Clean Energy Generation by Artificial Photosynthesis Based on Semiconductor Technology

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Semiconductor technology is upgrading solar panels, light-emitting diodes (LEDs) and so on. We are developing optical devices by using nitride semiconductors. The material has a great potential to realize highly efficient LEDs and photocatalysts since its bandgap can cover the visible light region varying its alloy composition. We have invented a nitride photocatalyst that can generate solar hydrogen gas by water splitting, and hydrocarbons such as C_2H_5OH, HCOOH by artificial photosynthesis. This technology will be useful for clean energy generation and storage.

The author's first nitride photocatalyst patent (Pat. 3730142, the filing date: July 2001) became the world's first basic patent with nitride as a photocatalyst. [1]. The idea of the nitride photocatalyst came from the fabrication of lasers and LEDs with ZnSe or GaN. These materials did not have an appropriate etching solution, and Cl-based dry etching was used. In other words, these materials are chemically tough. Moreover, although their bandgaps (Eg) are large, the value of Eg becomes small in the case of ZnCdSe or InGaN alloy. Based on these characteristics, it was considered to be suitable for photocatalyst utilizing visible light. The electrochemical measurement of the band edge positions of GaN revealed that those are ideal as shown in Fig. 1 [2]. By using InGaN, the water reduction/oxidation (redox) levels exist between its conduction band and valence band edges. It suggests a possibility of high efficiency in photocatalysis by InGaN, and water splitting without extra bias.

Hydrogen generation by nitride photocatalyst was announced for the first time in 2005 in the world [2]. There were great responses in television and newspapers as having opened up new possibilities. However, there were problems with photo-corrosion and low efficiency. Since the efficiency is low, a voltage of 1.0 V was applied between the nitride working electrode and the metal counterelectrode. Now, the efficiency has been improved by controlling the depletion layer, and hydrogen can be generated even with zero applied voltage [3, 4].

Photo-corrosion was serious. The materials are chemically tough, but not enough for the case with light. Electron-hole pairs are created by photoabsorption. When electrons move to the counterelectrode side and hydrogen is generated, holes are left on the semiconductor side. When holes oxidize water, oxygen evolution occurs. However, if holes oxidize the semiconductor itself, it becomes a photo-corrosion [5]. At our first research stage, we chose hydrochloric acid, which can generate chlorine with higher priority than oxygen generation and photo-corrosion reaction, as an aqueous solution. In hydrochloric acid, it is hydrogen evolution but not water splitting.

Discovery of NiO cocatalyst against nitride photocatalysts has realized the higher efficiency of water splitting, and long durability in 2009 [6]. Figure 2 indicates that the GaN-NiO photoelectrode shows better efficiency compared with GaN without NiO by about one order of magnitude. Durability was also improved, and the water splitting and artificial photosynthesis were realized [7, 8]. We confirmed durability for more than 500 hours (Fig. 3) [9]. We also demonstrated artificial photosynthesis of CO_2 reduction [10].

In the artificial photosynthesis, we observed the production of CO, HCOOH, CH_4, C_2H_4, C_2H_5OH, CH_3CHO, CH_2CHCH_2OH, C_3H_6OH, C_2H_5CHO from CO_2 reduction [11] (Fig. 4).

Produced substances will be more because our current instruments limit the detection of molecules. The evidence of more materials is that the total Faraday efficiency of these substances is only about 80%. Moreover, we suspected whether it is derived from CO_2 molecule or not. We have experimented with the $^{13}CO_2$ gas consisting of carbon isotope with the atomic weight of 13 and confirmed its origin [11].

There are two major research subjects in future to achieve high efficiency. (1) Surface structure: for example, structures with a large surface area and high light absorption such as nanocolumns are desirable. The surface of nanocolumns contains different planes other than c-plane. Durability against these surfaces except for c-plane has not yet been secured. (2) Thick InGaN layer: the 100-nm thickness is necessary for sufficient photoabsorption in the InGaN layer, but the critical thickness of high-In-content InGaN is less than 100 nm. The thickness of 100 nm is same with the light penetration depth in nitrides, and the amount of light absorption becomes insufficient unless it has such thickness [4]. When we grow InGaN layers more than the critical thickness, electron-hole recombination becomes large due to the introduction of defects, and the efficiency of separating electrons and holes is significantly reduced. Currently, we can increase In content in InGaN layers on sapphire substrates until 6% [12-15]. If we might realize In contents of 20% - 30% with a thickness of 100 nm, efficiency will make a big leap. The emergence of InGaN substrates and/or the development of new epitaxy techniques such as InGaN/BGaN strain-compensation-structure [16] are crucial.

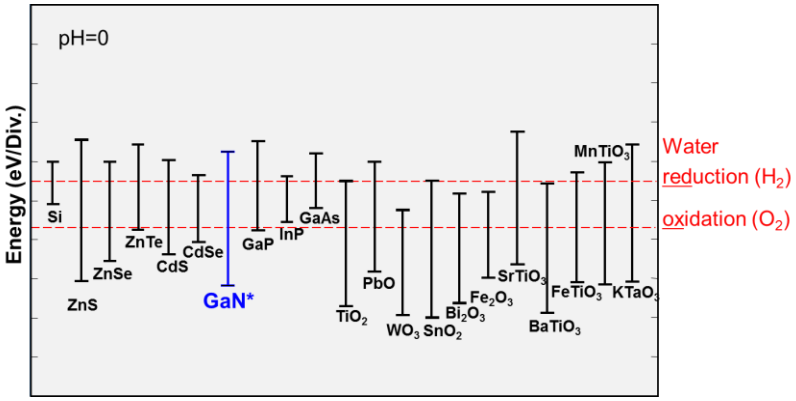

Fig. 1. The positions of the conduction band and the valence band position of various semiconductors. The water redox levels were included. The positions of GaN were originated from Ref. 2.

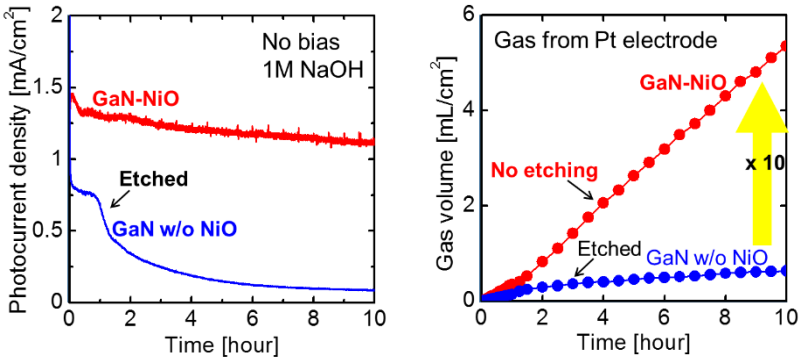

Fig. 2. GaN photocatalysis with and without NiO loading. The left shows photocurrent and the right shows hydrogen gas evolution. The GaN without NiO caused photo-corrosion from the initial stage and starts cutting off the current path in about 1 hour, so the photocurrent dramatically decreased. The light source was a Xe lamp, and the light intensity was 100 mW/cm^2.

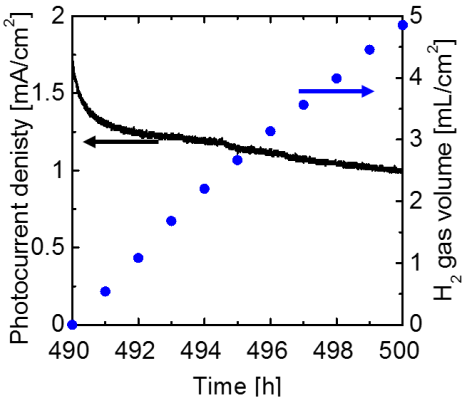

Fig. 3. Lifetime test of NiO-loaded GaN photocatalyst without bias [9]. The result is the 50th experiment of the 10-hour one. Stable H_2 generation was observed even after 500 hours. The sample structure was an n - GaN (n=1.2x10^{17} cm^{-3} at RT, 3 μm) layer grown on a c-plane sapphire substrate. The light source was a Xe lamp, and the light intensity was 100 mW/cm^2. The solution was 1 M NaOH aq.

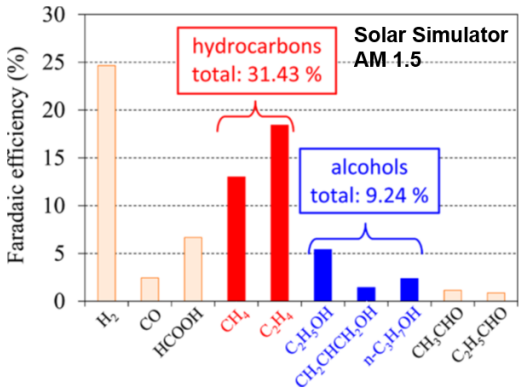

Fig. 4. An example of materials produced by artificial photosynthesis using nitride photocatalyst [11]. All of these products were from the reduction side. Solar-to-Fuels energy conversion efficiency was 0.408%. Faraday efficiencies to Hydrocarbons and alcohols were 31% and 9%, respectively. The light source was a solar simulator of AM 1.5.

References

[1] Kazuhiro Ohkawa, Japanese patent 3730142, the filing date: July 16, 2001.

[2] "Hydrogen gas generation by splitting aqueous water using n-type GaN photoelectrode with anodic oxidation", K. Fujii, T. Karasawa, K. Ohkawa, Japanese Journal of Applied Physics **44**, L543 (2005).

[3] "Photoelectrochemical reaction and H_2 generation at zero bias optimized by carrier concentration of n-type GaN", M. Ono, K. Fujii, T. Ito, Y. Iwaki, A. Hirako, T. Yao, K. Ohkawa, Journal of Chemical Physics **126**, 054708 (2007).

[4] "Nitride photocatalyst to generate hydrogen gas from water", Y. Iwaki, M. Ono, K. Yamaguchi, K. Kusakabe, K. Fujii, K. Ohkawa, physica status solidi (c) **5**, 2349 (2008).

[5] "Investigation of surface morphology of n-type GaN after photoelectrochemical reaction in various solutions for H_2 gas generation", K. Fujii, T. Ito, M. Ono, Y. Iwaki, T. Yao, K. Ohkawa, physica status solidi (c) **4**, 2650 (2007).

[6] 8th International Conference on Nitride Semiconductors, Oct. 18-23, 2009, Jeju, Korea, DD5. "H_2 Evolution from Water by GaN Photocatalyst with NiO Mictoelectrodes", F. Sano, T. Koyama, M. Sorimachi, A. Hirako, K. Ohkawa.
[7] "High stability and efficiency of GaN photocatalyst for hydrogen generation from water", T. Hayashi, K. Ohkawa, et al., Japanese Journal of Applied Physics **51**, 112601 (2012).
[8] "CO_2 conversion with light and water by GaN photoelectrode", S. Yotsuhashi, M. Deguchi, Y. Zenitani, R. Hinogami, H. Hashiba, Y. Yamada, K. Ohkawa, Japanese Journal of Applied Physics **51**, 02BP07 (2012).
[9] "Highly stable GaN photocatalyst for producing H_2 gas from water", K. Ohkawa, W. Ohara, D. Uchida, et al., Japanese Journal of Applied Physics 52, 08JH04 (2013).
[10] "Photo-induced CO_2 reduction with GaN electrode in Aqueous System", S. Yotsuhashi, K. Ohkawa, et al., Applied Physics Express **4**, 117101 (2011).
[11] "Analysis of products from photoelectrochemical reduction of $^{13}CO_2$ by GaN-Si based tandem photoelectrode", T. Sekimoto, H. Hashiba, S. Shinagawa, Y. Uetake, M. Deguchi, S. Yotsuhashi, K. Ohkawa, Journal of Physical Chemistry C **120**, 13970 (2016).
[12] "Photoelectrochemical properties of InGaN for H_2 generation from aqueous water", K. Fujii, K. Kusakabe, K. Ohkawa, Japanese Journal of Applied Physics **44**, 7433 (2005).
[13] "Tandem photo-electrode of InGaN with two Si p-n junctions for CO_2 conversion to HCOOH with the efficiency greater than biological photosynthesis", T. Sekimoto, K. Ohkawa,et al., Applied Physics Letters **106**, 073902 (2015).
[14] "InGaN photocatalysts on conductive Ga_2O_3 substrates", T. Ogita, Y. Uetake, Y. Yamashita, A. Kuramata, S. Yamakoshi, K. Ohkawa, physica status solidi (a) **212**, 1029 (2015).
[15] "Wireless InGaN-Si/Pt device for photo-electrochemical water splitting", T. Sekimoto, K. Ohkawa, et al., Japanese Journal of Applied Physics **55**, 088004 (2016).
[16] "Improvement of hydrogen evolution from InGaN/BGaN photoelectrodes", K. Shiohama, W. Ohara, H. Hayashi, D. Uchida, K. Ohkawa, Annual meeting of Japanese Society of Applied Physics, Sep. 16-20, 2013, Doshisya Univ., Kyoto, 16p-B5-3.