Realizing InGaN monolithic solar-photoelectrochemical cells for artificial photosynthesis

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InGaN alloys are very promising for solar water splitting because they have direct bandgaps that cover almost the whole solar spectrum. The demonstration of direct solar-to-fuel conversion without external bias with the sunlight being the only energy input would pave the way for realizing photoelectrochemical (PEC) production of hydrogen by using InGaN. A monolithic solar-PEC cell based on InGaN/GaN multiple quantum wells capable to directly generate hydrogen gas under zero bias via solar water splitting is reported. Under the irradiation by a simulated sunlight (1-sun with 100 mW/cm^2), a 1.5% solar-to-fuel conversion efficiency has been achieved under zero bias, setting a fresh benchmark of employing III-nitrides for artificial photosynthesis. Time dependent hydrogen gas production photocurrent measured over a prolonged period (measured for 7 days) revealed an excellent chemical stability of InGaN in aqueous solution of hydrobromic acid. The results provide insights into the architecture design of using InGaN for artificial photosynthesis to provide usable clean fuel (hydrogen gas) with the sunlight being the only energy input. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4871105]

Generating hydrogen gas via the process of solar energy conversion of water to gaseous hydrogen and oxygen (or solar water splitting) is highly attractive and potentially offers alternative, clean, nontoxic, and renewable fuels.[1–11] The most widely studied photoelectrode material for photoelectrochemical (PEC) solar water splitting is titanium dioxide (TiO_2). However, the wide band gap of this material (~3.2 eV) restricts the usable portion of the solar spectrum, limiting solar to hydrogen conversion efficiency.[3] Several oxide semiconductors such as $SrTiO_3$ and ZnO_2 have the potential to split water without applying external bias with relatively high corrosion resistance and acceptable band edge alignments relative to the redox potentials.[11] Yet, similar to TiO_2, these oxides also have large band gaps (3.4–3.5 eV) and are inefficient for solar energy conversion. Lower band-gap materials such as II-VI semiconductors (CdSSe, etc.) and III-V semiconductors (InGaAsP, etc.) absorb sunlight more effectively, but they easily corrode in acidic or basic solutions.[12–14] Finding new semiconductor materials meeting the criteria of an ideal semiconductor photoelectrode (high-efficiency, long-life, and low cost) has been challenging, but is highly desirable.

From the materials point of view, group III nitride semiconductors such as InGaN alloys are very promising for solar water splitting because they have direct bandgaps that cover almost the whole solar spectrum.[15–17] GaN has shown to be able to split water[10,18–20] under irradiation of ultraviolet (UV) light with considerable resistance to corrosion in an electrolytic solution.[21,22] Nonetheless, like TiO_2, the band gap of GaN is around 3.4 eV, which makes it an efficient photoreactive electrode for UV light with a wavelength of about 350 nm.[20] Alloying GaN with InN lowers the bandgaps and makes the bandgaps of $In_xGa_{1-x}N$ (E_g varied between 3.4 and 0.65 eV) to have an excellent spectral match to the solar spectrum while capable of shifting both the conduction and valence band edges closer to the redox potentials.[15–17] In addition, the smaller lattice constant or stronger bonding of In-N and Ga-N compared with other semiconductors (GaP, for example) also provides higher corrosion resistance. Furthermore, InGaN has been shown to be a radiation hard material.[15–17] Therefore, the use of InGaN as a photoelectrode material has recently generated considerable interest.[23–28] While a number of previous studies have shown PEC effects in InGaN and GaN, H_2 gas generation was demonstrated either via the assistance of external bias or under the irradiation by UV light.[10,18–20,23–26] More recently, water splitting under selective bands of visible light using multiband InGaN/GaN nanowire heterostructures has been demonstrated.[27] However, direct water splitting and H_2 generation using InGaN planar layer structures under zero external bias and full-spectrum solar irradiation have not been realized and the solar-to-fuel conversion efficiency has not been studied. The ultimate water splitting technology is the realization of direct solar-to-fuel conversion without external bias with the sunlight being the only energy input.

The concept of an integrated and monolithic PEC-solar cell device for direct water splitting has been previously proposed and demonstrated for the InGaAsP material system, which holds the record of solar-to-fuel conversion efficiency of 12.4%.[29] However, the further development of InGaAsP PEC devices has been limited by corrosion problems. More recently, solar water splitting was demonstrated by a hybrid system consisting of n-type InGaN working electrodes with bias supplied by a GaAs solar cell.[28] Here, we report on the realization of a monolithic integrated solar-PEC cell device based on the InGaN material system which is capable to directly generate H_2 gas via solar water splitting without external bias with the sunlight being the only energy input.

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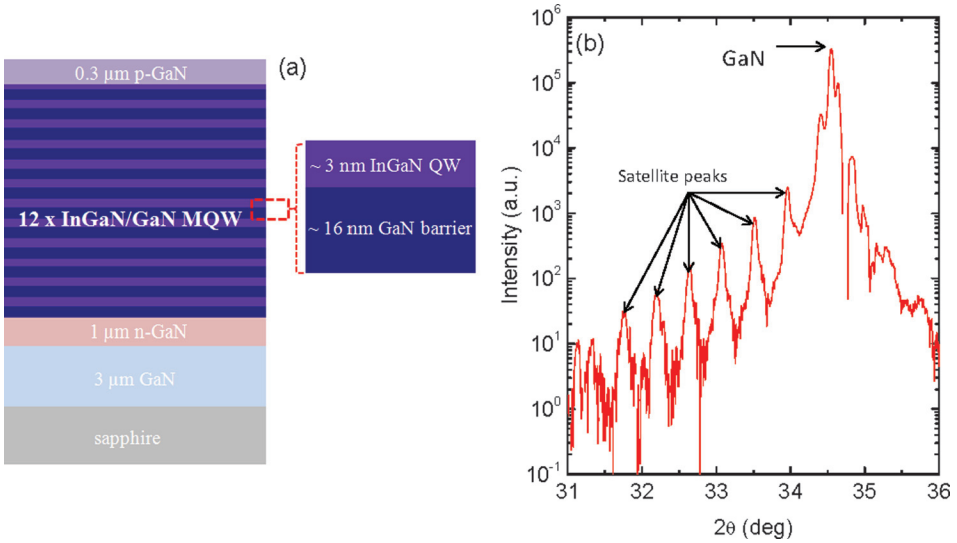

FIG. 1. (a) Schematic layer structure of a 12-period InGaN/GaN MQW solar cell; (b) XRD θ-2θ scan pattern of the 12-period InGaN/GaN MQW solar cell structure shown in (a). The presence of the distinct satellite peaks indicates the high interfacial quality between InGaN QW and GaN barrier layers.

The layer structure of the InGaN/GaN multiple quantum wells (MQWs) solar cell employed in this study is illustrated in Fig. 1(a) and was grown by metal organic chemical vapor deposition (MOCVD). By leveraging our previous InGaN/GaN MQW solar cell design,[30] the light absorbing region consists of twelve periods of $In_xGa_{1-x}N$ (3 nm)/GaN (16 nm) MQWs. Prior to the growth of the solar cell structure, an undoped GaN epilayer (3 μm) was first deposited on *c*-plane sapphire substrate. This is then followed by the growth of a highly conductive Si-doped *n*-GaN layer, followed by the InGaN/GaN MQW light absorbing region and then Mg-doped *p*-GaN layer. The MQWs were grown under the established MOCVD growth conditions of $In_xGa_{1-x}N$ epilayers[30,31] with the targeted *x* value of around 0.35. The thicknesses of the *p*-GaN and *n*-GaN contact layers are ~300 nm and ~1 μm, respectively. The x-ray diffraction (XRD) pattern (in θ-2θ scan) obtained from the solar cell structure shown in Fig. 1(b) exhibits distinct satellite peaks, indicating the high interfacial quality between the InGaN quantum wells (QW) and GaN barrier layers.

A schematic illustration of the fabricated InGaN/GaN MQW solar cells is shown in Fig. 2(a). The solar cell device fabrication process started with the deposition of a thin bilayer of Ni/Au (3/6 nm) by e-beam evaporation. Devices with mesa size dimensions of 2.3 mm × 2 mm were defined by etching down to *n*-type GaN using chlorine based inductively coupled plasma dry etching technique. Then a semi-transparent *p*-contact was annealed for 30 min in air at 450 °C to obtain the ohmic characteristic for *p*-contact. Then, grid *p*-contact Ni/Au electrode (6 μm width and pitch distance of 170 μm) bilayers (30/150 nm in thickness) were deposited on the mesa area. Ti/Al/Ni/Au (30/100/20/150 nm) *n*-contact was deposited by e-beam evaporation using optical lithography and lift-off techniques. The solar cell was characterized using a microprobe station, air mass 1.5 (AM1.5G) solar simulator (1 sun with 100 mW/cm^2), and Keithley 2400 source meter.

Figure 2(b) shows the current density versus voltage (*J*-*V*) characteristics of a fabricated $In_xGa_{1-x}N$/GaN MQW solar cell under the irradiation by a simulated sunlight (AM1.5G solar simulator with an incident light intensity of I_{int} ~ 100 mW/cm^2). This InGaN/GaN MQW solar cell exhibits an open circuit voltage (V_{oc}) of 1.80 V, short circuit current density (J_{sc}) of 2.5 mA/cm^2, fill factor (FF) of 64%, and solar-energy-to-electricity conversion efficiency of about 2.9%.

The photoelectrochemical properties of the InGaN/GaN MQW solar cell were studied in 1 mol/l of hydrobromic acid (HBr) solution. As schematically shown in Fig. 3(a), the PEC cell consists of the photoreactive working electrode (InGaN/GaN MQW solar cell), a counter electrode, and a reference electrode. The counter and reference electrodes were made of platinum (Pt) and Ag/AgCl/NaCl (Sodium-chloride-saturated silver-chloride electrode (SSSE)). The photoelectrochemical characteristics of the InGaN/GaN MQW solar cell were compared with those of *p*-InGaN and *p*-GaN epilayers deposited on a sapphire substrate. No surface treatments to the sample surfaces were employed. A Keithley source meter was used to apply bias voltage between the working and counter electrodes (V_{CE}). The photocurrent was recorded using an electrometer.

Figure 3(b) shows the photocurrent density (J_{ph}) as functions of V_{CE} measured under dark and under the irradiation

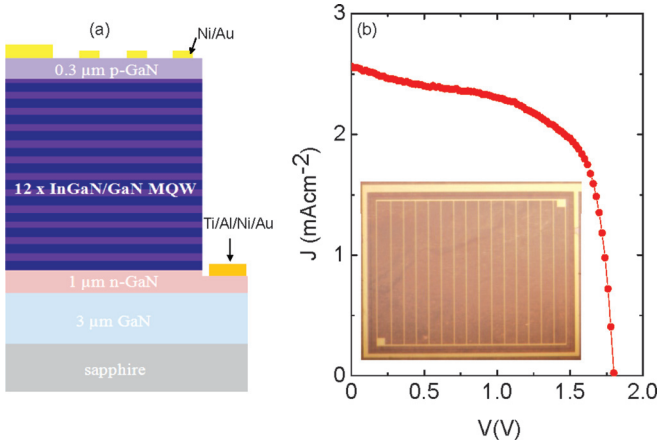

FIG. 2. (a) Schematic of the fabricated InGaN/GaN MQW solar cell. (b) Current density-voltage (*J*-*V*) characteristic of the 12 period InGaN/GaN MQW solar cell under irradiation by a simulated sunlight (1-sun solar simulator). The inset shows the photo of the fabricated solar cell.

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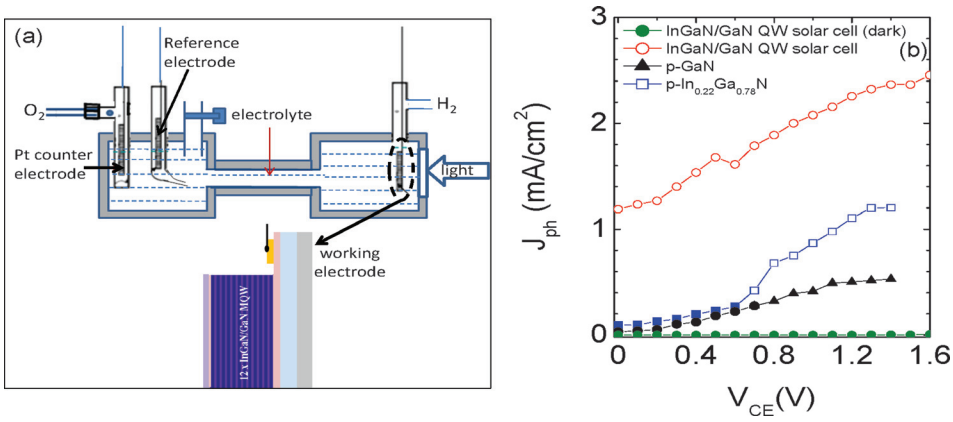

FIG. 3. (a) Schematic of the experimental setup for the photoelectrochemical properties characterization and hydrogen gas generation; (b) Current density-voltage characteristics measured under dark and under irradiation by a simulated sunlight (1-sun solar simulator) for InGaN/GaN MQW solar-PEC cell, *p*-InGaN epilayer photoelectrode, and *p*-GaN epilayer photoelectrode. Open and solid symbols, respectively, indicate H_2 generation and no H_2 gas generation under the irradiation by a simulated sunlight (1-sun solar simulator).

by a simulated sunlight (1-sun solar simulator) for the InGaN/GaN MQW solar cell, *p*-InGaN and *p*-GaN epilayer electrodes. Several features can be observed: (1) The measured J_{ph} values are much higher for the InGaN/GaN MQW solar cell structure than for *p*-InGaN and *p*-GaN epilayers, with *p*-GaN epilayer exhibiting the lowest values of (J_{ph}). (2) H_2 gas generation occurs in *p*-InGaN epilayer electrode at $V_{CE} = 0.6$ V, indicating that an additional external voltage is needed for *p*-InGaN epilayers to split water. (3) No H_2 gas was generated from *p*-GaN working electrode in the measured bias range, indicating the existence of a large surface potential due to band bending caused by the presence of surface states in *p*-GaN; a surface potential of about 1.6 V has been previously measured for *p*-GaN.[32] (4) Evolution of H_2 is established immediately without external bias ($V_{CE} = 0$ V) for the InGaN/GaN MQW solar cell electrode and H_2 gas generation was visible with plentiful amounts of gas bubbles accumulated on the surface of the solar cell. The measured PEC results indicate that InGaN/GaN MQW solar cells are capable to split water directly into usable hydrogen with the sunlight being the only energy input.

The stability of the InGaN/GaN MQW solar cell working electrodes in HBr solution was evaluated by recording the relative H_2 production photocurrent as a function of illumination time and the results are summarized in Figure 4.

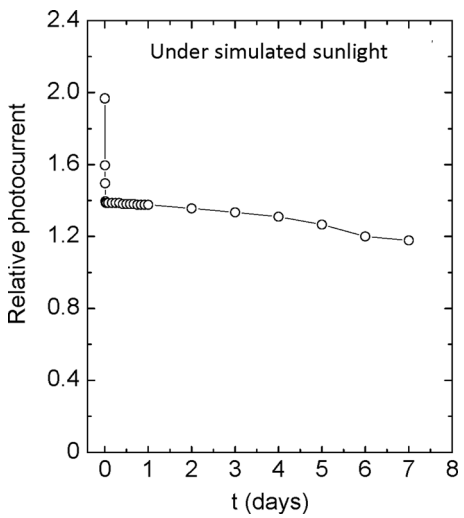

FIG. 4. The relative H_2 production photocurrent as a function of operating time (t) under the irradiation by a simulated sunlight (1-sun solar simulator).

The H_2 production photocurrent exhibits an initial sharp drop by about 40% and then becomes quite stable thereafter and drops by about 10% after 1 week of measurement time. We did not observe any etching effects or changes in morphology occurring on the surface of the InGaN/GaN MQW solar cell photoelectrode after the PEC measurements. This initial drop may be associated with absorption of the light by solvated electrons generated on the electrode surface, a scenario which has been previously reported.[33]

Assuming 100% photocurrent electrolysis efficiency, the efficiency (η) of H_2 production of the InGaN/GaN MQW solar cell electrode can be estimated using the following equation:[29]

$$\begin{aligned}\eta &= (\text{power out})/(\text{power in}) \\ &= 1.23\,\text{x}\,(\text{H2 production photocurrent density}) \\ &\quad /(\text{input optical power density}),\end{aligned} \tag{1}$$

where the multiplier factor 1.23 V is the ideal fuel cell limit at 25 °C (the lower heating value of hydrogen). The input power is the incident light intensity provided by the AM1.5G solar simulator which is ~100 mW/cm^2. For the output power, the H_2 production photocurrent is 1.2 mA/cm^2 at zero bias ($V_{CE} = 0$ V) for the InGaN/GaN MQW solar cell electrode. The calculation based on Eq. (1) yields the H_2 production efficiency of the InGaN/GaN MQW solar cell PEC system to be around 1.5%. Note that the output power is calculated assuming 100% Faradaic efficiency. This is based on the stability result shown in Fig. 4. If a fraction of the photocurrent was contributed by an undesirable photocorrosion reaction, the stable operation over this prolonged measurement time (7 days) will be unlikely. In fact, the 100% Faradaic efficiency assumption has been commonly used and verified for semiconductor photoelectrodes, including Si[34] and InGaAsP.[29]

In summary, a monolithic solar-photoelectrochemical cell based on InGaN/GaN multiple quantum wells has been fabricated and is shown to be capable to directly generate hydrogen gas under zero bias via solar water splitting. Under the irradiation by a simulated sunlight (AM 1.5 solar simulator), a 1.5% solar-to-fuel conversion efficiency has been achieved under zero bias. The hydrogen gas production photocurrent is found to be quite stable (decreases by about 10% after 7 days of operation), revealing an excellent chemical stability of InGaN in aqueous solution of HBr. With further

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development, the InGaN MQW solar cells appear to be an excellent artificial photosynthesis material which is expected to be capable to provide usable clean fuel (hydrogen gas) with the sunlight being the only energy input. Due to its chemical stability and radiation hardness, InGaN/GaN MQW solar cell PEC systems could be ideal for clean energy applications in harsh environments.

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