Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp1233-1234

Quantum Efficiency of H_2 Generation by Water Decomposition Using p-GaN Photoelectrode

Takahito Shimazaki[1], Naoki Kobayashi[1], Masahiro Kako[1],
Jun Yamamoto[2] , Yuzaburo Ban[2] and Koh Matsumoto[2]

[1]Department of Engineering Science, The University of Electro-Communications
1-5-1 Chofugaoka, Chofu-shi, Tokyo 182-8585, Japan
Phone: +81-42-443-5579 Fax: +81-42-443-5501 E-mail: shimazaki@cell.pc.uec.ac.jp
[2]TNEMC Ltd.
2008-2 Wada, Tama-shi, Tokyo 206-0001, Japan

1. Introduction

Renewable sources of energy, especially the use of solar energy, have become more important to realize the sustainable development in the human society. The artificial photosynthesis is attractive become the photon is directly converted to chemical energy such as hydrogen. Since the water photolysis using TiO_2 was reported by Honda and Fujishima [1], the semiconductor photoelectrode for high efficiency and visible light response has been actively studied. Group III-nitride semiconductors are one of semiconductor photoelectrode capable of visible light response.

Among group III-nitrides, GaN is a wide band gap (Eg=3.4eV) semiconductor. Unlike TiO_2, p-type is available for GaN in which photoexcited electrons are transported to the water/p-GaN interface by the bandbending and reduce protons to generate hydrogen. In addition, the conduction band edge of GaN is higher than the redox level of $2H^+ + 2e^- \rightleftarrows H_2$. From the flat-band potential measurement of n-GaN [2-4], the conduction band edge energy of GaN is located at about 0.4eV higher than the redox level. Due to this, photoexcited electrons in p-GaN can reduce protons without the reverse reaction [5]. For the flat-band potential measurement of $In_{0.17}Ga_{0.83}N$/GaN quantum well (QW), by taking piezoelectric polarization into energy band of quantum well, the conduction band edge of $In_{0.17}Ga_{0.83}N$ (Eg=2.6eV) with visible light response was estimated to be about 0.2eV higher than the redox level [6]. By the experiment using p-GaN and UV-light irradiation, the hydrogen generation was observed at zero bias and its quantum efficiency at 340 nm excitation was measured to be 4 ~ 6% in 1 M Na_2SO_4 (pH7) aqueous solution [7]. At the same time, the deterioration of p-GaN electrode was observed at acidic conditions.

In this study, about the p-GaN photoelectrode, the basic characteristics for the quantum efficiency of hydrogen generation and its dependence on pH are reported on the basis of the gas chromatography measurement of generated hydrogen.

2. Experimental

The working electrode, p-GaN (1μm) was grown by metal organic vapor phase epitaxy on undoped GaN/LT-GaN buffer/sapphire (c-plane) substrate. The hole concentration of p-GaN layer was measured as 5.7×10^{17} cm^{-3} by Hall effect measurement. The as-grown sample was annealed at 850°C in nitrogen and then annealed at 600°C in air after depositing Ni/Au as ohmic electrode. The counter electrode and reference electrode were Pt and Ag/AgCl, respectively. In quartz glass reactor, the electrolytes are 0.1M Na_2SO_4 for pH7, aqueous mixed solution of H_2SO_4 and Na_2SO_4 for pH4, and that of NaOH and Na_2SO_4 for pH10 and 13. After 30min N_2 bubbling, p-GaN electrode was irradiated by 365nm light from a 200W Hg-Xe lamp through a $CuSO_4$ solution filter transmitting $\lambda \geq$ 365nm at -2V bias. In this condition, dark current was neglected and photocurrent was dominant. Hydrogen was generated by water splitting by the p-GaN photoelectrode. The generated gas was accumulated at the headspace of the reactor. After 120min, the stored gas was pushed into the gas sampler with 0.60L/min N_2 flow, and sampled by 5ml. Hydrogen peak was detected by gas chromatography. The photocurrent spectrum was measured at 300-400nm.

3. Results and discussion

The quantum efficiency of H_2 generation was obtained by measuring the quantum efficiency of the photocurrent and the hydrogen gas generation efficiency per unit photocurrent. Fig.1 shows the pH dependence of the photocurrent spectra for p-GaN. The photocurrent starts to increase at

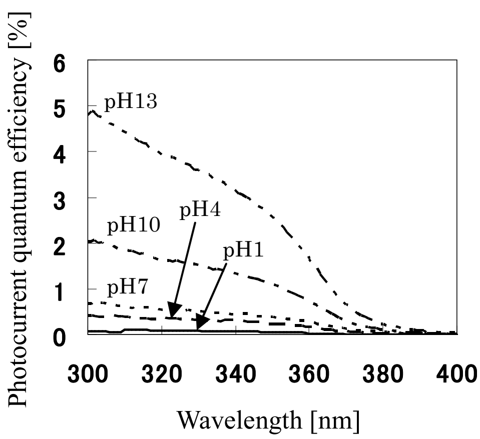

Fig. 1 Dependence on pH of photocurrent spectrum of p-GaN photoelectrode at 300-400nm.

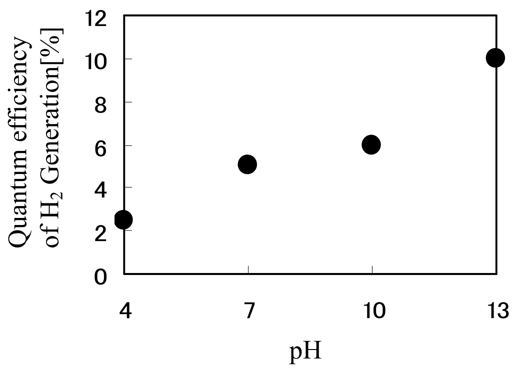

Fig. 2 Dependence on pH of quantum efficiency of hydrogen generation by photochemical water-splitting using p-GaN electrode at 365nm.

3.4eV, which is near the band gap of GaN. The quantum efficiency increases with pH.

Fig.2 indicates the dependence of quantum efficiency of hydrogen generation on pH by the product of quantum efficiency of photocurrent and hydrogen gas generation efficiency measured by gas chromatography. This result shows the higher pH, the higher quantum efficiency. That is, the quantum efficiency of hydrogen generation is lower at the acidic condition than the basic condition. At pH13, the quantum efficiency of hydrogen generation showed about 10%.

It is considered that the dependence on pH, the higher quantum efficiency in basic electrolyte, is caused by the hydrogen passivation of Mg acceptor in p-GaN electrode and hydrogen storing in p-GaN electrode. The former decreases the band bending of p-GaN electrode [8] and the latter decreases hydrogen gas generation efficiency.

4. Conclusions

Dependence of quantum efficiency of hydrogen generation on pH was measured. As a result, the higher pH, the higher quantum efficiency was observed. The quantum efficiency of about 10% at 365nm was observed at pH13.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (C) (Grant No. 20510101) from the Ministry of Education, Culture, Supports, Science and Technology.

References

[1] A. Fujishima, and K. Honda, *Nature*, **37** (1972) 238.
[2] K. Fujii, and K. Ohkawa, *Jpn. J. Appl. Phys.*, **44** (2005) L909.
[3] E. Harvey, and C. Hefferman, D.N. Buckley, C. O'Raifeartaigh, *Appl. Phys. Lett.*, **81** (2002) 3191.
[4] R. Morita, T. Narumi, and N. Kobayashi, *Jpn. J. Appl. Phys.* **45** (2006) 2525.
[5] S. Usui, S. Kikawa, N. Kobayashi, J. Yamamoto, Y. Ban, and K. Matsumoto, *Jpn. J. Appl. Phys.* **47** (2008) 8793.
[6] N. Kobayashi, R. Morita, T. Narumi, J. Yamamoto, Y. Ban, and K. Wakao, *J. Cryst. Growths,* **298** (2007) 515.
[7] N. Kobayashi, T. Narumi, and R. Morita, *Jpn. J. Appl. Phys.* **44** (2005) L784.
[8] D. Takagi, T. Narumi, N. Kobayashi, J. Yamamoto, Y. Ban, and K. Wakao, *Jpn. J. Appl. Phys.* **46** (2007) 572.