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InGaN/GaN multiple quantum well solar cells for energy and hydrogen generation

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InGaN alloys are promising for solar cells and solar water splitting because they have direct bandgaps that cover almost the whole solar spectrum. This paper provides a brief overview on recent advances made by our group in the area of III-nitrides for energy and hydrogen generation. Solar cells based on $In_xGa_{1-x}N$/GaN (x~0.35) multiple quantum well (MQW) structures have been fabricated and were shown exhibit an open circuit voltage (V_{oc}) of 1.80 V, short circuit current density (J_{sc}) of 2.5 mA/cm^2 and a solar-energy-to-electricity conversion efficiency (η) of 2.95% under the irradiation by a simulated sunlight (AM 1.5 G, 1-sun, 100 mW/cm^2). Under the irradiation of concentrated sunlight, V_{oc}, J_{sc} and η were found to increase with solar concentration. Furthermore, InGaN/GaN MQW solar cells were effectively monolithic solar-photoelectrochemical cells which are capable to directly generate hydrogen gas under zero bias via solar water splitting. Under the irradiation of 1 sun (AM 1.5 G), a 1.5% solar-to-fuel conversion efficiency has been achieved under zero bias with an excellent chemical stability.

Introduction

Photonic/electronic devices based on III-nitride semiconductors, including UV/blue/green/white light emitting diodes (LEDs), violet/blue laser diodes (LDs), UV detectors, and high power/temperature transistors, have reached very high performance level and made enormous impacts in almost all major sectors of society including lighting, energy, national security, and entertainment. It has also been recognized that InGaN ternary alloys are promising for the realization of solar energy conversion devices due to the fact that the energy gaps of InGaN alloys can be tuned to cover the entire solar spectrum (varying from 0.7 eV for InN to 3.4 eV for GaN) [1-3]. In additional to its direct bandgap match to the solar spectrum, the bandgap of InGaN alloys can also be engineered to optimally match with conditions necessary for direct hydrogen generation by water splitting using sunlight [4-7]. These properties together with other outstanding attributes of InGaN such as high carrier mobility, drift velocity, radiation resistance, and optical absorption of ~10^5 cm^{-1} near the band edge [2,8], make the InGaN alloys highly promising for solar energy conversion, such as solar cells [8-10], thermoelectric (TE) devices [11,12], and photoelectrochemical cells (PECs) for direct hydrogen production by sun light [4-7, 13-15].

In order to take advantages of the band gap tunability of the InGaN alloy system, the synthesis of high quality InGaN films with high In-contents is necessary, however, is

highly challenging. One of the biggest problems is attributed to the large lattice mismatch between InN and GaN, resulting in low solubility and phase separation [16]. Previous theoretical studies on the effects of elastic strain in InGaN epilayers (coherently grown on GaN templates) on the spinodal decomposition revealed that the miscibility gap in the strained ternary compound is reduced in comparison to the relaxed layers [17]. It was shown experimentally that InGaN alloys across the entire composition range without phase separation can be grown by employing strain engineering via embedding InGaN within a double heterostructure [18,19] or directly depositing on GaN or AlN epi-templates without buffer layers [20]. Utilizing the concept, $In_xGa_{1-x}N$/GaN MQW architecture was exploited for the construction of solar cells with the attempt to alleviate to a certain degree the phase separation issue [9,10]. We have grown, fabricated, and characterized InGaN based solar cells utilizing the InGaN/GaN MQW p-i-n structures [9,10,15]. The fabricated solar cells exhibited an open circuit voltage of about 1.8 V, fill factor of about 64% and overall efficiency of about 3% under AM 1.5 irradiation. The performance of these nitride solar cells under concentrated sunlight has also been investigated. When used as a monolithic solar-photoelectrochemical cell, direct solar water splitting and hydrogen gas generation under zero bias has also been realized. Our results indicate that InGaN alloys are promising for full spectrum solar cell and artificial photosynthesis applications with potential to provide usable clean energy/fuel (electricity and hydrogen gas) with the sunlight being the only energy input.

Experimental

The layer structure of the InGaN/GaN MQW solar cells employed in this study is shown in Fig. 1(a) and was grown by metal organic chemical vapor deposition (MOCVD) [9,10,15]. The light absorbing region consists of twelve periods of $In_xGa_{1-x}N$ (3 nm)/GaN (17 nm) MQWs. Prior to the growth of the MQW 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 cladding layer, followed by the InGaN/GaN MQW light absorbing region and Mg-doped *p*-GaN layer. The MQWs were grown under the established MOCVD growth conditions of $In_xGa_{1-x}N$ epilayers [20] 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 pattern (in θ-2θ scan) obtained from the solar cell structure exhibited distinct satellite peaks, indicating the high interfacial quality between the InGaN QW and GaN barrier layers [10]. 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 x 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 minutes in air at 450 ^{o}C to obtain the ohmic *p*-contacts. Then, grid *p*-contact Ni/Au electrode bilayers (30/150 nm in thickness) with 6 µm width and pitch distance of 170 µm were deposited on the mesa area. Ti/Al/Ni/Au (30/100/20/150 nm) *n*-contact was deposited by e-beam evaporation via optical lithography and lift-off techniques. The solar cell was characterized using a microprobe station, air mass 1.5 (AM 1.5 G) solar simulator (1 sun, 100 mW/cm^2) and Keithley 2400 source meter. The photoelectrochemical properties of the InGaN/GaN MQW solar cells were studied in 1 mol/L of hydrobromic acid (HBr) solution. 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.

Results and Discussion

Figure 1(b) shows the current density versus voltage (J_{sc}-V) and power density versus voltage (P-V) characteristics of a fabricated $In_xGa_{1-x}N$/GaN MQW solar cell under the irradiation by a simulated sunlight (AM 1.5 G, 1-sun, 100 mW/cm^2). From these measurements, V_{oc}, J_{sc}, fill factor (FF), and maximum power delivered by the devices were found to be 1.80 V, 2.56 mA/cm^2, 64% and 2.95 mW/cm^2, respectively. We have also studied the light intensity dependence of J_{sc}, V_{oc}, FF and η to explore the potential use of InGaN MQW for concentrator solar cells. It was found that the short circuit current density increases linearly and V_{oc} increases logarithmically with solar concentration (C). This is due to the fact that the number of charge carrier generated is directly proportional to the number of photons absorbed. However, FF was decreased with increasing in C, which is caused by the enhanced carrier recombination at the interface region under high carrier densities. The overall solar conversion efficiency as a function of C is shown in Fig. 1(c). The efficiency increases from 2.95 to 3.03% when C increases from 1 to 30 suns. The overall enhancement in efficiency up to 30 suns implies the suitability of InGaN MQW solar cells for concentrated photovoltaic applications.

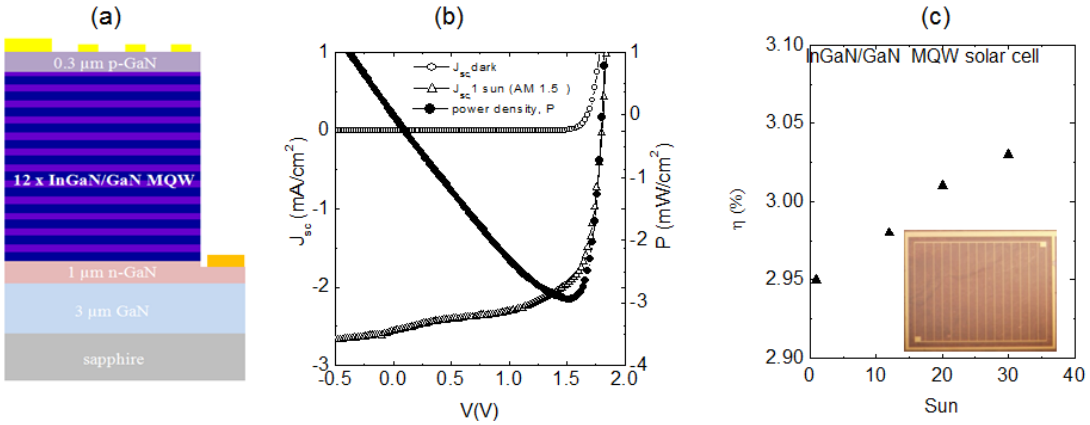

Fig. 1 (a) Layer structure of InGaN/GaN solar cells with twelve periods of 3 nm thick $In_xGa_{1-x}N$ (x≈0.35) QW and 17 nm GaN barrier. (b) Room temperature current density versus voltage (J_{sc}-V) and power density versus voltage (P-V) characteristics of $In_xGa_{1-x}N$/GaN MQW (x~0.35) solar cells under AM 1.5 irradiation. V_{oc}, J_{sc}, FF and η are 1.8 V, 2.56 mA/cm^2, 64% and 2.95%, respectively. (c) Solar-energy-to-electricity conversion efficiency, η, as a function of the solar concentration, C. The efficiency increases from 2.95 to 3.03 % as C increases from 1 to 30 suns. The inset is an optical microscopy image of a fabricated solar cell with 2.3 mm x 2 mm mesa size [after refs. 9 and 10].

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. 2(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. Figure 2(b) shows the photocurrent density (J_{ph}) as functions of V_{CE} measured under dark and under the irradiation by a simulated sunlight (AM 1.5 G, 1-sun, 100

mW/cm^2) for the InGaN/GaN MQW solar cell, *p*-InGaN and *p*-GaN epilayer electrodes. It can be seen that InGaN/GaN MQW solar cells outperform those of *p*-InGaN and *p*-GaN epilayers, with *p*-GaN epilayer exhibiting the lowest values of (J_{ph}). Figure 2(b) shows that the evolution of H_2 is established immediately without external bias (V_{CE} = 0 V) for the InGaN/GaN MQW solar cell electrode with plentiful amounts of H_2 gas bubbles accumulated on the surface of the solar cell. In comparison, 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; while 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. 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.

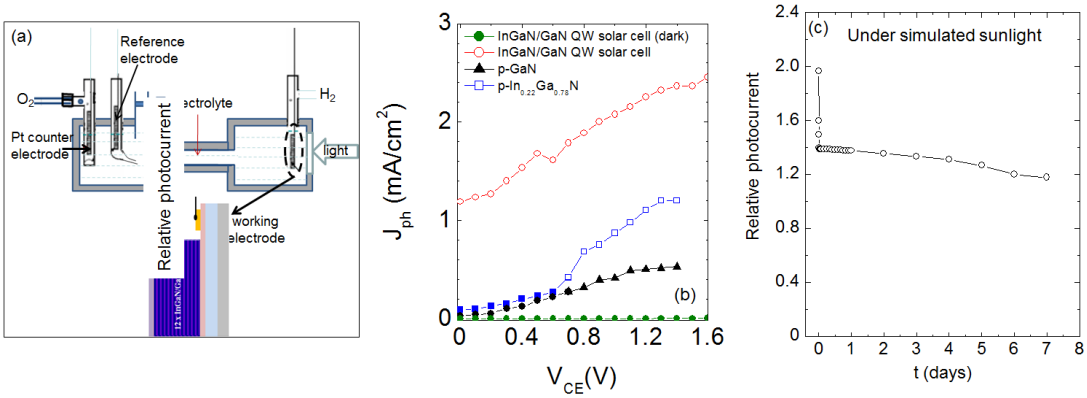

Fig. 2 (a) Schematic of the experimental setup for the photoelectrochemical properties characterization and hydrogen gas generation; (b) Current density-voltage characteristics measured under dark and under irradiation by a simulated sunlight (1-sun solar simulator) for InGaN/GaN MQW solar-PEC cell, *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). (c) The relative H_2 production photocurrent as a function of operating time (t) under the irradiation by a simulated sunlight (1-sun solar simulator) [after ref. 15].

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 [21]:

$$\eta = (\text{power out})/(\text{power in})$$
$$= 1.23 \times (H_2 \text{ production photocurrent density})/(\text{input optical power density})$$

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 yields the H_2 production efficiency of the InGaN/GaN MQW solar cell PEC system to be around 1.5%.

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 Fig. 2(c). 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. Based on the

stability result shown in Fig. 1(c), any contributions by undesirable photocorrosion reactions to the photocurrent can be precluded. Therefore, the 100% Faradaic efficiency assumption used in calculating the solar-to-fuel efficiency is valid.

In summary, a brief overview on recent advances made by the authors' group in the area of III-nitrides for energy and hydrogen generation was provided. InGaN/GaN MQW architecture was utilized to obtain the InGaN light absorbing region with a relatively high In-content or longer operating wavelength. Solar cells with an overall solar energy to electrical power conversion efficiency of about 3% have been obtained and the efficiency was observed to increase with the solar concentration. InGaN/GaN MQW solar cells have also been investigated as monolithic solar-photoelectrochemical cells. 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. Due to its chemical stability and radiation hardness, InGaN/GaN MQW solar cells and PEC systems could be ideal for clean energy applications in harsh environments.

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