Hydrogen generation by solar water splitting using p-InGaN photoelectrochemical cells

K. Aryal, B. N. Pantha, J. Li, J. Y. Lin, and H. X. Jiang[a)]
Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, Texas 79409, USA

Photoelectrochemical effects in p-$In_xGa_{1-x}N$ ($0 \leq x \leq 0.22$) alloys have been investigated. Hydrogen generation was observed in p-InGaN semiconducting electrodes under white light illumination with additional bias. It was found that p-InGaN alloys possess much higher conversion efficiencies than p-GaN. Time dependent photocurrent density characteristics showed that the stability of p-InGaN in aqueous HBr is excellent. The photocurrent density was found to increase almost linearly with hole mobility and excitation light intensity. © 2010 American Institute of Physics.
[doi:10.1063/1.3304786]

The generation of hydrogen gas by splitting water has attracted tremendous research work in recent years, with the hope of fulfilling demands for environmental friendly energy.[1] Among the various potential technologies for efficient and nontoxic hydrogen production, photoelectrochemical (PEC) technology is recognized as one of the most promising. The currently known photocatalytic materials, however, are either too inefficient in sunlight due to large band gaps, or too unstable in aqueous solutions for practical implementation.[2–6] For example GaInP and GaAsPN, have shown promising efficiency but suffer from poor stability.[3] Currently, the favored material for the photoanode in a PEC is TiO_2 due to its high corrosion resistance.[6] However, TiO_2 has an energy band gap of about 3.2 eV and can only be activated by light energy equal to or greater than 3.2 eV. Such an energy range is present in less than 3% of the solar spectrum. TiO_2 is thus intrinsically inefficient. Maximum solar absorption can be attained by minimizing the semiconductor band gap.[7] However, if the band gap becomes too small, the cell will not generate enough potential to drive the water splitting reaction. In order to split water in a PEC cell, the conduction band-edge potential of a semiconductor electrode must be lower than that of the hydrogen-evolving half-reaction and its valence band-edge potential must be higher than that of the oxygen-evolving half reaction.[8,9]

$In_xGa_{1-x}N$ is a very promising candidate for solar water splitting because of its direct band gap, which can be tuned to cover the entire solar spectrum through band gap engineering. This system not only has the appropriate band gap energy for water splitting, but also has high corrosion resistance in aqueous solutions.[10–14] Between n-and p-type semiconductors, if the band-edge potentials are the same, they should have similar capabilities for water splitting. However, they could have different stabilities in an electrolyte solution. In an n-type semiconductor, photogenerated holes acting as strong oxidizing agents can oxidize the semiconductor itself. In p-type semiconductors, the surface exhibits electron accumulation under irradiation, so using p-type semiconductor materials as a working electrode offers self-protection against photocorrosion caused by semiconductor oxidization. In addition, a p-type semiconductor material has characteristics of hydrogen production at the surface, in contrast to oxygen production in n-type semiconductors.[15] When p-$In_xGa_{1-x}N$ electrode is excited by light irradiation, photo-excited electrons move toward the p-$In_xGa_{1-x}N$/electrolyte interface and react with H^+ to generate H_2 by a reduction reaction; $2H^+ + 2e^- \rightarrow H_2$.[16] Semiconductors are more resistant to reduction than oxidation reactions, making p-type materials more stable than n-type materials. Thus, p-type semiconductors are preferred over n-type semiconductors as photocatalytic materials.[17,18] However, there has not been any work done regarding the use of p-InGaN as the working electrode in PEC cells. This is because p-type InGaN is notoriously hard to make. Recently, our group has succeeded in producing p-$In_xGa_{1-x}N$ by metal organic chemical vapor deposition (MOCVD) for x up to 0.35.[19]

In this letter, we report on the studies of PEC effects in p-$In_xGa_{1-x}N$ alloys and the observation of hydrogen generation by solar water splitting using p-$In_xGa_{1-x}N$ alloys as working electrodes in a PEC cell. p-$In_xGa_{1-x}N$ epilayers of about 0.25 μm in thickness were epitaxially deposited on semi-insulating c-GaN/AlN/sapphire templates using MOCVD. Trimethylgallium, trimethylindium, and bicyclopentadienyl were used as the precursors for Ga, In, and Mg, respectively. For an active nitrogen source, high purity ammonia gas was used. The In content in p-$In_xGa_{1-x}N$ alloys was increased by reducing the growth temperature. Ohmic contacts on p-$In_xGa_{1-x}N$ working electrodes were prepared by e-beam evaporation of Ni (30 nm)/Au (120 nm) with subsequent rapid thermal annealing at 550 °C for 90 s in air. Hall effect measurement results for the set of samples used in this study are summarized in Table I. These results showed that the Mg-doped $In_xGa_{1-x}N$ epilayers are p-type. The metal contact was protected by using clear epoxy resin to avoid direct contact with the electrolyte solution.

TABLE I. Electrical properties of p-$In_xGa_{1-x}N$ alloys employed in this study.

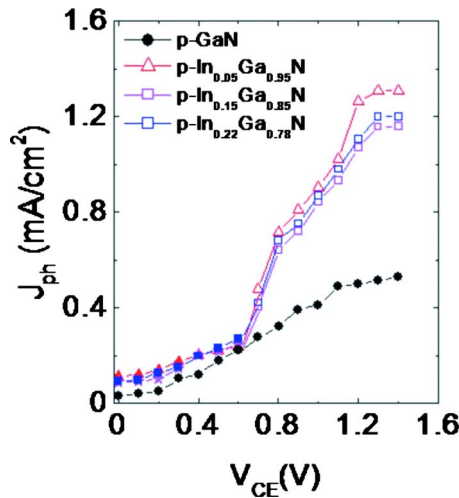| Samples	Mobility (cm^2/V s)	Hole Concentration (cm^{-3})	Resistivity (Ω cm)
GaN	15	2.0×10^{17}	2.1
$In_{0.05}Ga_{0.95}N$	13	3.0×10^{17}	1.6
$In_{0.15}Ga_{0.85}N$	2	2.4×10^{18}	1.3
$In_{0.22}Ga_{0.78}N$	3	5.0×10^{18}	0.4

[a)]Electronic mail: hx.jiang@ttu.edu.

FIG. 1. (Color online) Photocurrent densities (J_{ph}) as a function of V_{CE}, the voltage applied between working and counter electrodes under white light illumination using a standard AM1.5 solar simulator. The light intensity at the sample surface was about 132 mW/cm^2. Open symbols indicate generation of H$_2$ gas, while solid symbols indicate no H$_2$ gas generation.

FIG. 3. (Color online) Photocurrent densities (J_{ph}) of p-In$_x$Ga$_{1-x}$N electrodes at V_{CE}=1.2 V as a function of the measurement time (t). The light intensity at the sample surface was about 132 mW/cm^2.

The PEC cell consists of a working electrode (p-In$_x$Ga$_{1-x}$N), 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). The light source was a standard AM1.5 solar simulator. 1 mol/L of hydrobromic acid (HBr) solution was used as the electrolyte. 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. H$_2$ gas generation was visible when V_{CE} exceeded 0.7 V and bubbles accumulated on the surface of the p-In$_x$Ga$_{1-x}$N electrodes.

Figure 1 shows the photocurrent density (J_{ph}) as a function of V_{CE} under white light irradiation using an AM1.5 solar simulator. The measured J_{ph} values are much higher in p-InGaN than in p-GaN. However, an apparent dependence of J_{ph} on the In-content is not seen here. This is most likely due to the fact that the material quality of p-In$_x$Ga$_{1-x}$N dominates over all other factors so that the advantage of the lower
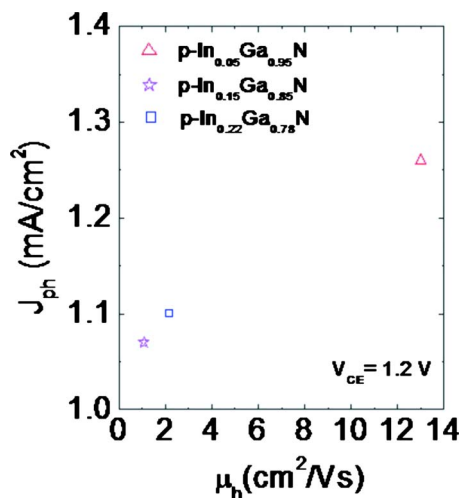
band gap is not noticeable in present p-InGaN materials. This speculation is corroborated by the results shown in Fig. 2, where a clear correlation between J_{ph} and hole mobility (μ_h) is presented. It was found that J_{ph} increases almost linearly with μ_h, which is reasonable because higher hole mobility would help the photogenerated holes to move faster in semiconductor electrodes, which would result in higher photocurrents.

The stability of p-In$_x$Ga$_{1-x}$N working electrodes in an HBr solution was tested by recording J_{ph} for a prolonged period of time (24 h). Figure 3 shows J_{ph} as a function of light irradiation time (t). The results show that the stability of p-In$_x$Ga$_{1-x}$N in an HBr solution is excellent. It was observed that J_{ph} dropped quickly in the first few seconds and became completely stable after about 10 min. Further, we did not observe any etching effects occurring on the surface of the p-In$_x$Ga$_{1-x}$N working electrodes. The reason for the excellent stability of p-In$_x$Ga$_{1-x}$N in an electrolytic solution is that p-type conductivity provides a reduction reaction and prevents the photocorrosion of p-In$_x$Ga$_{1-x}$N electrodes.

The dependence of J_{ph} on light intensity was measured. Figure 4 shows J_{ph} (at V_{CE}=1.2 V) for p-In$_{0.05}$Ga$_{0.95}$N as a function of light intensity. Maximum J_{ph} was observed at

FIG. 2. (Color online) Photocurrent densities (J_{ph}) as a function of hole mobility of p-In$_x$Ga$_{1-x}$N electrodes at V_{CE}=1.2 V. The light intensity at the sample surface was about 132 mW/cm^2.
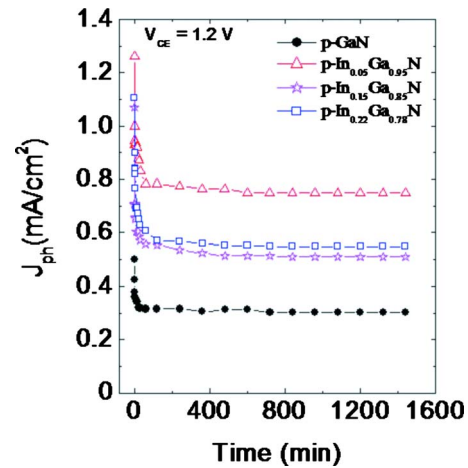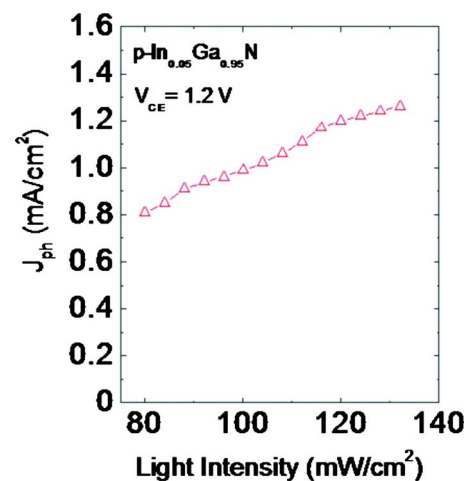

FIG. 4. (Color online) Photocurrent densities (J_{ph}) of p-In$_{0.05}$Ga$_{0.95}$N as a function of light intensity at V_{CE}=1.2 V.

intensity 132 mW/cm^2. Further increase in light intensity is limited by our light source. Higher light intensity would generate more electron-hole pairs, resulting in a higher photocurrent. The linear dependence implies that it is possible to adopt concentrator solar cell concept for PEC to further enhance conversion efficiency.

In summary, PEC effects in p-In$_x$Ga$_{1-x}$N alloys have been investigated. p-type In$_x$Ga$_{1-x}$N alloys exhibit much higher conversion efficiency compared to p-GaN. Continuous hydrogen bubbles evolved from the surface of p-InGaN samples when the bias voltage exceeded 0.7 V. The time dependent photocurrent density measurement showed that no morphological degradation of the surface of p-In$_x$Ga$_{1-x}$N electrodes was visible and the stability of p-In$_x$Ga$_{1-x}$N electrodes in an aqueous solution of HBr is excellent. Further enhancement of conversion efficiency is anticipated upon further improvements in the material quality of p-InGaN.

[1] A. Fujishima and K. Honda, Nature (London) **238**, 37 (1972).

[2] M. Tomkiewicz and H. Fay, Appl. Phys. (Berlin) **18**, 1 (1979).

[3] T. G. Deutsch, C. A. Koval, and J. A. Turner, J. Phys. Chem. B **110**, 25297 (2006).

[4] J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar, Mater. Res. Bull. **10**, 1023 (1975).

[5] J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar, Appl. Phys. Lett. **28**, 241 (1976).

[6] A. J. Nozik and R. Memming, J. Phys. Chem. **100**, 13061 (1996).

[7] A. Bott, Current Separations **17**, 87 (1998).

[8] K. Fujii and K. Ohkawa, Phys. Status Solidi C **3**, 2270 (2006).

[9] M. Pourbaix, *Atlas of Electrochemical Equilbria in Aqueous Solutions*, 2nd ed. (National Association of Corrosion Engineers, Houston, 1974), p. 97.

[10] J. W. Ager III, W. Walukiewicz, K. M. Yu, W. Shan, J. Denlinger, and J. Wu, "*Materials and Technology for Hydrogen Storage and Generation*," MRS Symposia Proceedings (Materials Research Society, Warrendale, 2005), Vol. 884E, GG6.6.

[11] I. M. Huygens, K. Strubbe, and W. P. Gomes, J. Electrochem. Soc. **147**, 1797 (2000).

[12] L. H. Peng, C. W. Chuang, J. K. Ho, C. N. Huang, and C. Y. Chen, Appl. Phys. Lett. **72**, 939 (1998).

[13] C. H. Ko, Y. K. Su, S. J. Chang, W. H. Lan, J. Webb, M. C. Tu, and Y. T. Cherng, Mater. Sci. Eng., B **96**, 43 (2002).

[14] J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **93**, 162107 (2008).

[15] K. Fujii and K. Ohkawa, Jpn. J. Appl. Phys., Part 2 **44**, L909 (2005).

[16] S. Usui, S. Kikawa, N. Kobayashi, J. Yamamoto, Y. Ban, and K. Katsumoto, Jpn. J. Appl. Phys. **47**, 8793 (2008).

[17] X. Gao, S. Kocha, A. J. Frank, and J. A. Turner, Int. J. Hydrogen Energy **24**, 319 (1999).

[18] N. Kobayashi, T. Narumi, and R. Morita, Jpn. J. Appl. Phys., Part 2 **44**, L784 (2005).

[19] B. N. Pantha, A. Sedhain, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **95**, 261904 (2009).