previously reported metal oxide photoanodes showed cut-off wavelengths ~550 nm for hematite,^{33, 186, 202} 500

nm for BiVO₄,³⁵ and 450 nm for WO₃.^{34, 203} For photocathodes made by Cu₂O,¹¹³ the cut-off wavelength is 600 nm. Clearly, the presented InGaN nanowire photoanode can extend the photo-response of previously reported metal oxide photoanodes by ~200 nm, *i.e.*, from 550 nm to 750 nm, enabling the majority of visible light photons to be harvested.



Figure 5-9. Incident-photon-to-current efficiency (IPCE) of the InGaN nanowire photoanodes made from Sample A (reproduced from Ref. [54] with permission), Sample B and Sample C at 1 V vs. NHE in 1 M HBr solution. A 300 W Xenon lamp with monochromatic filters was used as the excitation source for the IPCE experiment.

To evaluate the stability of the InGaN nanowire photoanode, chronoamperometric experiments were conducted at 1.2 V vs. NHE under AM1.5G one sun illumination for a period of 4 hours. Shown in Fig. 5-10, the photocurrent dropped by 25% over 4 hours. Gas samples were manually taken from the sealed PEC chamber and injected into a gas chromatography system with a thermal conductivity detector (Shimadzu GC-8AI) to evaluate the amount of evolved H₂. About 175 μ mol H₂ was produced in 4 hours. After 1 hour's illumination, the Faradaic efficiency was calculated to be in the range of 97% and 105%. Considering an error bar of ~5% due to manual gas injection, it is concluded that nearly unity Faradaic efficiency for the InGaN nanowire

photoanode is achieved. The turnover number, which is defined as the molar ratio of evolved H_2 to $In_{0.5}Ga_{0.5}N$, was estimated to be ~110 after 4 hours' illumination.



Figure 5-10. H₂ generation on the InGaN nanowire photoanode made from Sample C at 1.2 V vs. NHE under AM1.5G illumination of 100 mW/cm². Red dots represent the amount of H₂ produced at the sampling time; the black curve represents photocurrent over time; and the blue curve is the theoretical amount of H₂ over time based on the photocurrent, by assuming a 100% Faradaic efficiency. The sample area is ~0.4 cm².

The elemental and chemical composition of the InGaN nanowire arrays after the stability test of 4 hours was further studied by XPS. The XPS spectra of the InGaN nanowire arrays before and after the stability experiment in 1 M HBr were compared in Fig. 5-11a. No evident change can be observed in the XPS spectrum after the PEC reaction, indicating that the surface properties of InGaN nanowires have remained largely unchanged during the experiment. In Fig. 5-11b, detailed analysis of the high resolution XPS spectrum with the binding energy in the range of 13-23 eV revealed that ~5% of bromine was present on the sample surface after the experiment, which could be related with the oxidation of Br⁻ on the surface of InGaN nanowires. The residual bromine on the InGaN nanowire surface could be one reason for the PEC performance degradation over time.



Figure 5-11. a) Comparison of the XPS spectra of the InGaN nanowire arrays in Sample C before (red curve) and after (black curve) the 4 hours' stability test under illumination. b) Fitting of the high resolution XPS spectra revealed the emergence of Br 4s spectrum after the experiment, represented by the dashed blue curve. The content of Br was quantified as \sim 5% after the experiment.

5.5 Summary on the In_{0.5}Ga_{0.5}N photoanode

In summary, we have demonstrated the epitaxial growth of superior quality InGaN nanowires with In compositions as high as 50%, which can exhibit nearly homogeneous In distribution and are free of GaN-like shell structure. We have further shown that the photocurrent density of such InGaN nanowire photoanodes can be dramatically enhanced from ~0.4 mA/cm² to ~7.3 mA/cm² at 1.2 V *vs.* NHE under AM1.5G one sun illumination in 1 M HBr. At 650 nm, the incident-photon-to-current-efficiency (IPCE) of the InGaN nanowire photoanode is >10%, surpassing those of previously reported metal oxide and metal nitride photoelectrodes.^{33-35, 51a, 113} Compared to the previously reported metal oxide photoanodes, the presented InGaN nanowire photoanode can extend the photo-response by ~200 nm, *i.e.*, from 550 nm to 750 nm. Moreover, H₂ evolution with a nearly unity Faradic efficiency was measured for a duration of four hours. The InGaN nanowire photoanode can be directly applied in a HBr, HCl or HI solar fuel cell system.¹⁰⁶⁻¹⁰⁷ By loading suitable oxidation reaction co-catalysts, it is expected that the InGaN nanowire photoelectrodes can split water at such high photocurrent density, which, together with the monolithic integration with Si solar cells, can enable high efficiency solar-to-hydrogen conversion at zero electric energy

input. Moreover, heterostructures based on such superior quality InGaN nanowires also hold tremendous promise for realizing deep visible and near-infrared light emitting diodes and lasers on a Si platform for full color displays and on-chip optical communications.

To produce such In-rich InGaN nanowires on a scale of the same order as CdTe photovoltaics industry, there are several challenges to be addressed, including the low growth rate of InGaN nanowires, low throughput capacity and high cost related to the high vacuum environment of MBE growth. Nonetheless, to transfer such a growth technique of In-rich InGaN by MBE to more scalable systems such as remote plasma-assisted MOVPE could be a viable way. However, the kinetics of indium/gallium metal atoms in MBE growth could not be directly applied for metalorganic compounds in MOVPE growth. A drastic paradigm-shift of the kinetic growth process is required to enable In-rich InGaN of equivalent or superior optoelectronic properties, including the role of precursor flow rate and flow direction, the chamber pressure, and the carrier gas.
Chapter 6 An InGaN-nanowire/Si tandem photoanode approaching the ideal bandgap configuration of 1.75 eV/1.13 eV

6.1 An introduction to the use of multiple light absorbers for unassisted water splitting

To date, a STH of 15.0% has been achieved by coupling the GaInP/GaInAs tandem solar cell with electrolyzer under CSP.²⁶ However, the goal of implementing solar hydrogen production urges research on the balance of upper-bound efficiency, device complexity and cost.

Considering the overpotential for water splitting, only wide-bandgap semiconductors such as GaN, TiO₂ and GaN:ZnO can split water unassistedly as a single light absorber.^{49d, 50, 204} Following the convention used by Brillet, J. *et. al.*,^{177e} the approach of using a single light absorber to absorb two photons in order to produce one hydrogen molecule can be categorized as the S2 approach. Generally, the S2 approach only utilizes UV photons and a fraction of short-wavelength visible light photons. In contrast, better management of visible light photons in the AM1.5G solar spectrum can be realized by using tandem dual-absorber structures (the D4 approach). The D4 approach can be realized in various schemes: 1) using a tandem solar cell to drive water splitting in an electrolyzer, *i.e.*, the PV+electrolyzer scheme; 2) pairing a photoanode with a photocathode in a PEC cell, the paired-photoelectrode scheme; and 3) monolithically integrating a photoelectrode.

The pioneering work on the D4 approach paired a p-type TiO₂ photocathode with an n-type TiO₂ photoanode and achieved unassisted water splitting with a STH of 0.3%, about a quarter of the theoretical upper-bound STH of TiO₂.²⁰⁵ Using the same semiconductor TiO₂ twice in the D4 approach inevitably reduces the upper-bound STH by half while better management of the solar

spectrum requires the use of two light absorbers harvesting photons of different wavelengths. Jiang, J. et. al. demonstrated a STH of 0.91% by pairing an a-Si/Pt photocathode with a α-Fe₂O₃/NiFeO_x photoanode.⁴³ The STH efficiency is one order of magnitude lower than the upper-bound STH of α -Fe₂O₃ (16%), mainly due to the low IPCE of α -Fe₂O₃. As for the paired-photoelectrode scheme of a BiVO₄/Co-Pi photoanode and a Cu₂O/RuO_x photocathode with a STH of 0.5%, the overlapping absorption spectrum of BiVO₄ (2.5 eV) and Cu₂O (2.0 eV) indicates irrational management of useful photons.²⁰⁶ For tandem photoelectrodes, one example is that the integration of a dye-sensitized solar cell (DSSC) with a WO₃ photoanode witnessed a STH of 3.1%, with the absorption edge of the DSSC at 650 nm (corresponding to 1.9 eV, in comparison with the energy bandgap of WO₃: 2.6 eV).^{177e} Another example is that the integration of a Mo-doped BiVO₄/Co-Ci photoanode with a perovskite solar cell enabled a STH of 4.3%, representing rational management of solar photons with BiVO₄ (2.5 eV) and CH₃CH₂PbI₃ (1.55 eV).^{125, 207} The record STH of 12.4% for the PEC D4 approach was held by a GaAs/GaInP₂/Pt tandem photocathode under CSP of 12-13 suns, which utilized two light absorbers GaInP₂ (1.83 eV) and GaAs (1.42 eV) to obey the current matching condition strictly.⁶⁵ However, the STH of GaAs/GaInP₂/Pt tandem photocathode is far from the ideal STH for the D4 approach because of the insufficient use of the infrared light. Besides, compared to other aforementioned D4 devices, the GaAs/GaInP₂/Pt tandem photocathode entails high cost, high fabrication complexity and inadequate stability. A rational choice of light absorbers for the D4 approach should aim at energy bandgaps for the lowest total photovoltage to drive unassisted water splitting, based on HER/OER catalysts with the minimal overpotential loss, and for the strict current matching condition, based on the highest achievable photocurrent density under terrestrial solar irradiation. These criteria lead to the ideal energy bandgap configuration of 1.75 eV/1.13 eV discussed in Section 1.2.2, corresponding to a semiempirical STH of ~28%. In the same principle, the ideal energy bandgap configuration for a trijunction solar cell is 1.88 eV/1.40 eV/0.67 eV,²⁰⁸ and the use of tri-junction solar cells (the T6 approach) for water splitting was fundamentally limited to by the theoretical-limited J_{ph} of ~16 mA/cm² under the illumination of AM1.5G one sun, corresponding to a STH of ~19.7%.

The energy bandgap of Si (1.12 eV) suits the ideal choice of the bottom cell in a tandem photoelectrode. As for the top cell, the energy bandgap of 1.75 eV can be achieved by high Incontent InGaN alloy, as described in Chapter 5. Herein, we focus on the design and optimization of tandem photoelectrodes using InGaN and Si as dual light absorbers.

6.2 The design of InGaN-nanowire/Si tandem photoanode

As we have discussed in Chapter 1, an ideal tandem structure with an energy bandgap configuration of 1.75 eV for the top cell and 1.13 eV for the bottom cell has the potential to sustain a STH efficiency up to 28%. In this section, we designed a monolithically integrated tandem cell by using high In-content *n*-type InGaN nanowires demonstrated in Chapter 5 as the top cell, and a Si solar cell with a p^+ -emitter as the bottom cell (in contrast to the Si solar cell with an n^+ -emitter discussed in Chapter 4). The charge separation in the InGaN nanowire top cell was driven by the upward band bending at the InGaN/liquid interface. The challenges facing the design of such a tandem structure include 1) the design of a tunnel junction at the InGaN-nanowire/Si interface and 2) the use of a hole blocking layer to avoid the diffusion of photoexcited holes in the top cell to reach the InGaN-nanowire/Si interface.

Based on our discussion over charge carrier transfer at the (In)GaN/Si interface in Chapter 3 (*Section 3.4*), the only case of Ohmic contact at the (In)GaN/Si interface is to have adjacent n^+ -(In)GaN and n^+ -Si to facilitate the transfer of conduction band electrons. Hence there are two

scenarios for the design of a tunnel junction between the nanowire top cell and the planar Si bottom cell, that is, 1) to grow an n^+ -GaN nanowire template on n^+ -Si and then to grow the polarizationenhanced n^+ -GaN/InGaN(4nm)/ p^+ -GaN tunnel junction⁷² or even an n^+ -GaN/Al(4nm)/ p^+ -GaN tunnel junction²⁰⁹ within each nanowire, as discussed in Chapter 4; and 2) to promote a p^+ -Si/ n^+ -Si tunnel junction in the surface of the Si substrate and then to grow n^+ -(In)GaN nanowires. As for the first scenario, the photoelectrode was intended to provide photoexcited electrons into the electrolyte; therefore, it is suitable for the design of photocathode, as validated in Chapter 4. In contrast, the second scenario provides a solution for the transfer of photoexcited holes from the Si bottom cell to the (In)GaN nanowire top cell, which is to be discussed in the following context for the design of InGaN/Si tandem photoanode. The Si bottom cell requires a p^+ -emitter to collect photoexcited holes below the Si tunnel junction and an n^+ -Si back surface field (BSF) layer to reduce surface recombination rate at the back surface.

To utilize the high In-content *n*-type InGaN nanowires in Chapter 5 as the top cell of the tandem photoanode, it is crucial to block the photoexcited holes in InGaN to diffuse towards the tunnel junction at the nanowire/Si interface. By first growing an n^+ -GaN nanowire template on top of the Si tunnel junction prior to the growth of high In-content InGaN nanowires, the large valence band offset of ~0.5 eV between GaN (E_g =3.43 eV) and high In-content InGaN (E_g ~1.7 eV) can effectively block the diffusion of photoexcited holes towards the Si tunnel junction and the band bending at the *n*-InGaN/ n^+ -GaN interface can also facilitate the separation of photoexcited charges in the *n*-InGaN, resembling the use of a BSF layer in solar cells.

We have envisioned the design structure of the tandem photoanode, as shown by the schematic representation of the monolithically integrated tandem device and the corresponding energy band diagram under illumination in Fig. 6-1.



Figure 6-1. a) The schematic representation of the monolithically integrated InGaN nanowire/Si double-band photoanode with the nearly ideal energy bandgap configuration of 1.75 eV and 1.12 eV for the top and bottom cells, respectively. b) Energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illumination. c) Lateral energy band diagram of the InGaN/Si double-band photoanode under illuminating double-band photoa

6.3 The fabrication of Si solar cells with a Si tunnel junction

Since the invention of Si solar cells by Daryl Chapin, Calvin Fuller and Gerald Pearson at Bell Labs in 1952, the efficiency of crystalline Si (c-Si) solar cells has been boosted by several innovations. Those inventors of Si solar cells realized that it is crucial to fabricate the p-n junction close to the surface to harvest most incident photons; by introducing boron into an ultrathin surface layer of an arsenic-doped Si sheet and making Ohmic contacts for boron/arsenic-doped Si, they

achieved a power conversion efficiency of 6%.²¹⁰ Later Hoffman Electronics increased the efficiency of Si solar cells to >10% by using grid metal contact to reduce the series resistance. The next wave of innovations on c-Si solar cells include the fabrication of back surface field to reduce surface recombination at the rear contact, the use of surface-texturing to enhance light absorption and the introduction of passivation layers to reduce surface recombination velocities at both front and rear contacts. A. W. Blakers and M. A. Green reported 20% c-Si solar cells with microgrooved surface and a thin oxide surface passivation layer in 1985.²¹¹ Until 2000s, improvement on the passivation of emitter and sophisticated engineering of heavily-doping under contacts further improved the efficiency to 25%, (area: 4 cm^2) with an open-circuit voltage of 706 mV, a short-circuit current density of 42.7 mA/cm² (theoretical limit: 43.5 mA/cm²), and a fill factor of 0.828.²¹² In 1994, Sanyo Electric Co. demonstrated a 21% efficiency based on a novel Si solar cell structure of amorphous-Si (a-Si)/c-Si heterojunction with an intrinsic a-Si thin layer of 1-2 nm, named as the HIT structure.²¹³ By 2014, the same research group (acquired by Panasonic) achieved an efficiency of 25.6% from HIT Si solar cells of interdigitated back contacts, (area: 143.7 cm²) with an open-circuit voltage of 740 mV, a short-circuit current density of 41.8 mA/cm², and a fill factor of 0.827.²¹⁴ With both front and rear contacts, the open-circuit voltage had also reached 750 mV, unprecedentedly reducing the bandgap-voltage offset of Si to 370 mV,²¹⁵ which was made possible by the excellent passivation of c-Si by the thin layer of a-Si and effective retention of photoexcited carriers at the *c*-Si/*a*-Si heterointerface (surface recombination velocity <1 cm/s). Another distinctive advantage of HIT Si solar cells is the low process temperature of 200 °C by PE-CVD.

A controlled amount of dopants can be introduced into Si by thermal diffusion and ion implantation. Thermal diffusion at elevated temperature (900-1000 °C) makes a gradient doping

profile in Si. In contrast, bombardment of ions into Si can implant a certain amount of dopants at a desired depth, creating a large density of defects and the dopants which are most probably interstitially inserted into the Si lattice; therefore, a subsequent step of thermal curing at elevated temperature is required to form substitutional dopants. Depending on the temperature and duration of the thermal curing process, both abrupt and gradient dopant profiles can be engineered by ion implantation. In the following content, we will also elaborate the fabrication of abrupt junction as tunnel junction in Si by thermal annealing. The thermal diffusion process is determined by Fick's second law of diffusion, shown in Eq. (6-1).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial^2 x}$$
 Equation (6-1)

where *C* is the dopant concentration (~ 10^{21} cm⁻³ at elevated temperature for boron and phosphorous in Si) and *D* is the temperature-dependent diffusion coefficient.

The diffusion coefficient is determined by the Arrhenius equation in Eq. (6-2).

$$D(T) = D_o \cdot \exp(-\frac{E_a}{kT})$$
 Equation (6-2)

where E_a is the Arrhenius activation energy (~2 eV for interstitial diffusion of B/P in Si).

The diffusion coefficient for B/P in Si at 950 °C is $\sim 3 \times 10^{-15}$ cm²/s. With constant supply of the dopant at the surface, the concentration at the Si surface is determined by the solubility of the dopant at the annealing temperature. We used a liquid source of B/P spin-coated on pristine polished Si wafers; the solubility for P in Si at 950 °C is $\sim 8 \times 10^{20}$ cm⁻³, and the solubility for B in Si at 950 °C is $\sim 1.5 \times 10^{20}$ cm⁻³. Assuming a constant surface concentration of the dopant *C_s*, the solution to Eq. (6-1) is shown as below.

$$C(x,t) = C_S \cdot erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$
 Equation (6-3)

Generally lightly *n*-doped Czochralski (CZ) Si(100) wafers with a resistivity of 1-10 Ω ·cm, corresponding to a doping concentration of 0.5-5 ×10¹⁵ cm⁻³, are used for the fabrication of a top p^+ -doped emitter. In the experiment, we have determined that the optimal performance of Si solar cells with p^+ -doped emitter requires 210 min annealing at 950 °C. Therefore, the junction depth was calculated to be 392 nm, as shown in Eq. (6-4).

$$x_j = 2\sqrt{Dt} \cdot erfc^{-1}\left(\frac{c_o}{c_s}\right)$$
 Equation (6-4)

where $C_o = 1 \times 10^{15} \text{ cm}^{-3}$, $C_s = 1.5 \times 10^{20} \text{ cm}^{-3}$, $D = 3 \times 10^{-15} \text{ cm}^2/\text{s}$ and $t = 1.26 \times 10^4 \text{ sec}$.

An optimal CZ Si solar cell with p^+ -doped emitter generally requires slightly shallower junction depth (~200 nm) in lightly *n*-doped Si wafers (1-10 Ω ·cm) with an optimal thickness of ~200 µm. Herein, we can obtain 2" Si epi-ready wafers with a default thickness of 254-304 µm, which requires a slightly deeper junction depth of 392 nm. Besides, the performance of the Si solar cell could be further improved by annealing at higher temperature to reach a higher surface solubility of B in Si; however, we prepare the Si solar cell for the promotion of n^+ - p^+ Si tunnel junction to construct the tandem device so that a slightly lower B surface concentration of ~1.5×10²⁰ cm⁻³ benefits the conversion of the top few nanometers p^+ -doped Si into n^+ -doped Si.

To fabricate an n^+ - p^+ Si tunnel junction on top of the Si solar cell, the annealing temperature and duration should be restricted to form an abrupt doping profile. In addition, we have to guarantee a high surface solubility of the liquid source of P used in our experiment, which must be at least several times higher than the surface concentration of B in the p^+ -doped emitter (~1.5×10²⁰ cm⁻³). We found that at 825 °C the solubility of P is ~5×10²⁰ cm⁻³, and the diffusion coefficient of P is ~5×10⁻¹⁶ cm²/s. Thereafter, we optimized the annealing duration at 825 °C to be 120 s based on the Si solar cell performance. Using Eq. (6-4), we determined the depth of the tunnel junction is ~3.6 nm.

We fabricate c-Si solar cells by spin-coating double-side-polished prime CZ n-Si(100) (1-10) Ω cm) with liquid source of B on one side (front side) and liquid source of P on the other side (back side) and annealing at 950 °C for 210 min. The sheet resistivity of the p^+ -doped emitter layer was in the range of 30-60 Ω/sq , corresponding to an acceptor concentration of ~1.5×10²⁰ /cm³. For the n⁺-doped back surface field layer, the sheet resistivity was in the range of 8-14 Ω/sq , corresponding to a donor concentration of $\sim 5 \times 10^{20}$ /cm³. The n^+ - p^+ Si tunnel junction was realized by spin-coating the p^+ -doped emitter layer with liquid source of P and annealing at 825 °C for 2 min. The front(rear) contact of the Si solar cell without the n^+-p^+ Si tunnel junction was formed by subsequently depositing 20 nm Ni(Ti) and 50 nm Au in an E-beam evaporation system, followed by rapid thermal annealing (RTA) at 550 °C for 1 min under Ar flow of 200 sccm. A window of ~ 1 cm² on the front p^+ -doped emitter layer was reserved without metal contact for incident light. For the Si solar cell with the n^+ - p^+ Si tunnel junction, both front and rear contacts are Ti(20nm)/Au(50nm). The performance of Si solar cells is determined by the current density vs. voltage (J-V) characteristics under illumination and dark. To fundamentally understand the critical factors on the junction performance, diagnosis over the dark J-V characteristic can reveal the ideal factor, the series resistance, the shunt resistance and the dark saturation current, which was out of the scope of the discussion. The *J*-*V* characteristics of the *c*-Si solar cell with/without the n^+ - p^+ Si tunnel junction were compared in Fig. 6-2 and Tab. 6-1.



Figure 6-2. The *J*-*V* characteristics of the *c*-Si solar cell with the n^+ - p^+ Si tunnel junction under AM1.5G illumination of 100 mW/cm² (green curve) and dark (gray curve); the *c*-Si solar cell without the n^+ - p^+ Si tunnel junction under AM1.5G illumination of 100 mW/cm² (red curve) and dark (black curve) were also shown for comparison.

Table 6-1. The open circuit voltage, short circuit current density, fill factor and efficiency of the *c*-Si solar cell with and without tunnel junction under AM1.5G one sun illumination.

	Voc(V)	Jsc(mA/cm ²)	FF	Eff
w./o. TJ	0.505	31.2	0.676	10.7%
w. TJ	0.535	26.7	0.644	9.20%

The *c*-Si solar cell reached an efficiency of ~10%, similar to what had been achieved by Hoffman electronics, considering that we did not employ surface texturing (J_{sc} = 31.2 mA/cm², ~30% loss compared to the theoretical limit of 43.5 mA/cm²) or passivation layers (dark current density reached 3×10⁻⁵ A/cm² at 0.2 V). The Si solar cell with tunnel junction showed a reduced photocurrent density of 26.7 mA/cm², because the photoexcited carriers in the tunnel junction region cannot be extracted for photocurrent. Photons with short wavelengths are strongly absorbed at the top few nanometers. Upon the growth of the top cell, such photons can be absorbed by the top cell; therefore, the absorption in the Si tunnel junction region would not severely impair the photocurrent of the tandem device.

Since the Si bottom cell needs to be epi-ready for the growth of GaN/InGaN nanowires, there are some practical limitations on the fabrication of Si solar cells. Firstly, surface texturing cannot be employed, since it severely affects the nucleation of GaN seeds and the surface diffusivity of Ga/In adatoms. Therefore, the surface reflection of Si lead to ~30% loss of the incident light. However, the light trapping effect of InGaN/GaN nanowire arrays can enhance the light absorption of the Si bottom cell, as explained in Chapter 4 and to be further verified in the following context. Secondly, to guarantee Ohmic conductivity at the Si/GaN interface, passivation layers cannot be employed as well. Nonetheless, the N-atmosphere inside the growth chamber passivates the surface region of Si amidst GaN nanowires with a thin layer of SiN_x during growth. Lastly, to retain the abrupt doping profile of the tunnel junction, the growth temperature needs to be lower than 800 °C.

6.4 The growth and PEC performance of the monolithically integrated tandem photoanode

Prior to the fabrication of metal contacts, the *c*-Si solar cell with the n^+ - p^+ Si tunnel junction (size: 2" wafer) was soaked in acetone for 1 min and then in methanol for 1min under ultrasonic cleaning to dissolve organic contaminants. After rinsed by deionized water, the wafer was soaked in buffered hydrofluoric acid (6:1) for 2 min to dissolve surface oxide. After rinsed by deionized water again, the wafer was loaded into the introduction chamber of the GEN II MBE system immediately. The wafer was degassed at 550 °C for 60 min but without oxide desorption (~800 °C) to avoid the activation of P/B diffusion in the Si wafer. The subsequent growth of GaN at 750 °C and InGaN at 550 °C was compatible to keep the junction structure in the Si wafer, following the

growth process elaborated in Chapter 5 and further increasing the indium content. The SEM image of the as-grown sample was shown in Fig. 6-3. The InGaN nanowires in Fig. 6-3a are 200-300 nm in diameter and ~1.2 μ m in height, with irregular morphologies. The relatively thin *n*⁺-GaN nanowire template was shown in Fig. 6-3b. The highly compacted *n*⁺-GaN nanowire nanowires have a thickness of ~100 nm, serving as the seeding layer for the growth of InGaN nanowires and as a hole blocking layer in the tandem device.



Figure 6-3. 45° tilted SEM images of the InGaN/GaN nanowire arrays grown on the Si solar cell with the tunnel junction. The SEM image in (a) showed the large InGaN nanowire arrays on the small GaN nanowire template; the SEM image in (b) enlarged the bottom region in (a) to show the small GaN nanowire template.

To probe the optical property of the InGaN/GaN nanowire arrays, room temperature photoluminescence spectrum from the nanowire samples were obtained using a 325 nm He-Cd laser as the excitation source, a high-resolution spectrometer to resolve the emission light spectrally, and a photomultiplier tube to detect the emitted light. The photoluminescence emission spectrum from the sample was shown in Fig. 6-4. The emission peak is at 725 nm, corresponding to an optical energy bandgap of 1.71 eV, which is suitable to split the solar spectrum with Si to provide a theoretical photocurrent density of 21.7 mA/cm².



Figure 6-4. RT PL from the InGaN/GaN nanowire array sample.

The PEC performance of the tandem photoanode was studied in the 3-electrode configuration afore-described in Chapter 5 with 1M HBr as electrolyte. The LSV curves of the InGaNnanowire/Si tandem photoanode and the InGaN-nanowire-on- n^+ -Si-substrate photoanode under AM1.5G one sun illumination and dark were compared in Fig. 6-5. Under illumination, the photovoltaic from the Si bottom cell significantly shifted the onset potential cathodically from 0.58 V *vs.* NHE to 0.18 V *vs.* NHE (take J_{ph} = 0.1 mA/cm² for the onset potential). Besides, the accumulation of photoexcited holes beneath the tunnel junction in the Si bottom cell facilitates the tunneling of photoexcited electrons in the InGaN nanowires so that a well-defined saturated photocurrent density of 16.2 mA/cm² was reached, consistent with the half of the photocurrent density of 31.2 mA/cm² observed from the Si solar cell. Two factors could deviate the saturated photocurrent density of the tandem photoanode from the half of the J_{sc} of the Si solar cell. Firstly, the light trapping effect of the InGaN nanowire arrays due to the sub-micrometer modulation of the refractive index significantly enhances the absorption of infrared light by the Si bottom cell. Secondly, after the visible light filtered by the InGaN nanowires, a portion of the infrared light photons (<1.71 eV) is absorbed by the top few nanometers of Si tunnel junction, which does not contribute to the photocurrent, though infrared light has an optical depth of 10-100 μ m in Si.



Figure 6-5. The LSV curves of the InGaN-nanowire/Si tandem photoanode under AM1.5G one sun illumination (red curve: with Si bottom cell) and dark (black curve). The LSV curve of the InGaN-nanowire-on- n^+ -Si-substrate photoanode (green curve: without Si bottom cell) was shown as well for comparison.

A more concrete experiment to confirm the tandem effect of the InGaN-nanowire/Si photoanode is to measure the photovoltage produced from the photoanode. The open circuit potential (OCP) was measured in the 3-electrode configuration with 1M HBr as electrolyte and an Ag/AgCl reference electrode as well. The electrical potentials of the tandem photoanode *vs*. the Ag/AgCl reference electrode under illumination and dark were by switching the shutter of the solar simulator on and off once every 60 seconds. A duration of 60 seconds was essential for the semiconductor-electrolyte interface to reach the equilibrium under illumination/dark. The open circuit potentials of the tandem photoanode was converted to potentials *vs*. NHE and shown in Fig. 6-6. It is seen that the potential of the photoanode under illumination is -0.229 V *vs*. NHE, and that

under dark is +0.647 V vs. NHE. The absolute potential change upon illumination (Δ OCP) is 0.876 V, which was still much lower than the expected photovoltage from a tandem photoelectrode with the ideal energy bandgap configuration. Caution should be exerted for the photovoltage measured in a PEC cell, because under illumination, a fraction of the photovoltage is applied to the Helmholtz layer, unpinning the energy band edge at the semiconductor/electrolyte interface, thus reducing the observed photovoltage (reduction >0.5V in the case of SiC and CdS).³¹ However, when photocurrent is flowing in the closed circuit loop, the photovoltage may drive the kinetic process of water splitting half reactions; (the loss due to potential drop across Helmholtz layer was represented by the OCP under dark but not by Δ OCP) hence the photovoltage defined by the difference between E(O₂/H₂O) or E(O₂/OH⁻) and the onset potential of photocurrent in CV/LSV scans is commonly larger than the (Δ OCP measured under open circuit condition. One example to illustrate the discrepancy is that the BiVO₄/Co-Pi photoanode with an onset potential of 0.25 V vs. NHE, corresponding to a photovoltage of 0.98 V, only sustained a Δ OCP of 0.29 V.⁴²



Figure 6-6. The open circuit potentials of the InGaN-nanowire/Si tandem photoanode under illumination and dark in 1 M HBr solution.

We further compared the ABPE of the InGaN-nanowire/Si tandem photoanode with the InGaN nanowire photoanode. Since the anodic half reaction was dominated by bromide ion oxidation, $(E_0(Br_2/Br^-)= +1.09 \text{ V } vs. \text{ NHE})$, the ABPE was calculated in Eq. (6-5). The ABPE for HBr splitting was compared in Fig. 6-7. The InGaN-nanowire/Si tandem photoanode demonstrated an ABPE of 8.3% at 0.5 V vs. NHE; in comparison, the ABPE of InGaN-nanowire-on- n^+ -Si-substrate photoanode is 0.68% at 0.85 V vs. NHE.



Figure 6-7. The ABPE of the InGaN-nanowire/Si tandem photoanode and the InGaN-nanowire-on- n^+ -Si-substrate photoanode (green curve).

6.5 The monolithically integrated tandem photoanode with NiFeO_x co-catalyst for water splitting in strong base electrolyte

To date, most studies on (In)GaN used hydrobromic acid (HBr) or hydrochloric acid (HCl) as electrolyte and focused on the photoresponse from (In)GaN and its potential as photoanode in strong acidic condition.^{146a-g, 146i, 146j, 146l, 146n, 146o} (In)GaN photoanodes are stable in HBr solutions, as evidenced by previous publications as well as the comparison of XPS spectra before and after

reaction in Section 5.3. It has been well studied that both (In)GaN and Si cannot sustain stable photocurrent for water oxidation. Under illumination, (In)GaN decomposes to form N₂ gas as well as to sustain O₂ evolution in both acidic and base electrolytes, as shown in Eq. (1-18).^{67, 94b} Si is rapidly oxidized when a positive bias is applied.²¹⁶ Recent studies have shown that (In)GaN can be kinetically protected by NiO_x for water oxidation in strong base solution.^{49c, 148} Stable water oxidation for over 500 h was demonstrated.^{148a} In addition, the Si substrate needs to be capsulated to avoid photodecomposition.^{76, 83, 97-98}

We tested the InGaN-nanowire/Si tandem photoanode in 1M KOH solution for water oxidation, with the CV scans under illumination and dark shown in Fig. 6-8. It was observed, however, that the photocurrent density was significantly lower in 1M KOH compared to that in 1M HBr. Besides, the photocurrent degraded rapidly; it took 175 sec for each CV scan, which already led to a severe hysteretic curve in the 1st CV scan and a dramatic decrease of the photocurrent in the 2nd scan under illumination. We further tested the tandem photoanode in 1M HClO₄ for water oxidation. The CV scans and CA curve at an applied bias of 0.9 V *vs.* NHE were shown in Fig. 6-9. The CV scan under illumination in 1M HClO₄ also showed a severe hysteretic curve, and the following CA experiment witnessed a rapid decrease of photocurrent density from 0.55 mA/cm² to 0.12 mA/cm² in 5 min. The very rapid degradation could be related to the etching of Si in KOH at anodic bias. In conclusion, bare InGaN on Si photoanodes undergo rapid degradation in strong acidic or base electrolyte under illumination.



Figure 6-8. The CV curves of the InGaN-nanowire/Si tandem photoanode in 1M KOH under AM1.5G one sun illumination (red curve: the 1st scan; green curve: the 2nd scan) and dark (black curve). Scan from negative to positive bias with a rate of 20 mV/sec.



Figure 6-9. (a) The CV curves of the InGaN-nanowire/Si tandem photoanode in 1M HClO₄ under AM1.5G one sun illumination (red curve) and dark (black curve). Scan from negative to positive bias with a rate of 20 mV/sec. (b) The degradation of photocurrent density over time at an applied bias of 0.9 V *vs*. NHE.

To enable the InGaN-nanowire/Si tandem photoanode for water oxidation, we attempted to couple OER catalysts with the photoanode. Generally, an unstable light absorber can be passivated by conform coating of stable hole transfer layers or be kinetically protected by OER catalyst

particles dissipated on the surface of the light absorber. Si photoanode requires conform passivation layers considering the the deleterious Si oxidation process occurring at -0.8 to -0.9 V *vs.* NHE. We have extensively discussed the passivation of Si by ALD-TiO₂, ITO, Ni and NiO_x in *Section 1.2.4.* We have also probed the viability of kinetical protecting the InGaN nanowires on Si substrate, following standard procedures in literature to prompt NiO_x nanoparticles onto (In)GaN nanowires by depositing 5-10 nm Ni in an e-beam evaporation system and subsequently annealing in air; the photoanode underwent degradation showing identical characteristic in Fig. 6-7. In contrast, the stable (In)GaN photoanodes using NiO_x as cocatalyst in literature were mainly grown on Sapphire substrates.^{94a, 148} Therefore, we postulate that the degradation of the photoanode made by InGaN nanowires grown on Si substrate is primarily due to the collapse of the InGaNnanowire/Si-substrate interface or the oxidation of Si substrate, which rapidly turns the part of the Si substrate adjunctive to InGaN nanowires into an electrical insulator.

Recently, a novel approach to form thin film metal oxide OER layers called photochemical metal organic deposition (PMOD) has been developed.^{19d, 217} Metal oxide precursors including nickel(II) 2-ethylhexanoate, iron(II) 2-ethylhexanoate, cobalt(II) 2-ethylhexanoate and iridium(III) 2-ethylhexanoate can be dissolved into organic solvents and coated onto substrates. Under deep UV illumination (<254 nm), such metal organic precursors decompose and produce conform amorphous metal oxide or mixed metal oxide thin films on the substrate. Dunwei Wang's group had used NiFeO_x cocatalyst by the PMOD approach to significantly improve the onset potential of hematite photoanodes and the improved onset potential was attributed to the reduced voltage drop across the Helmholtz layer.³² Herein, we applied the PMOD approach to prompt NiFeO_x cocatalyst to the InGaN-nanowire/Si tandem photoanode. A 300 W Xenon lamp was used as the

UV excitation source; therefore the precursor was simultaneously heated to >200 °C during the UV curing process, which could impact the catalytic performance of the metal oxide cocatalysts.^{19d}

The PEC experiment was conducted in 1M KOH electrolyte using an Ag/AgCl reference electrode and a Pt wire counter electrode. As shown in Fig. 6-10a, the water oxidation overpotential for 1 mA/cm² under illumination is -0.23 V, (1.0 V vs. NHE) similar to the previously reported value of -0.171 V for a *c*-Si coated with ALD-TiO₂ and Ir cocatalyst for water oxidation in 1M NaOH.⁷⁶ The saturated photocurrent density of 13.7 mA/cm² seems to be also determined by the absorption of Si after visible light (>1.71 eV) was filtered by InGaN nanowires. Such characteristic, however, did not correspond to the expected PEC performance of the tandem photoanode. One plausible reason could be that the metal precursors penetrated through the space among InGaN nanowires and reached the *n*⁺-GaN nanowire hole blocking layer. Therefore, the NiFeO_x cocatalyst shunt the InGaN nanowires so that the photovoltaic effect of the top cell cannot be observed. This conclusion can also be verified by the open circuit potential measurement shown in Fig 6-10b. The absolute potential change upon illumination is 0.473 V, which is close to the V_{oc} of the *p*⁺-*n* Si. The stability of the tandem photoanode with was significantly improved for water oxidation, shown in Fig. 6-10c.



Figure 6-10. PEC characteristics of the tandem photoanode with NiFeO_x cocatalyst in 1M KOH. (a) CV curves of the photoanode under illumination (red curve) and dark (black curve). (b) The open circuit potentials of the photoanode under illumination and dark. (c) The change of photocurrent density over the duration of 1 hour at an applied bias of 1.23 V *vs*. NHE.

Tandem performance began to show up after 2 hour of PEC experiment in 1M KOH solution, as shown in Fig. 6-11. The CV experiment was conducted in a 2-electrode system with electric bias applied against the Pt wire counter electrode. The ABPE for water splitting *vs*. Pt counter electrode is 0.85-1.3% under AM1.5G illumination of 100 mW/cm² with a MMP at 0.53 V. However, the photocurrent density at 1.23 V *vs*. the Pt counter electrode is merely 3.8 mA/cm². The emergence of tandem performance over the course of PEC experiment could be related to photoinduced reconfiguration of the (In)GaN/NiFeO_x interface. However, further study is required to unveil the mechanism and to empower the potential of the tandem photoanode for water splitting.



Figure 6-11. The CV curves of the tandem photoanode with NiFeO_x cocatalyst vs. the Pt wire counter electrode under AM1.5G one sun illumination (red curve) and dark (black curve) after 2 hours of PEC experiment.

6.6 Summary on the InGaN-nanowire/Si tandem photoanode

In this chapter we realized an InGaN-nanowire/Si tandem photoanode with an ABPE of 8.3% for hydrogen generation in HBr solution. The photocurrent density of the tandem photoanode reached 16.2 mA/cm², and the onset potential was 0.18 V vs. NHE, both of which were significantly improved compared to the photoanode made merely by the InGaN nanowire top cell. However, the absolute change of the potential on the tandem photoanode upon illumination is only 0.876 V, leaving a large margin for improvement considering that the upper limit of the photovoltage should be ~1.8 V. We further coupled the tandem photoanode with NiFeO_x OER catalyst using the PMOD method. We observed an initial photovoltage of 0.23 V in the PEC experiment in 1M KOH solution, mainly determined by the p^+ -n Si; after two hours of catalyst aging in the KOH solution, the tandem photoanode can sustain a substantial photocurrent at electric bias <1 V in a 2-electrode system vs. the Pt counter electrode. We observed an ABPE (vs. Pt counter electrode) of 1.3% at 0.53 V. The photocurrent density, however, is much lower compared

to that observed from the PEC experiment in HBr solution. The loss of photocurrent could be due to the poor interface between InGaN nanowires and the NiFeO_x OER catalyst. Kim *et. al.* demonstrated that the photocurrent of a nanoporous $BiVO_4$ photoanode can be improved by inserting a layer of FeOOH as hole transfer layer between $BiVO_4$ and the NiOOH OER catalyst. Herein, a hole conductive interface layer which can interface well with both InGaN and the NiFeO_x OER catalyst may be the key to achieve the same LSV performance in KOH as that in HBr.

Chapter 7 Solar fuels beyond hydrogen

7.1 Photocatalytic CO₂ reduction over GaN nanowires

The promising hydrogen energy system is limited considering the challenges to integrate hydrogen into the current energy infrastructures, which gives chemical fuels like methanol or CH₄ an advantage over hydrogen as energy carrier. One of the major challenges facing solar-to-fuel conversion is the sluggish water oxidation process; in comparison, the selective activation of CO₂ reduction pathway imposes more crucial requirements on the catalytic system. Unlike photocatalytic H₂ production, the conversion of CO₂ to chemical fuels involves a far more complicated chains of proton-coupled electron transfer reactions, producing a wide range of chemicals at much more sluggish rates. The thermodynamic requirement for CO₂ reduction is similar to that for H₂ production, as shown by Eqs. (7-1)-(7-5) (25 °C, at *p*H=7 in aqueous solution).²¹⁸ However, the activation energy to kinetically drive CO₂ reduction could be very high, which will be discussed later in this section.

$$2H^{+} + 2e^{-} \rightarrow H_{2}, E_{o} = -0.41 V vs. NHE$$
Equation (7-1)
$$CO_{2} + 8H^{+} + 8e^{-} \rightarrow 4H_{2}O + CH_{4} \uparrow, E_{o} = -0.24 V vs. NHE$$
Equation (7-2)
$$CO_{2} + 2H^{+} + 2e^{-} \rightarrow H_{2}O + CO \uparrow, E_{o} = -0.53 V vs. NHE$$
Equation (7-3)
$$CO_{2} + 6H^{+} + 6e^{-} \rightarrow H_{2}O + CH_{3}OH, E_{o} = -0.38 V vs. NHE$$
Equation (7-4)
$$CO_{2} + 6H^{+} + 6e^{-} \rightarrow H_{2}O + HCOOH, E_{o} = -0.61 V vs. NHE$$
Equation (6-5)

Halmann *et. al.* first demonstrated that the reduction of CO_2 to a mixture of formic acid, formaldehyde, and methanol on *p*-GaP photocathode.²¹⁹ Using semiconductor particles in aqueous suspension, Inoue *et. al.* found formaldehyde, methanol and methane were produced, and the

production rate increased by using semiconductors of higher CBM.²²⁰ Besides H₂O, CH₄²²¹ and H2²²² are utilized to reduce CO₂ under illumination as well. Photocatalytic conversion of CH₄ with CO₂ requires elevated temperature at 373~473K to thermally activate the reactants, with hydrocarbon, CO or oxygenates as primary products depending on the reaction temperature and catalysts. When H₂ is used as reducing agent for CO₂ photoreduction, the main product is CO. For all the photocatalytic CO₂ reduction reactions, the reductive reaction involves multiple steps of electron transfer and hydrogenation. As a result, depending on reaction conditions, multiple reaction pathways can be simultaneously involved in experiment, producing carbon monoxide, hydrocarbons (including methane, ethane and ethylene), alcohols (including methanol, ethanol and propanol), aldehydes (of formaldehyde and acetaldehyde), formate, acetate and higher carboxylic acids.²²³ To perform CO₂ reduction in PEC cells, the electron transfer process could be highly sensitive to the applied electric potential, which further complicates CO₂ photoreduction process. Another concern related to PEC CO₂ reduction is the predominance of hydrogen and formate production at the solid-liquid interface.²²⁴ In this perspective, we started with CO₂ reduction experiment over GaN nanowires as photocatalyst, with more in-depth study on the role of GaN nanowires in PEC system to be elaborated in Section 7.3. At the solid-gas interface in a photocatalyst system, the mixture of CO_2 and water vapor in gas phase can relatively suppress H_2 evolution, which was deduced from the comparison of studies on TiO₂ as photocatalyst, and the availability of both reductive reaction sites and oxidative reaction sites at nanoscale makes it viable to probe the reaction mechanism.

Generally, photocatalysts were adhered in optical fibres or embedded in zeolites to increase the optical cross section and surface reaction sites. In our circumstance, highly oriented GaN nanowires arrays grown on Si wafer with a mass density of ~90 μ g/cm² can sufficiently absorb

photons within the depth of 1 μ m; the non-polar sidewalls of nanowires increase the surface area to 6 to10 times of the geometric surface area of the wafer. The CO₂ reduction and product evaluation experiments were performed in an air-tight gas circulation system (~450 mL). The wafer-level undoped GaN nanowires identical to the GaN nanowires studied in Section 3.2 (area \sim 3.5 cm²) were carefully washed before putting at the bottom of the Pyrex reaction cell. The circulation system was first well evacuated and then filled with pure CO₂ until reaching a pressure of 80 kPa. 2 mL of distilled water was then added into the reaction cell. The added water was vaporized under the illumination of a 300 W Xe lamp (ILC Tech, CERMAX LX-300), which was also used as the light source for the reaction. The products were measured by a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector (FID) followed by hydrogenation reactor for the evaluation of potential products, including CO, hydrocarbon and other small organic molecules. The sensitivity of the FID for the projected products can reach 10's of part per billion (ppb). The analysis on gas sampling after a duration of 24 hours under illumination revealed that 25.5 part per million (ppm) of CO and 1.2 ppm of CH₄ were present in the air-tight system. Each experiment was repeated by three times using different pieces of the same sample, and the production of CO and CH4 was confirmed while the quantification of the products exhibited an error bar of ~10%. After normalized by the mass density of wafer-level GaN nanowires, the production of CO and CH₄ were presented in Fig. 7-1 in the unit of µmol per gram of catalyst. As a comparison, the natural atmospheric level of CO and CH₄ are 0.1 ppm and 1.8 ppm, respectively. In control experiment, the gas circulation system was filled with pure N_2 but no CO_2 to reach identical pressure of 80 kPa. Neither CO nor CH₄ was detected, excluding air leakage and carbon residuals on the sample as the carbon source of these two products.



Figure 7-1. The photoreduction of CO_2 towards CO and CH_4 over undoped wafer-level GaN nanowires under the illumination of a 300 W Xe lamp.

As shown in Fig. 7-1, the detected amount of CO and CH₄ normalized to the weight of the GaN nanowire photocatalyst (0.3-0.5 mg) in the closed system increased linearly over the irradiation duration, with a CO-to-CH₄ ratio of ~35. The evolution rates of CO and CH₄ were 47.1 μ mol/(g·hr) and 1.33 μ mol/(g·hr), respectively. The evolution rate of H₂ analyzed separately by a thermal conductivity detector (TCD) in the GC-8AI, however, reached 1250 μ mol/(g·hr), which is about 25 times higher than that of CO and about 3 orders higher than that of CH₄. As a comparison, CO and CH₄ are also the main products from photocatalytic CO₂ reduction on TiO₂ of various crystalline phases and nanostructures, with the evolution rates of CO and CH₄ in the range of 0.8-12 μ mol/(g·hr) and 0.15-2.5 μ mol/(g·hr) in similar reaction conditions, respectively,²²⁵ while the evolution rate of H₂ on TiO₂ is just slightly higher than CO₂ reduction.²²⁶

We further studied CO₂ photoreduction on GaN nanowires with Pt nanoparticles formed by photodeposition. As shown in Fig. 7-2, Pt nanoparticles in diameters of 2-3 nm were uniformly distributed on the lateral surface of one GaN nanowire after the photodeposition, with a loading amount of 1-2 μ g/cm². The CO₂ photoreduction experiment was repeated with the Pt-decorated

GaN nanowires under afore-described conditions, and the amount of CH₄ and CO during the irradiation time was shown in Fig. 7-3. Compared to pristine undoped GaN nanowires, the evolution rate of CH₄ was significantly increased from 1.33 μ mol/(g·hr) to 14.8 μ mol/(g·hr) while that of CO was slightly reduced from 47.1 μ mol/(g·hr) to 41.2 μ mol/(g·hr). As expected, the H₂ evolution rate was increased by a factor of 10 as well. In comparison with studies under similar conditions, Pt-loaded TiO₂ nanostructures can improve the rate of CH₄ to 1.4-8 μ mol/(g·hr) while the rate of CO is similar with or without Pt and the rate of H₂ is increased by a factor of over 10;²²⁵⁻²²⁶ specifically, one study had shown that single crystalline TiO₂ nanorod arrays with Pt nanoparticles deposited by CVD could reach a photocatalytic CH₄ production rate up to 1400 μ mol/(g·hr) and the rate of CO was ~200 μ mol/(g·hr).²²⁷



Figure 7-2. An undoped GaN nanowire decorated with Pt nanoparticles on the sidewall.



Figure 7-3. The photoreduction of CO_2 towards CO and CH_4 over Pt-nanoparticle-decorated GaN nanowire arrays under the illumination of a 300 W Xe lamp.

Our preliminary experiment demonstrated the feasibility of photocatalytic CO₂ reduction over GaN nanowires, though H₂ evolution predominated over the reductive reactions. The change of reaction rate upon photodeposition of Pt was also consistent with Pt-loaded TiO₂, indicating the change of reaction mechanism. Two reaction mechanisms were proposed for the reduction of CO₂ to CH₄ on TiO₂, the formaldehyde pathway and the carbene pathway, illustrated in Fig. 7-4.²²⁸ Both of the proposed mechanisms start with the activation of CO₂ by one electron transfer towards adsorbed CO₂ molecules, leading to the formation of bent CO₂⁻ on the surface. The standard potential for the CO₂/CO₂⁻ couple is -1.9 V *vs. NHE*,²²⁹ as shown in Eq. (7-6). Such a high activation energy is required because the addition of one electron to the π^* orbital of CO₂ breaks the molecular symmetry. Studies have shown that the binding of CO₂ molecular to the surface of TiO₂ stretches the original molecular structure, which reduces the energy barrier for the one-electron-transfer process.²³⁰ In addition, the activation energy can be further reduced when the electron transfer process is coupled with proton incorporation.



Figure 7-4. Two proposed reaction mechanisms for photocatalytic reduction of CO_2 with H₂O, the formaldehyde pathway and the carbene pathway.²²⁸

 $CO_2 + e^- \rightarrow CO_2$, $\overline{}, E_0 = -1.9 V vs. NHE$ Equation (7-6)

The reaction mechanism may be related to the way how CO₂ and reaction intermediates are bound on the reaction sites. The distinction between the formaldehyde pathway and the carbene pathway is determined by the relative sequence of hydrogenation and the cleavage of C-O bonds. If the cleavage of C-O bonds is preferential, the reaction follows the carbene pathway. In another perspective, after one electron transfer, if the O atom is tightly bonded to the active site, the following proton incorporation process can be realized on the C atom to form C-H bond, which is related to the chemisorption energy of the C-H bond on the surface, to be elaborated in Section 7.2; then the cleavage of C-O bonds is primarily driven by the facile dehydration of two adjacent hydroxyl groups, which leads to the formaldehyde pathway; otherwise, if the C atom is tightly bonded to the active site, the higher electronegativity of the O atom could prevent the incorporation of proton to the C atom, so the cleavage of C-O is realized at an early stage with CO as the product. Whether further photoreduction of CO can proceed or not is determined by the chemisorption of CO on the photocatalyst. In the case of photocatalytic CO₂ reduction on GaN nanowires, the predominance of CO production indicates the reduction reaction follows the carbene pathway, and the relatively high ratio of CO over CH₄ might further implies that the desorption of CO from GaN is a facile process. As for GaN nanowires with Pt nanoparticles, photoexcited electrons are mainly extracted from GaN nanowires into Pt nanoparticles. Pt can from strong bonding with the C atom of the CO molecule;²³¹ therefore it is plausible the CH₄ was formed on Pt nanoparticles following the carbene pathway as well. Meanwhile the photocatalytic CO₂ reduction towards CO occurred at reaction sites on GaN not covered by Pt. Under illumination, the abundance of energetic electrons in Pt nanoparticles did not convert all the evolved CO into CH₄, indicating the rate-determining step for CH₄ formation could be the oxidation of CO.

7.2 Photoconversion of CH₄ towards benzene on GaN nanowires

In Section 7.1, we demonstrated that the photocatalytic reactions over pristine GaN nanowires in the presence of CO₂ and H₂O vapor produced a mixture of H₂, CO and CH₄ at the ratio of $875(H_2)$: 35(CO): $1(CH_4)$. The sluggish evolution of CH₄ implied that the formation of C-H bond is unfavorable over illuminated GaN nanowires. In this section, we proceeded to test the interaction of C-H bond with GaN nanowires under UV illumination.

In this experiment, a slice of pristine wafer-level GaN nanowires shown in the SEM image of Fig. 3-1 (area: ~3.5 cm²) was placed on the bottom of an air-tight quartz reactor in vacuum (Pressure <1.0 Pa), followed by introduction of 150 μ mol pure CH₄ gas (99.999% purity). The experiment was conducted under moisture-free condition by passing pure CH₄ gas through a column of MgSO₄ and CuSO₄ prior to illumination. Considering that the energy to break C-H bond in CH₄ is 434 kJ/mol (4.5 eV), we have scrutinously confirmed that the CH₄ is stable under the illumination of UV photons with wavelengths between 290 nm and 380 nm. A 300 W Xenon lamp equipped with a 290 nm long pass filter and a 380 nm short pass filter was used as the excitation source and the light intensity was calibrated to be 7.5 mW/cm², using a photodiode sensor (818-ST2-UV/DB, Newport) with attenuator.

After an illumination duration of 12 hours, we use an air-tight syringe to sample 1 mL of the gas and injected into the GC-8AI with TCD, the GC-2014 with FID and another GC system with mass spectrometry (GC-MS) to analyze the composition. Besides CH₄, we detected H₂, C₂H₄, C₂H₆ and C₆H₆ (benzene), as shown by the screenshots of the output component spectra from three GC systems in Fig. 7-5.



Figure 7-5. The output component spectra of (a) GC-8AI with TCD; (b) GC-2014 with FID and (c) GC-MS. Note: the peaks for O_2 and N_2 in (a) were due to leakage of trace of air into the reactor.

To accurately evaluate the molar amount of each product, the sealed reactor were heated gradually up to 200 °C and at this temperature for 60 min to thermally desorb all the organic compounds adsorbed in the chamber wall, and then gas samplings were analyzed in those GC systems again. The amount of H₂, C₂H₄, C₂H₆ and C₆H₆ was calibrated to be 0.886 μ mol, 1×10⁻⁴ μ mol, 0.01 μ mol and 0.594 μ mol, respectively. Based on carbon balance in the reactions, the selectivity for methane-to-benzene conversion over the formation of alternative hydrocarbon

products (CH₄ and C₂H₆) was measured to be 96.5%, leading to a benzene-to-hydrogen stoichiometric ratio close to 1:9. It is evident that CH₄ could be photocatalytically dissociated over GaN nanowires to form H₂, and the ruminant methyl group produced C₂H₆. The presence of C₂H₄ and the final product of C₆H₆ implied that dehydrogenation reaction of C₂H₆ can occur photocatalytically over GaN nanowires to form C₂H₄, which might be a reaction intermediate of the overall methane dehydroaromatization (MDA) reaction to form C₆H₆.

To date, significant efforts have been devoted to the MDA reaction and several efficient heterogeneous catalysts have been developed and well investigated, such as Mo-,²³² Zn-,²³³ Re-²³⁴ and Ga-modified²³⁵ ZSM-5 zeolites. The MDA reaction over such zeolite-based catalysts occurred at elevated temperatures (>500 °C) to drive methane conversion under thermodynamic equilibrium state. It has been evidenced that the reaction mechanism involves the C-H bond stretching of light alkane molecules (CH₄ and C₂H₆) upon their chemisorption by the metal ion species dispersed in the zeolite, coined as alkane dissociative adsorption.^{233, 235-236} Under elevated temperature, heterolytic dissociation of the light alkane forms metal-alkane species as reaction intermediates and hydrogen. The intensity of the C-H stretching is related to the polarizing ability of dipolars between metal ions and their zeolite frameworks.^{236b} Wurtzite structure GaN exhibits strong ionic characteristic and its surface polarizing ability highly depends upon the exposed crystal planes. The polarization in terms of chemisorption is determined by the local arrangement of cations and anions in the exposed surface, which is different from the spontaneous and piezoelectric polarizations elaborated in Section 3.4. If the *m*-plane (1-100) is exposed, alternating positively charged Ga and negatively charged N atomic planes can form strong electrostatic bipolar along the *c*-direction, which is particularly favorable for methane dissociative adsorption; otherwise if the *c*-plane (0001) for the Ga-polar *c*-plane, (000-1) for the N-polar *c*-plane) is exposed, the C-H bond in CH_4 is less likely to be heterolytically stretched.

We have conducted thorough structural characterization of the GaN nanowires to examine the exposed surfaces. As shown in Figs. 7-6a-b, the SEM image (the same image of Figs. 3-1a-b) and the TEM image clearly show the lateral surface of nanowires accounts for over 97% of the total surface area of the sample. Figure 7-6d illustrates the statistical distribution of the diameters of nanowires based on the SEM image in Fig. 7-6a. The hexagonal cross section and the highly oriented growth direction of nanowires indicate that the GaN nanowires are of wurtzite crystal structure and the growth direction is along *c*-axis, which is evidenced by the distance between atomic planes on the lateral surface of nanowires in the high-resolution TEM image (Fig. 7-6c). The electron beam diffraction pattern in Fig. 7-6c revealed that the lateral surface is the (1-100) *m*-plane. The XRD diffraction pattern of the GaN nanowires was shown as the blue curve in Fig. 7-6f, which only exhibits the (002) and (004) peaks of GaN due to the vertically-oriented GaN nanowire arrays grown on Si substrate. We have also confirmed the exposed nanowire top surface is N-polar *c*-plane in Section 3.4.

We also prepared Ga-polar GaN thin films with thickness of 650 nm grown over an AlN buffer layer on Sapphire substrate and GaN nanoparticle powders (Sigma-Aldrich) for XRD measurement, as shown by the red curve and black curve in Fig. 7-6f. The (002) peak for AlN and the (004) peak for GaN verified that the growth direction is (0001), while the GaN nanoparticle powders (TEM images shown in Fig. 7-7a) exhibited almost all of the essential XRD peaks of GaN, indicating the presence of surface active sites in all the primary crystal planes, including *m*plane and *c*-plane, which was further confirmed by selected area electron diffraction pattern under TEM mode in Fig. 7-7b-c.



Figure 7-6. (a) SEM, (b) low- and (c) high-resolution TEM images, (d) diameter distribution, and (e) RT PL spectrum of the pristine wafer-level GaN nanowire arrays. The inset of (a) shows the top view of one nanowire. The inset of (c) is the selected area electron diffraction pattern of the lateral facet of the nanowire in (b). (f) X-ray diffraction patterns of wurtzite GaN samples in the forms of nanowire arrays, thin film, and nanoparticle powders (from top to bottom).



Figure 7-7. (a) TEM image of the GaN nanoparticle powders and the corresponding selected area electron diffraction patterns of (b) *c*- and (c) *m*-planes.
Besides, to compare the photocatalytic performance of wafer-level GaN nanowires, GaN thin films and GaN nanoparticle powders, we have analyzed the surface area of these samples. The surface of wafer-level GaN nanowires (~90 μ g/cm²) is essentially the exposed *m*-plane of nanowire lateral surface, whose area is about 6 times of the geometric area of the wafer surface (~3.5 cm² in this experiment). In contrast, the GaN thin film (~400 μ g/cm²) with exposed Ga-polar *c*-planes and some semi-polar crystal planes due to surface pits, roughly has the same surface area as its geometric area of the wafer surface (~10 cm² in this experiment). As for GaN nanoparticle powders, the Brunauer-Emmett-Teller (BET) specific surface area was measured to be 3.2 m²/g, and the use of 0.35 mg GaN nanoparticle powders corresponds to a surface area of 11 cm². As a control experiment, we also prepared another GaN nanowire array sample with the heights of nanowires ~500 nm, which is half of that shown in Fig. 7-6a. Compared to GaN nanowire samples with heights of ~1 μ m, the GaN nanowire sample with reduced heights of ~500 nm roughly have about half of the area of exposed lateral surface in *m*-plane.

The four samples were tested under identical conditions as described above for photocatalytic CH₄ conversion. The photocatalytic MDA activity of each sample is presented in Fig. 7-8. The molar amount of CH₄ converted over the long nanowire sample is slight more than twice of that converted over the short nanowire sample, which is consistent with the area ratio of their exposed *m*-planes. The GaN nanoparticle powder exhibited much lower photocatalytic MDA activity while no methane conversion was detected over the GaN thin film sample. The experiment result confirmed that the lateral surface of GaN nanowires with exposed *m*-plane are the active sites for the photocatalytic MDA reaction.



Figure 7-8. The amount of CH₄ consumed in 12 hours (left *y*-axis) in the photocatalytic MDA reaction over 1- μ m GaN nanowire arrays (~0.3 mg), 500-nm GaN nanowire arrays (~0.15 mg), GaN nanoparticle powders (0.35 mg) and GaN thin film on AlN buffer layer on Sapphire (~4 mg). The *y*-axis on the right is for the surface area in each sample. The green bar represents converted CH₄ in the MDA reaction, black bar represents the area of exposed *m*-planes and the shadowed bar represents the area of exposed *c*-planes in each sample.

We have also noted that the aluminosilicate zeolites (-AlO₄/-SiO₄) used in most heterogeneous catalysts for the MDA reaction is insulating, which were studied for catalyzing MDA because of their shape-selective adsorption properties.²³⁷ Therefore the electronic structure of the zeolite is shielded from its surface adsorption properties. However, the *d*-band center theory developed by Hammer and Norskov revealed that the binding energy of various adsorbates on the surface metal species largely depends on the electronic structure of the surface, or more specifically the *d*-band center of the species (corresponding to the Fermi level of metal).²³⁸ In the same principle, as for methane dissociative adsorption on GaN nanowires, the chemisorption energy of methane on lattice Ga³⁺ exposed on the lateral surface can be related to the Fermi level of GaN. To verify this point, we prepared *n*-type GaN nanowires by incorporating Si dopant and *p*-type GaN nanowires by incorporating for the Sindoped *p*-type GaN nanowires were estimated to be on the order of $n = 5 \times 10^{18}$ cm⁻

³ and $p = 1 \times 10^{18}$ cm⁻³, respectively. The photoluminescence spectra of undoped (black curve), *n*-type (red curve), and *p*-type (blue curve) wafer-level GaN nanowire samples under the excitation of 325 nm Cd-He laser were compared in Fig. 7-9. The introduction of dopants (Si or Mg) compromised the optical quality of the nanowire arrays but did not affect the energy band gap of GaN. The photocatalytic MDA activity of each GaN nanowire sample was shown in Fig. 7-10. All the GaN nanowire samples facilitated the MDA reaction with a selectivity of ~97%. However, the reaction rates exhibited a ratio of 12.5(*n*-type): 2.1(undoped): 1(*p*-type). Therefore, the increase of Fermi level towards the conduction band edge of GaN can significantly increase the photocatalytic MDA activity, which could be due to the optimal chemisorption energy for methane dissociation on the exposed *m*-planes of *n*-type GaN.



Figure 7-9. RT PL spectra of undoped (black curve), *n*-type (red curve), and *p*-type (blue curve) wafer-level GaN nanowire samples under the excitation of a 325 nm Cd-He laser.



Figure 7-10. Methane conversion rate and benzene selectivity over a slice of undoped GaN nanowires, *n*-type GaN nanowires, *p*-type GaN nanowires, and the Si substrate under UV irradiation (290-380 nm) for 12 h. The area of each slice is 3.5 cm².

We further evaluated the dependence of the photocatalytic MDA reaction rate of the *n*-type GaN nanowires over the incident light intensity, as shown in Fig. 7-11. The reaction rate is proportional to the square of the incident light intensity, which implies that the rate-determining step of the MDA reaction is linearly dependent on the photoexcited carriers in GaN nanowires. A plausible reaction mechanism consists of the following steps, 1) the C-H bond of the adsorbed CH₄ was stretched by the neighboring positive charge Ga atomic plane and negatively N atomic plane to form $H^{\delta+}$ -CH₃^{$\delta-$} polarization; 2) the transfer of photoexcited holes towards the stretched C-H bond dissociates the CH₄ to form H⁺ and adsorbed Ga-methyl group on the exposed lattice Ga³⁺; which is linearly dependent on the light intensity; 3) the coupling of methyl groups at adjacent lattice Ga³⁺ ions is a relatively rapid process, followed by much easier dehydrogenation reactions since the methyl group no long possesses the symmetry of CH₄, while traces of C₂H₄ and C₂H₆ are released into gas phase; and 4) aromatization. The rate of coupling of methyl groups in Step 3)

depends on the square of the formation rate of methyl groups in Step 2). Therefore, the overall reaction rate depends on the square of incident light intensity. The quantum efficiency, defined by Eq. (7-7), was proportional to the incident light intensity, as shown in the inset of Fig. 7-11.

$$QE = \left(N_A \cdot \left|\frac{dn[CH_4]}{dt}\right|\right) \div \frac{P_{incident} \cdot A}{hc/\lambda} \times 100\% \qquad \text{Equation (7-7)}$$



Figure 7-11. Plot of the methane consumption and quantum efficiency (inset) over n-type GaN nanowires in 12 h as a function of the light intensity.

To sum up, we have discovered that direct photocatalytic conversion of CH₄ to benzene can be realized on the exposed *m*-planes of GaN nanowire lateral surface. The MDA reaction mechanism involves the dissociative adsorption of CH₄ at the exposed lattice Ga³⁺ and the neighboring N³⁻ sites. The cleavage of the first C-H bond in the CH₄ molecule could be the rate-determining step, leading to the square dependence of overall quantum efficiency on the incident light intensity. The MDA reaction rate was correlated with the Fermi level of GaN nanowires, because the GaN Fermi level could affect the chemisorption energy of C-H bond, which in turn affects the rate-determining

step. Such a novel photocatalytic MDA reaction promises great potential for future chemical synthesis.

Chapter 8 Conclusion and outlook

8.1 Summary of the thesis work

III-nitride nanostructures hold tremendous potential for solar-to-fuel production. In this thesis, we systematically investigated the synthesis of III-nitride nanowires by PA-MBE, the structural and optical properties of III-nitride nanowires, and the application of III-nitride nanowires in PEC water splitting, photocatalytic CO_2 reduction and photocatalytic CH_4 conversion.

The versatility of PA-MBE enabled our design of nanostructures such as tunnel junction in nanowires and the growth of high quality InGaN nanowires with In-content of ~50%. We have demonstrated that both highly efficient InGaN nanowire photocathode and photoanode can be realized on Si platform for solar water splitting. A solution-based photodeposition process for promoting Pt nanoparticles on III-nitride nanowires was adopted and perfected for the fabrication of nanowire photocathode. We realized an n^+ -GaN/InGaN(4nm)/ p^+ -GaN polarization-enhanced tunnel junction in nanowire arrays for the first time. By using an InGaN-nanowire/polarizationenhanced-tunnel-junction/ n^+ -p-Si tandem photocathode, we achieved an ABPE of 8.7%, which matches or exceeds the highest achievement of c-Si based photocathodes. With comprehensive investigation over the kinetic properties of InGaN nanowire synthetic process, we realized nearly homogenous 50%-In-content InGaN nanowire arrays on Si substrate, which could sustain a photocurrent density as high as 7.3 mA/cm² as a photoanode under AM1.5G one sun illumination at 1.2 V vs. NHE in 1 M HBr. Such high In-content InGaN and the corresponding photocurrent is unprecedented in the published literature, extending the absorption edge of metal oxide photoanodes towards deep visible spectrum by ~200 nm. Furthermore, we realized an InGaNnanowire/Si tandem photoanode for HBr splitting, with a saturated photocurrent density of 16.2 mA/cm² and an ABPE of 8.3% at 0.5 V vs. NHE under the illumination of AM1.5G one sun. Once

again, such a saturated photocurrent density settled down a new benchmark for the PEC community, representing a substantial step towards a STH of > 20% under terrestrial solar irradiation. By adopting the photochemical metal organic deposition process, a solution-based synthetic approach to produce NiFeO_x cocatalyst on the tandem photoanode, we have achieved 1.3% ABPE at 0.53 V *vs.* the Pt counter electrode for water splitting in 1M KOH electrolyte. This work demonstrated for the first time that InGaN can be coupled with an OER catalyst for water oxidation with stable photocurrent.

Besides, we studied the photocatalytic CO₂ reduction on GaN nanowires and tuned the activity by promoting Pt nanoparticle co-catalyst, which proved that 1) the formation of C-H bond for valuable solar fuel products is not favored on pristine GaN nanowires, and 2) it is viable to reduce CO₂ to CO on GaN with or without Pt nanoparticles; 3) Pt nanoparticles as co-catalyst could significantly enhance the formation of C-H bond but simultaneously reinforced the predominance of hydrogen production. Such insights laid down the foundation for future exploration on using III-nitrides for photocatalytic CO₂ reduction and motivated our inquiry on the activation of C-H bond on GaN nanowires. As expected, we observed photocatalytic heterolysis of CH₄ on GaN nanowires; the final reaction products were benzene and hydrogen. This experiment revealed that 1) methane dehydroaromatization reaction can occur on the non-polar sidewall of GaN nanowires under UV illumination (290-380 nm); 2) the reaction activity is affected by the type of doping in GaN nanowires; and 3) the reaction requires the absorption of two photons to dissociate one CH₄ molecule. The research on the fundamental photocatalytic property and mechanism over GaN nanowires sheds light on III-nitride based photocatalysts.

8.2 Future work

8.2.1 Enabling the InGaN-nanowire/Si tandem photoanode for water splitting

The InGaN-nanowire/Si tandem photoanode discussed in Chapter 6 exhibits a $\triangle OCP$ of 0.876 V, much lower than the expected photovoltage of 1.8 V. The loss of the photovoltage could be attributed to several factors. Firstly, the band bending of InGaN at InGaN-nanowire/electrolyte interface may not be large enough to sustain a photovoltage of > 1V from the top cell. To this point, the doping concentration and the doping profile of the InGaN nanowires need to be further optimized to maximum the surface band bending. Secondly, there could be a large potential drop within the Helmholtz layer of the InGaN-nanowire/electrolyte interface in equilibrium under dark, which restricts the extent of surface band bending and in turn clamps the achievable photovoltage; the OCP under dark should be aligned with $E_0(Br_2/Br^-)$ (=+1.09 V vs. NHE) in the absence of potential drop in the Helmholtz layer in comparison to the measured OCP of 0.647 V vs. NHE under dark, and OCP under dark in 1M KOH was measured to be 0.42 V vs. NHE after promoting NiFeO_x OER catalyst, which indicates even higher voltage drop across the Helmholtz layer formed by InGaN/NiFeO_x/KOH electrolyte. Thirdly, the presence of a native SiO_x layer is unavoidable since the manual operation process commonly exposes wafers in air for about 20 min prior to loading the wafers into MBE, which may affect the carrier transfer at the Si tunnel junction. By annealing the Si substrate at 800 °C for 10 min before the deposition of GaN/InGaN, the RHEED pattern of the Si substrate changed from blur concentric circles into clear striking lines, indicating the desorption of surface oxides. The onset potential of the corresponding tandem photoanode in 1M HBr was reached the highest value of our observation, -0.2 V vs. NHE shown in Fig. 8-1a, and unassisted photolysis of HBr in a 2-electrode setup was observed, shown in Fig. 8-1b. However, the photocurrent was quite low and the CV curve under illumination in Fig. 8-1a reveals that the

low current density at 0 V *vs.* NHE could be due to a limited tunneling current density of the Si tunnel junction. The degradation of the Si tunnel junction may be caused by the oxide desorption duration of 10 min at 800 °C, which can activate the diffusion of phosphorous dopants and destroy the abrupt doping profile for the Si tunnel junction. To solve this issue, hydrogen or argon plasma should be used to strip away the native Si oxide layer *in situ* at a reduced temperature of 750 °C.



Figure 8-1. The PEC characterization of the InGaN-nanowire/Si tandem photoanode with oxide desorption at 800 °C for 10 min prior to the growth of GaN/InGaN. (a) CV curves under AM1.5G illumination of 100 mW/cm² and dark in 1M HBr in a 3-electrode setup. (b) Photocurrent density under AM1.5G illumination of 100 mW/cm² at 0 V vs. the Pt counter electrode in a 2-electrode setup in 1M HBr.

The V_{oc} of 0.535 V and fill factor of 0.644 from the p^+ -n Si corresponds to a bandgap-voltageoffset of 0.59 V, while the state-of-art HIT Si solar cell with both front and rear a-Si contact can achieve V_{oc} of 0.75 V and an improved fill factor of 0.832,²¹⁵ which has the potential to shift the V_{MPP} of the tandem photoanode by 0.3 V. However, the a-Si thin layers require a deposition temperature of ~200 °C, which will be definitely destroyed at the growth temperature of InGaN nanowires (~550 °C). To integrate the InGaN nanowires with HIT Si solar cells, we have to remove the InGaN nanowire arrays from the Si substrate and transfer them to the HIT Si solar cell. As for transferring ordered nanowire/microwire arrays, Sun, Y. *et. al.* developed a method by 1) embedding top-down fabricated GaAs and InP microwire arrays in a polydimethylsiloxane film and 2) mechanically removing the embedded wires from the growth substrate.²³⁹ Warren, E. L. et. al. applied the same method for the transfer of vapor-liquid-solid-grown Si microwire arrays.²⁴⁰ Concerns on the mechanical method include incomplete removal of wire arrays from the growth substrate, mechanically induced wire fracture and the uncontrollable contact of the embedded wire arrays with the new substrate. In our growth of high In-content InGaN nanowire arrays, we discovered that the InGaN nanowire arrays detached from the Si substrate upon a slightly increase of the GaN base template growth temperature by 30 °C; the thermal-induced tension led to a thorough detachment of nanowire arrays. Based on this observation, we simultaneously increased the Ga and In flux at the first 10-30 nm of InGaN nanowire growth, which induced the growth of a thin film at the root of InGaN nanowires, and the thermal-induced detachment of the thin film from the Si substrate did not seem to affect the subsequent growth of InGaN nanowires. Because of the growth temperature gradient towards the very edge of the 2" Si substrate, an ring with a width of 2-5 mm at the edge of the 2" Si substrate was not affected by the thermal-induced strain, and retained InGaN nanowires on the Si substrate. Shown in Fig. 8-2 is the SEM image of the InGaN nanowire arrays transferred onto a copper tape foil. To show the side view of the nanowire arrays, the image was taken with a 45° tilted angle by choosing the overlapping interface of two pieces of InGaN nanowire arrays attached on the same piece of copper tape foil (Area of each piece: 0.2-0.5 cm²). From the SEM image, it is seen that bottom of the InGaN nanowire arrays are interconnected, resembling a thin film, and the morphology and the order of InGaN nanowires within the array was not affected during the transfer process. Such an elegant and unique method of transferring InGaN nanowire arrays paves the way towards the integration of the InGaN nanowire arrays with HIT Si solar cells to form large-area tandem photoanodes. Besides, the

engineering of the bottom cell and the tunnel junction were no longer restricted by the growth of InGaN top cells; the interconnection of InGaN nanowire base also promises effective isolation of OER catalyst with the bottom Si cell and improved stability of the tandem photoanodes. Future work on the fabrication of high In-content InGaN solar cells with ultra-high flexibility becomes viable based on specifically-designed contact fabrication process of the stand-alone InGaN nanowire arrays.



Figure 8-2. The 45° tilted SEM image of the overlapping interface of two pieces of InGaN nanowire arrays attached on a copper tape foil.

As we have discussed in *Section 6.4*, the monolithically integrated InGaN-nanowire/Si tandem photoanode with NiFeO_x cocatalyst could not reach the saturated photocurrent density of ~16 mA/cm² at an applied bias lower than 1.23 V in a 2-electrode PEC system with Pt wire as counter electrode. The photovoltaic effect of the InGaN nanowires could be partially shunted due to the penetration of NiFeO_x towards the n^+ -GaN hole blocking layer; that is, photocurrent from the Si bottom cell leaks into the electrolyte via the n^+ -GaN hole blocking layer. The issue could be addressed by controlling the PMOD process to selectively form ultrathin coating on InGaN nanowires. Another issue is related to the lack of a hole transfer layer which can interface well with both InGaN and the NiFeO_x OER catalyst; one of the candidate could be TiN, considering its identical valence band configuration of N 2p orbitals²⁴¹ as III-nitrides. A conform TiN layer can be formed on top of InGaN nanowires by 1) E-beam deposition of 1-5 nm Ti and 2) subsequent N₂ plasma treatment at 400 °C in vacuum.

As we have elaborated in *Section 1.2.2*, practical PEC cells for water splitting requires the use of the highly conductive proton exchange membrane in strong acidic condition. Therefore, it is essential to empower the tandem photoanode for water splitting in strong acidic electrolyte. We aim to prompt IrO_x cocatalyst to the tandem photoanode using the PMOD approach. IrO_x is stable in strong acid and can sustain water oxidation current density of 1 mA/cm² at an overpotential of <200 mV. However, IrO_x in its oxidized status exhibits dark blue color, blocking a fraction of short wavelength visible light, which can severely limit the saturated photocurrent density of the tandem photoanode. So the challenge to prepare IrO_x cocatalyst is also to form ultrathin conform coating on the InGaN nanowires.

8.2.2 Enabling tandem behavior from the InGaN-tunnel-junction-nanowire/Si tandem photocathode

We have realized an InGaN-tunnel-junction-nanowire/Si tandem photocathode in Chapter 4. However, the top cell of InGaN nanowire segments only reduced the HER resistance of the whole device. It would be crucial to add up the photovoltage from the InGaN-nanowire/electrolyte junction and the Si solar cell substrate to realize zero-bias water splitting. Again, the challenge is to avoid current leakage from the bottom n^+ -GaN nanowire section. Herein, our future work on the tandem photocathode is to engineer an approach to capsulate the bottom n^+ -GaN nanowire section and the tunnel junction, with only the top *p*-InGaN nanowire segments exposed to

electrolyte for HER. Besides, we will apply the growth technique of high In-content InGaN nanowires to p-InGaN for the photocathode, aiming at a saturated photocurrent density of 20 mA/cm². A tentative capsulizing scheme is to follow the process developed by Gao et. al. to capsulate the bottom segment of InP nanowires.⁵⁷ Firstly, a thin layer of SiO₂ can be deposited on the InGaN nanowires and Si substrate by PECVD. Secondly, a thick layer of benzocyclobutene (BCB) photoresist should be applied to fill up the gap of nanowires and bury the top of nanowires. Thirdly, dry-etching of BCB by reactive ion etch (RIE) with controlled rate should be conducted to expose the top part of InGaN nanowires and to keep the n^+ -GaN and the tunnel junction at the bottom part of InGaN nanowires embedded. Fourthly, etch the SiO₂ layer on the top part of InGaN nanowires by HF solutions. Lastly, prompt Pt nanowires on the top part of InGaN nanowires by photodeposition. One challenge facing this process is the relative high nanowire density and tapered-nanowires formed by the spontaneous nanowire growth process. The relative large nanowire top can have a shadowing effect on the deposition of SiO₂ by PECVD. Such an issue needs to be addressed by controlling the morphology and density of nanowires during the MBE growth process.

In this thesis, the research focused on the design of InGaN nanowire structures and the integration of InGaN nanowires with Si solar cells to improve the energy conversion efficiency and photocurrent density of PEC solar-to-fuel conversion. Short-term stability of few hours' operation was demonstrated. However, the application of such PEC devices requires a lifetime comparable to those of current commercial solar cells. Future work on the long-term stability of InGaN nanowire based PEC devices is crucial.

List of publications

Peer Reviewed Journal Articles

- Shizhao Fan, Ishiang Shih, and Zetian Mi^{*}, "A Monolithically Integrated InGaN Nanowire/Si Tandem Photoanode Approaching the Ideal Bandgap Configuration of 1.75 eV/1.13 eV", 2016, manuscript submitted.
- Shizhao Fan, Steffi Y. Woo, Srinivas Vanka, Gianluigi A. Botton, and Zetian Mi^{*}, "An InGaN Nanowire Photoanode with Enhanced Hydrogen Generation under Deep Visible Light Irradiation", APL Mat., 2016, in press.
- Bandar AlOtaibi, <u>Shizhao Fan</u>, Srinivas Vanka, Mohammad Kibria, Zetian Mi^{*}, "A Metal-Nitride Nanowire Dual-Photoelectrode Device for Unassisted Solar-to-Hydrogen Conversion under Parallel Illumination", *Nano Lett.*, **2015**, *15*, 6821-6828.
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- <u>Shizhao Fan</u>, Bandar AlOtaibi, Steffi Y. Woo, Yongjie Wang, Gianluigi A. Botton, and Zetian Mi^{*}, "High Efficiency Solar-to-Hydrogen Conversion on a Monolithically Integrated InGaN/GaN/Si Adaptive Tunnel Junction Photocathode", *Nano Lett.*, **2015**, *15*, 2721-2726.
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Conference Presentation

 Shizhao Fan, Bandar AlOtaibi, and Zetian Mi, "Full-Solar-Spectrum InGaN/Si Nanowire Photoelectrochemical Water Splitting", *31st North American Molecular Beam Epitaxy* (NAMBE), Mayan Riviera, Maxico, October 04-07, 2015.

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