Flexible InGaN nanowire membranes for enhanced solar water splitting

RAMI T. ELAFANDY, MOHAMED EBAID, JUNG-WOOK MIN, CHAO ZHAO, TIENT KHEE NG, AND BOON S. OOI

King Abdullah University of Science and Technology (KAUST), Photonics Laboratory, Thuwal 23955-6900, Saudi Arabia
boon.ooi@kaust.edu.sa

Abstract: III-Nitride nanowires (NWs) have recently emerged as potential photoelectrodes for efficient solar hydrogen generation. While InGaN NWs epitaxy over silicon is required for high crystalline quality and economic production, it leads to the formation of the notorious silicon nitride insulating interface as well as low electrical conductivity which both impede excess charge carrier dynamics and overall device performance. We tackle this issue by developing, for the first time, a substrate-free InGaN NWs membrane photoanodes, through lift-off and transfer techniques, where excess charge carriers are efficiently extracted from the InGaN NWs through a proper ohmic contact formed with a high electrical conductivity metal stack membrane. As a result, compared to conventional InGaN NWs on silicon, the fabricated free-standing flexible membranes showed a 10-fold increase in the generated photocurrent as well as a 0.8 V cathodic shift in the onset potential. Through electrochemical impedance spectroscopy, accompanied with TEM-based analysis, we further demonstrated the detailed enhancement within excess charge carrier dynamics of the photoanode membranes. This novel configuration in photoelectrodes demonstrates a novel pathway for enhancing the performance of III-nitrides photoelectrodes to accelerate their commercialization for solar water splitting.

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OCIS codes: (160.4236) Nanomaterials; (260.5130) Photochemistry; (350.6050) Solar energy.

References and links
1. Introduction

Urged by increasing energy demands and rising average global temperature, there are enormous global efforts to shift the world energy dependence from fossil fuels to renewable energy sources [1]. Conventional solar electricity in particular, while representing an abundant energy source, suffers from intermittency and dependence on weather conditions and thus require an efficient energy storage and transport system [2,3]. In this regards, solar water splitting represents a clean, renewable and storable energy source where solar energy is converted into hydrogen chemical energy through splitting water molecule into hydrogen and oxygen [4].

The semiconductor photoelectrodes required to constitute an efficient kinetic path for such a reaction, need to fulfil several optical, chemical and morphological criteria [5]. Having proper energetics as well as a tunable energy bandgap, indium gallium nitride (InGaN) semiconductor alloy efficiently absorbs solar radiation while straddling the electrochemical potentials of the oxygen and hydrogen evolution reactions, allowing for an efficient solar hydrogen generation [6–8]. Furthermore, InGaN nanowires (NWs) have large surface-to-volume ratio and are capable of withstanding high indium incorporation without defects nucleation [9], and therefore, are excellent candidate for solar hydrogen generation photoelectrodes [10–14]. To achieve high crystalline quality as well as economic production, InGaN NWs, previously employed for solar hydrogen generation, were epitaxially grown on silicon (Si) substrates [11,15,16]. Unfortunately, besides having a comparatively low electrical conductivity, growth of InGaN NWs on Si leads to the formation of an amorphous insulating silicon nitride (SiNx) interfacial layer, during the nitrogen rich nucleation phase [17,18]. These issues highly impede transport of excess charge carriers from the NWs to the counter electrode and thus reduce the device performance.

We present an unconventional technique to resolve the detrimental effect of growing InGaN NWs on Si substrate without risking their high crystalline quality. Specifically, we fabricated the first substrate-free InGaN NWs membrane photoanodes, based on lift-off and transfer techniques for solar hydrogen generation (Fig. 1). The membrane photoelectrodes consisted of lifted-off InGaN/GaN NWs forming an ohmic contact with a high electrical conductivity metallic layer and thus, allowing for an efficient excess charge carrier extraction and transport towards the counter electrode (inset of Fig. 1). As further presented below, due to their large aspect ratio, the prepared membranes could be efficiently bended and thus be attached to a plethora of media including rigid and flexible platforms. The presented strategy represents a novel pathway to enhance the solar water splitting efficiency of InGaN NWs to further drive III-nitride photoanodes towards commercialization.
In this investigation, a detailed scanning electron microscopy (SEM) images were presented to demonstrate the detailed fabrication and lift-off processes. Several optical spectroscopy measurements affirmed that the fabrication process did not affect the optical properties of the pristine NWs and thus did not degrade device performance. Structural and chemical properties of the NWs membrane were studied using transmission electron microscopy (TEM) alongside electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX). The photoanodic behaviour of the fabricated substrate-free InGaN NWs membrane was evaluated against the conventional InGaN NWs on bulk silicon substrate through several electrochemical measurements. While both samples had comparable dark currents densities (less than 0.022 mA/cm²), the measured NWs membrane photocurrent density (0.8 mA/cm²) exhibited a 10-fold increase compared to NWs on silicon (0.052 mA/cm²) at 0.5 V applied bias versus Ag/AgCl reference electrode. Finally, based on the electrochemical impedance spectroscopy (EIS) studies, along with the respective Bode plots, we derived equivalent electrical circuits for the NWs membrane and the NWs on silicon samples. These equivalent circuits demonstrated the higher performance of the NWs membrane photoanode due to the much reduced capacitance and interfacial resistances as compared to those originated from the silicon/NWs interface and the silicon substrate.

![Diagram of a flexible InGaN NWs membrane photoanode](image)

**Fig. 1.** Flexible InGaN NWs membrane photoanode comprising of lifted-off InGaN NWs attached to a flexible metal film. Inset: A single NW (n-doped) having an ohmic contact with a TiN/Ti/Al/Ti/Au metal layer allowing for an efficient carrier extraction and transport.

### 2. Experimental methods

#### 2.1. NWs MBE growth

InGaN NWs were grown in a plasma assisted molecular beam epitaxy (PA-MBE) reactor. After nucleating GaN seeds on silicon (100) substrate under nitrogen rich conditions, vertically aligned 20 nm-long Si-doped GaN NWs templates were grown. Then, approximately one μm of Si-doped InGaN NWs were grown which constitute the optically active component in the water splitting reaction. A 600 nm Si-doped GaN was then grown, under metal (Ga) rich conditions to promote lateral growth. The purpose of this expanded top GaN layer, as further elaborated later, was to prevent the formation of short circuits between the back metal contact and the electrolyte solution during the water splitting process. Finally, the NWs were capped with approximately 5 nm of n⁺ GaN to enhance ohmic contact with the deposited metals. Top view SEM of the NWs reveals their densely packed GaN top (Fig. 2(a)). Furthermore, the cross-sectional SEM view of the NWs, in Fig. 2(b), shows their slim
InGaN stems (average diameter = 78 nm) underneath their expanded GaN tops (average diameter = 273 nm). The measured photoluminescence (PL) signal from the as-grown NWs sample (Fig. 2(c), red curve) peaked at 580 nm (2.14 eV – In0.35Ga0.65N) [19], which is close to the optimum bandgap energy (2.0 eV) required to overcome reaction overpotential and other experimental potential drops, while maintaining an efficient absorption of solar spectrum [20]. The collected Raman spectrum of the same NWs sample showed a strong silicon peak at 519 cm\(^{-1}\) as well as two broader peaks at longer Raman shifts (red curve, Fig. 2(d)). One peak was resolved into 567 cm\(^{-1}\) and 553 cm\(^{-1}\) peaks, ascribed to the high branch of the \(E_2\) phonon mode (\(E_2^N\)) and \(E_1(\text{TO})\) of GaN, respectively [21]. The other peak was resolved into 721 cm\(^{-1}\) and 696 cm\(^{-1}\) peaks, which are both ascribed to A1, longitudinal optical phonon modes (A1(LO)) of InGaN crystal having different indium compositions [22]. These peaks are evidence of phase separation within the InGaN NWs which is a common phenomenon in high indium compositions nanostructures [23]. After lift-off, as detailed later, the silicon peak was not observed in the Raman spectrum (blue curve, Fig. 2(d)) demonstrating the full removal of silicon in the substrate-free NWs membrane.

2.2. NWs membrane photoanode fabrication

After growing the InGaN NWs, the metal contact layer, consisting of Ti (20 nm), Al (60 nm), Ti (60 nm) and Au (300 nm), was deposited using an electron-beam evaporator (Fig. 3(a)) [24]. Since any contact between this metal layer and the electrolyte would short circuit our fabricated devices, the expanded GaN top was intentionally grown to limit chemical diffusion to the contact layer. The structure was then annealed at 750 °C to form an ohmic contact through nitrogen out-diffusion from GaN (as detailed later) leading to the transfer of charge.
carriers through thermionic field emission and thus increasing charge carrier collection efficiency [25]. Then a layer of 10 µm thick SU-8 photoresist was spin coated onto the metal contact layer to provide mechanical support for the final device. The SU-8 was however patterned with Vias to allow for an electric back contact of the device as presented in Fig. 3(b). Finally, silicon was etched away in a xenon difluoride (XeF₂) reactor. Due to the decreased flexural rigidity of the resulting substrate-free NWs membrane, it was successfully attached to a flexible plastic sheet and bent to a 7 mm radius of curvature without any crack formation or subsequent device failure (as optically imaged in Fig. 3(c)). SEM image of the metal side (marked with black square in Fig. 3(c)), presented in Fig. 3(d), revealed the successful formation of a quasi-continuous metal layer on the expanded GaN top, which highly increased the homogeneity and electrical conductivity of the back contact. Moreover, SEM image of the InGaN NWs side (marked with white square in Fig. 3(c)), revealed the complete etching of silicon substrate, which enabled the water splitting reaction to directly proceed at the InGaN NWs surface (Fig. 3(e)).

In the later presented electrochemical measurements, the membrane photoanode was flipped over a polyimide film covered with gold and attached to it using a conductive epoxy. Figure 3(f) contains false-coloured cross-sectional SEM image of the flipped NWs, showing their uncovered InGaN stems, GaN expanded region, annealed metal contact and conductive epoxy (from top to bottom). Finally, a layer of poly(dimethylsiloxane) (PDMS) was coated on the gold layer for proper electrical insulation. The optical image of the finalized NWs membrane photoanode is presented in Fig. 3(g).

![Fig. 3. NWs membrane photoanode fabrication. (a) Cross-sectional SEM (false-coloured) of the NWs after electron beam evaporation of the metal contacts. (b) Optical image of the sample surface showing the Via pattern through the SU-8 photoresist layer and the underlying metal contacts. (c) Optical image of the NWs membrane attached to a plastic sheet and bent to a 7 mm radius of curvature. Top view SEM images of the (d) metal side and (e) NWs side of the NWs membrane photoanode. (f) Cross-sectional SEM (false-coloured) of the NWs after flipping over a conductive medium. (g) Optical image of a NWs membrane attached to a polyimide film covered with gold.](image-url)
3. Results and discussion

3.1. TEM imaging and analysis of the NWs membrane

Following the fabrication process of the NWs membrane photoanode, a cross-sectional specimen was prepared through focused ion beam (FIB) milling and analysed through TEM (Fig. 4(a)). The collected TEM image clearly showed the InGaN/GaN NWs attached to the metal contact layer which itself is in contact with the conductive epoxy. The top carbon layer was deposited before the FIB milling process for the NWs protection. Collected EDX signals from the stem and expanded region (Fig. 4(b)), red and blue curves, respectively, showed peaks assigned to In, Ga and N within the stem while only peaks assigned to Ga and N were present within the expanded region. This clearly demonstrated that the NWs stem and expanded region were composed of InGaN and GaN, respectively. The Cu peak in the EDX spectra originated from the TEM sample holder. Since the novelty of the presented work is to extract the excess charge carrier through the deposited metal layer instead of silicon, elemental mapping of the GaN/metal contact interface was performed. EELS and EDX signals were collected under scanning mode from the region marked with the red vertical line in Fig. 4(a). Variations along the Ga ka, Ti ka, Al ka and Au La signals were extracted from the EDX spectra while variations in the N signal, due to the low N atomic number, were extracted from the EELS spectra and the collected profile were plotted in Fig. 4(c). Ga and N line profiles revealed a smoother decrease in the N peak compared to the Ga peak which is attributed to N out-diffusion during the annealing process [24]. This process leads to the formation of TiN as well as N vacancies, which act as donor sites, in the GaN layer. Therefore, the interfacial GaN becomes highly n-doped which is required for ohmic contacts based on thermionic field emission [26]. It should be noted that while Al/Au diffusion is expected, the Al EDX peak lies on the low energy spectrum of the EDX spectrum where it is highly affected by the x-ray continuum caused by the heavier atomic number Au atoms. Therefore, as observed in Fig. 4(c), a false reading of Al is expected to occur in regions with high Au compositions.

Fig. 4. (a) Cross-sectional TEM image of the NWs membrane. (b) Collected EDX spectra from the NWs stem (top red) and the expanded region (bottom blue). (c) EDX and EELS elemental mapping of the NWs/metal contact interface collected from the red vertical line in (a).

3.2. Electrochemical performance of the NWs membrane photoanode

To investigate the band alignment at the interfacial region, without potentially photocorrodng the surface by the generated photocurrent under reverse bias [27], the open circuit potential (OCP) of the membrane photoanode was studied [28]. The photoanode was thus submerged...
in potassium phosphate buffer solution (PH = 7) and irradiated by a 900 mW/cm² solar simulator through an AM1.5G filter. In response to a light pulse, the OCP of the membrane photoanode increased from −0.115 V (under darkness) to −0.31 V (under illumination) (Fig. (a)) evidencing the n-doping within the InGaN NWs and the presence of an upward band bending in the interfacial surface charge region [29, 30]. Since OCP corresponds to the electron quasi Fermi level of the n-doped InGaN NWs, the presence of surface states, which pin the surface Fermi level, is also reflected in the OCP behaviour. Therefore, OCP, under illumination, was measured at increasing illumination intensity and plotted in Fig. (b). At low intensities, (below 4 mW/cm²) increasing the excitation intensity has no effect on the OCP which suggests the presence of interfacial surface states which pin the n-quasi Fermi level [28]. Increasing the illumination intensity (above 4 mW/cm²) seems to unpin the Fermi level through filling the states with the photogenerated charge carriers. In this intensity domain, the OCP gets cathodically shifted with increasing intensity due to the screening effect of the photogenerated carriers’ electric field. Therefore, within the subsequent studies, the illumination intensity was chosen to fully unpin the fermi-level during water splitting operation.

![Graphs](image)

Fig. 5. (a) OCP profile measured from the NWs membrane in response to a light pulse. (b) OCP value dependence over increasing illumination intensity. Current density from the NWs membrane (red) and NWs on silicon substrate (blue) under c) continuous illumination, darkness and d) chopped illumination. All potentials are measured versus an Ag/AgCl/3M KCl reference electrode.

To assess the performance enhancement of the NWs membrane photoanode, it was compared to a reference sample consisting of InGaN NWs grown on silicon substrate, of similar chemical compositions and morphology, but without the GaN expanded region. Without any liftoff or transfer processes, metal contacts were made to the back side of the silicon wafer of the reference and then properly insulated. Linear sweep voltammetry (LSV)
scans of the NWs membrane (red curves) and the reference sample (NWs on silicon substrate—blue curves) were performed under illumination and darkness (Fig. (b)). While the dark current densities of the two structures, were comparably negligible (less than 0.02 mA/cm$^2$, dashed curves in Fig. (b)), the photocurrent densities were quite different. The NWs membrane structure showed much increased current density compared to the NWs on silicon as well as having a higher cathodic onset potential (−0.2 V, compared to 0.62 V). LSV scan of the two structures under chopped illumination (Fig. (d)) further demonstrates the improved performance of the NWs membrane over the NWs on silicon. At increasing anodic potentials, no plateau in the photocurrent density was observed, which denoted that not all of the photogenerated holes take part of the charge carrier transfer across the InGaN/electrolyte interface [31]. The presence of surface states, which were investigated by previous OCP measurements, is the main cause for the trapping/recombination of the photogenerated charge carriers. Indeed, several published reports showed similar photocurrent behaviour for InGaN NWs (and other nanostructures) in solar-based water splitting [11, 12, 32–34].

To shed light on the kinetics of charge carriers, responsible for the enhanced performance of the NWs membrane, the dynamic behaviour of the devices was studied through EIS. Under illumination and zero applied bias, a single frequency perturbation potential (10 mV), alternating from 1 Hz to 10 kHz, was applied over the samples and the platinum counter electrode and the changes in impedance were recorded. Figures (a) and (b) showed the collected Nyquist plot of the NWs on silicon substrate (blue dots) and NWs membrane (red dots), respectively. The insets, present the equivalent electrical circuits used to model the charge carrier dynamics which provided a good fitting (black lines) for the EIS data. The circuits were derived based on the photo-stationary state of the electronic charge carriers within the photoanodes during water splitting, depicted in Fig. (c) and (d). The first RC element in the equivalent circuit for the NWs on silicon substrate ($R_{CT}Q_{CT}$) represented the hole transfer process from the InGaN NWs to the electrolyte, where $R_{CT}$ describes the resistance to charge transfer and $Q_{CT}$ is a constant phase element (CPE) which describes the double layer capacitance [35]. While the double layer capacitance, generated from the bulk space-charge region and the Helmholtz layer is ideally modelled by capacitor, the surface roughness and non-uniform chemical composition associated with NWs, caused the interface to be best described by a CPE [36,37]. The second RC element ($R_2Q_2$) described the GaN/silicon interface which hinders electron transfer due to the presence of the large bandgap insulating SiNx interfacial layer, Fig. 5(b) [17,18]. Finally, there is a series resistance ($R_{sol,sub}$), which describes the solution and substrate cumulative resistance. The values of the fitting parameters are presented in Table 1.

On the other hand, the equivalent electrical circuit, which presented a good fitting of the NWs membrane EIS data (black curve), only contained $R_{CT}$, $Q_{CT}$, and $R_{sol,sub}$ elements (Fig. 6(b)). The absence of the series $R_2Q_2$ elements in the equivalent circuit revealed that indeed, an ohmic contact formed between the NWs and the back-metal contact which could facilitate excess charge carriers transfer. Furthermore, the values of the CPE elements ($Q_{CT}$) from both structures were within the same range, which demonstrated that the main difference in performance was not due to the charge transfer layer, but rather due to the enhancement of the collection of the excess charge carriers. Finally, the difference in magnitude between $R_{sol,sub}$ for the membrane (46 Ω) and for the NWs on silicon (1.3 kΩ), demonstrated the higher resistance from the comparatively lower substrate electrical conductivity and its effect on the charge carrier dynamics, as previously anticipated.
Fig. 6. EIS measurements for the (a) NWs on silicon and b) NWs membrane (dots). The insets in (a) and (b) represent the equivalent electric circuit used to fit (black curves) the experimental data. Energy band diagram of the (c) NWs on silicon and (d) NWs membrane under photo-stationary equilibrium during solar water splitting. $E_F$ represents the bulk Fermi level while the $E_{Fp}$ and $E_{Fe}$ represent the quasi electron and hole Fermi levels under optical excitation, respectively.

Table 1. Fitting parameters for the Nyquist plots.

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<tr>
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<th>NWs on silicon</th>
<th>NWs membrane</th>
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<tbody>
<tr>
<td>$R_{ct}$</td>
<td>23 kΩ</td>
<td>27 kΩ</td>
</tr>
<tr>
<td>$Q_{ct}$</td>
<td>$2 \times 10^{-6}$; 0.86</td>
<td>$4.5 \times 10^{-6}$; 0.87</td>
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<tr>
<td>$R_s$</td>
<td>332 kΩ</td>
<td>-</td>
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<tr>
<td>$Q_s$</td>
<td>$93 \times 10^{-9}$; 0.79</td>
<td>-</td>
</tr>
<tr>
<td>$R_{sol,sub}$</td>
<td>1.3 kΩ</td>
<td>46 Ω</td>
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Having established the higher performance of the NWs membrane, compared to the NWs on silicon, the stability of the samples was studied under continuous operation (Fig. 7). The samples were biased at 0.4 V, where the dark current densities were $11 \times 10^{-6}$ and $8 \times 10^{-6}$ mA/cm$^2$ for the NWs membrane and NWs on silicon, respectively. While, the InGaN NWs on Si-substrate showed a rapid degradation of the current density, the NWs membrane showed a higher equilibrium for the generated current density which can be attributed to the previously described mechanisms [38].
4. Conclusions

In conclusion, we have demonstrated the fabrication of a flexible substrate-free novel InGaN NWs membrane photoanode structure. The LSV characterization of the NWs membrane photoanode revealed an enhancement of the photocurrent densities as well as a lower turn on potential, as compared to regular NWs on bulk silicon substrate. As confirmed by the EIS measurements, such an increase in performance was ascribed to more efficient excess charge carrier extraction from the NWs due to the Ohmic contact formed by the deposited metals, as compared to the silicon wafer which forms the interfacial SiNx insulating layer. The demonstrated membrane technique represents a novel pathway for enhancing InGaN NWs photoanode performance that could be implemented alongside other techniques, such as co-catalysts [39], sidewall passivation [34], surface protection [40, 41] or bandgap engineering [11] to further drive III-nitride photoanodes towards commercialization.

Funding

BSO, TKN and CZ acknowledge funding support from King Abdulaziz City for Science and Technology (KACST) Technology Innovation Center (TIC) for Solid State Lighting, grant no. KACST TIC R2-FP-008. King Abdullah University of Science and Technology (KAUST) baseline funding, grant no. BAS/1/1614-01-01.

Disclosures

The authors declare that there are no conflicts of interest related to this article.