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Photocatalytic activity of gallium nitride for producing hydrogen from water under light irradiation

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Photocatalytic activity of powdered GaN for decomposing water into hydrogen under light irradiation was investigated. It was found that GaN has activity for producing hydrogen from water containing electron donors (Na_2S-Na_2SO_3, CH_3OH) without a loading of a noble metal; the obtained H_2 yield was ca. 150 μmol for a 200 h-Xe lamp (300 W) irradiation. The activity was increased by adding NaOH in the reaction solution due to the photo-etching of GaN by NaOH and concomitant removal of the native oxide from the surface, as confirmed by XPS, XRD, and PL measurements. The band energy scheme for GaN suggests that the conduction band edge of GaN is positioned at 0.5 V higher than the redox potential of H^+/H_2. This large energy difference (overpotential) makes the photocatalytic H_2 evolution over GaN from water possible.

1. Introduction

In heterogeneous photocatalysis, electrons and holes produced in a light-irradiated semiconductor are utilized, respectively, for reductive and oxidative reactions; this has been recognized as a promising less-energy-consuming method for producing a wide variety of valuable chemicals [1]. In particular, water-splitting into hydrogen and oxygen over photocatalysts under light irradiation has been attracting much attention over the past decades from the viewpoint of solar energy conversion into clean hydrogen energy [2]. To date, a large number of semiconductors, such as TiO_2, $SrTiO_3$, $Na_2Ti_6O_{13}$, $BaTi_4O_9$, ZrO_2, Ta_2O_5, $NaTaO_3$, $K_4Nb_6O_{17}$, $K_2La_2Ti_3O_{10}$, CdS, ZnS, and so on, were reported to have

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activity for producing hydrogen from water [3, 4]; most of the catalysts so far developed are metal oxide semiconductors. However, their activities still remain insufficient to practically generate hydrogen from water under sunlight. Accordingly, extensive work is being in progress for developing new active photocatalysts [5–8]. Under these circumstances, some metal oxynitrides and nitrides have recently been developed as visible-light sensitive catalysts; for example, $TiO_{2-x}N_x$ [9], $LaTiO_2N$ [10], TaON [11], and Ta_3N_5 [12] are active for water-splitting because of their narrow band gaps. Thus the above findings opened a new field for developing active photocata lysts.

Here, we report photocatalytic activity of gallium nitride (GaN) for splitting water into hydrogen. GaN is a well-known blue-light emitting semiconductor having wide band gap of 3.4 eV [13]. Although this wide band gap is a drawback for splitting water under sunlight, GaN has considerably high flat-band potential (approximately equal to conduction band edge for n-type conductors) [−1.5 V (vs. SCE; pH = 14)] [14], which is advantageous for reducing water because in this case photogenerated electrons in the conduction band must have high reduction potential. Furthermore, it has been reported that GaN has an excellent chemical stability in acid or base solutions [15], which properties are expected to enable continuous H_2 production without degradation. However, it has recently been reported that an aqueous alkaline solution can etch the GaN surface under illumination [16] and in the dark [17]. The treatment is performed for cleaning and removing surface impurities and is thus expected to improve the photocatalytic activity of GaN. In this study, the effect of the photo-chemical etching of GaN on the photocatalytic activity was also investigated. Moreover, in order to improve the light absorption property of GaN and thus the photocatalytic activity, doping of foreign elements into GaN was also carried out.

2. Experimental

GaN powders used in the present study were of reagent grade, purchased from Wako Pure Chemical Industry. Indium doping was carried out as follows; 0.1 g of GaN powders were suspended in 30 mL of water containing a designated amount of $In(NO_3)_3.3H_2O$ for 3 h, and the above suspension was dried under vacuum. The obtained powders were calcined at 873 K for 1 h under N_2 flow. The loading of Pt on GaN was carried out by a photochemical deposition method [18], in which 0.1 g of GaN was dispersed in 30 mL of water containing Na_2S (0.1 M) and a designated amount of H_2PtCl_6, and then the above solution was irradiated with a 150 W Hg lamp for 1 h.

Photocatalytic H_2 production over GaN was carried out in a closed gas circulation system using a 300 W Xe lamp; 0.1 g of GaN powders were dispersed in 60 mL of water containing Na_2S (0.1 M) — Na_2SO_3 (0.5 M) - NaOH (0.1 M) or CH_3OH (50 vol%) in a quartz reaction cell, into which 13.3 kPa of Ar gas was introduced after evacuating the system. The reaction was carried out under vigorous stirring using a magnetic stirring rod, which is sealed by PTFE (polytetrafluoroethylene, Tefron®). The amount of H_2 evolved was analyzed using an on-line gas chromatograph. The incident light energy from the Xe lamp to the reactor was measured with an optical power meter (NOVA, 2A-SH).

The surface morphology and particle size of GaN were observed by means of scanning electron microscope (SEM; alfha-25A, ABT) and the surface area was determined by an N_2 adsorption isotherm at 75 K. The diffuse reflectance spectra of samples were measured using a spectrometer (V-550, Jasco). The obtained reflectance spectra were converted into absorption (F(R)) spectra on the basis of the Kubelka Munk theory. The band gap was calculated from the liner correlation between $[F(R)h\nu]^2$ and $h\nu$ (Tauc plot).

For photo-etching experiments, GaN powders were treated with 60 mL of an aqueous NaOH solution (0.1 M) for 24 h under UV light irradiation using a 150 W Hg lamp. The photo-etching was performed under vigorous stirring using a magnetic stirring rod coated with PTFE in an Ar atmosphere (13.3 kPa). The surface states of the treated GaN powders were analyzed by XPS (ESCA-3400, Shimadzu) using an Mg Kα source. The Ga/N ratios were estimated from the integrated area of Ga 3d, N 1 s, and O 1 s peaks in the obtained XPS spectra, taking into account the relative sensitivity factors (RSF). The binding energies of the spectra were referred to that of C 1 s peak (285.0 eV). The photoluminescence properties of the treated GaN were examined on a spectrometer (FP-750, Jasco) at room temperature. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (RINT-1000, Rigaku) with Cu Kα radiation.

3. Results and discussion

3.1. Characterization of GaN powder

Fig. 1 shows the SEM surface morphology of GaN powders used for photocatalytic reactions. The particle size of GaN was found to be in the range of 4–20 μm and the BET surface area was measured to be 1.04 m^2/g. Fig. 2 a shows diffuse reflectance spectrum (inset) and Tauc plot for GaN powders. GaN is known to be a direct band gap semiconductor. Thus the band gap was calculated to be ca. 3.3 eV from the intercept in the energy ($h\nu$) axis for the straight line $\{[F(R)h\nu]^2$ vs. $h\nu\}$. This value is in relatively good agreement with the reported value of 3.4 eV for single crystalline GaN films [14].

3.2. Photocatalytic activity of GaN

Fig. 3 shows the amount of H_2 produced over GaN as a function of light irradiation time. We first investigated H_2 evolution over GaN in pure water but only observed

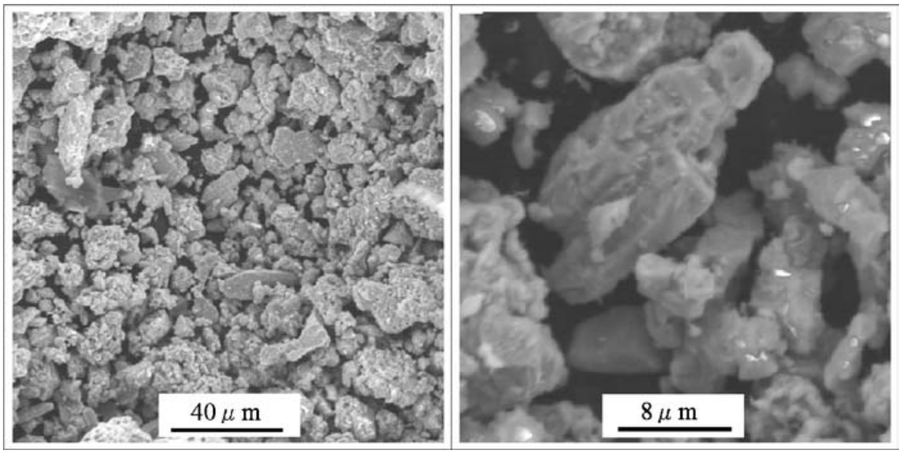

Figure 1. SEM photographs of GaN powders used for the production of H_2 from water.

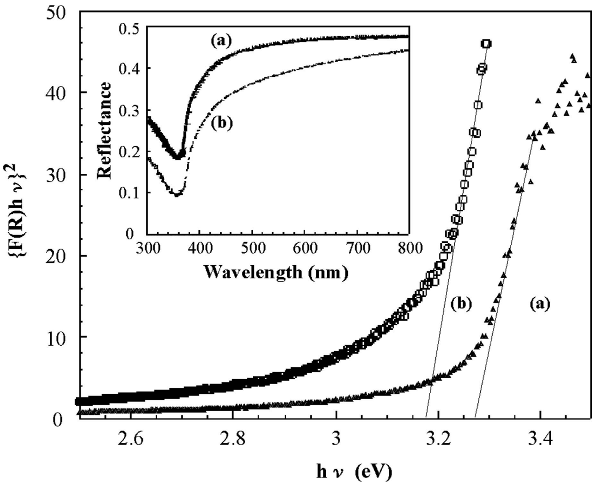

Figure 2. Diffuse reflectance spectra (inset) and Tauc plot for (a) GaN and (b) $In_{0.1}Ga_{0.9}N$.

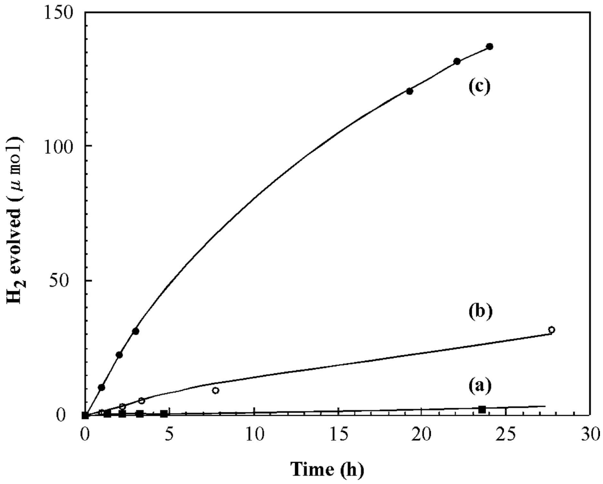

Figure 3. The amount of H_2 evolved over GaN from water containing (a) CH_3OH, (b) CH_3OH-NaOH, and (c) Na_2S-Na_2SO_3-NaOH under Xe lamp irradiation as a function of reaction time.

quit a low amount of hydrogen evolved (ca. 0.1 μmol for 24 h). However, when an electron donor of Na_2S was used with Na_2SO_3, ca. 150 μmol of H_2 was formed for a 24 h-reaction. The apparent energy conversion efficiency, defined as the ratio of the combustion heat of H_2 obtained to the radiation energy to the reactor, was found to be 0.12%. On the other hand, when an electron donor of CH_3OH was used, the H_2 yield was significantly decreased but improved to some extent by adding NaOH (0.1 M) into the reaction solution. The above results clearly indicate that the photocatalytic activity of GaN is largely dependent on the electron donors used and the pH of the reaction solution used. Such phenomena are frequently reported for many photocatalytic systems and the reaction mechanism is normally interpreted in terms of the band structure of the photocatalyst used.

Kocha et al. reported the energetic position of the conduction band edge of GaN, which was dependent on the pH of a solution as follows [14]:

$$Ec = -0.49 - 0.055.\mathrm{pH}(\mathrm{vs.\ NHE}) \qquad (1)$$

This pH dependence is associated with the interaction of H^+ and OH^- with the GaN surface and has been determined electrochemically by using a GaN epitaxial layer on a (0001) sapphire substrate [14]. It is known that wurtzite GaN has two polar faces along the c axis, Ga-polar (0001) and N-polar (000-1) faces, and thus the dependence of the polarization-induced surface charges on the two faces upon a pH change should be different. The reported values may be obtained with a sample with the Ga-polar face. Therefore, the above energetic band edge position is only applicable to a sample with the Ga-polar face. However, since powdered GaN must have the two polar faces along with other non-polar faces, we tentatively use the reported band edge position to estimate the band energy scheme for GaN in the reaction solution used. Fig. 4 shows the band energy scheme estimated on the basis of the results reported by Kocha et al. [14] together with the redox potentials of Na_2S, CH_3OH, and O_2/H_2O at pH 7 and 14. This scheme shows that the conduction band edge is ca. 0.5 V higher than the redox potential of H^+/H_2 in natural and alkaline solutions, which means that photo-

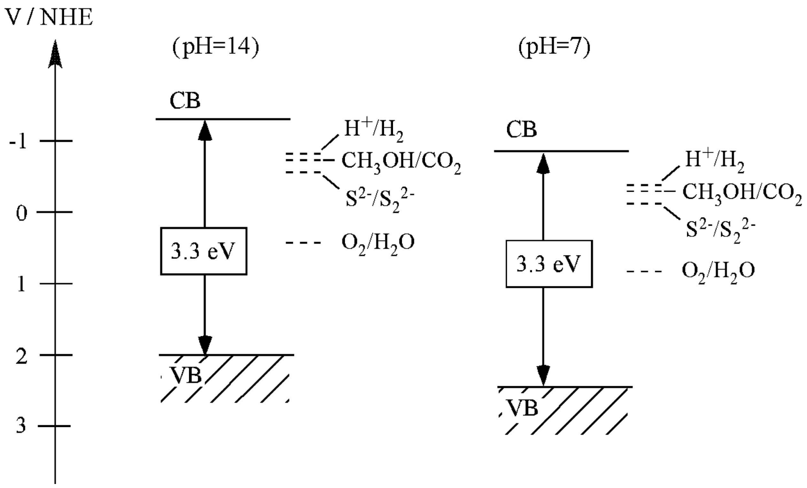

Figure 4. Band energy schemes for GaN in different pH solutions and redox potentials of related reactions.

generated electrons in the conduction band can react with water to produce H_2:

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

Because the valence band edge is much lower than the redox potentials of Na_2S and CH_3OH, electron donors of Na_2S and CH_3OH can react with photogenerated holes in the valence band:

$$2S^{2-} + 2h^+ \rightarrow S_2^{2-} \quad (3)$$

$$CH_3OH + H_2O + 6h^+ \rightarrow CO_2 + 6H^+ \quad (4)$$

These reactions can prevent the charge-recombination between the photogenerated electrons and holes and facilitate the reaction (2). On the other hand, the redox potential of O_2/H_2O is much lower than those of Na_2S and CH_3OH, which is probably the reason why the H_2 yield over GaN in pure water was much lower than that in water containing electron donors. In addition, the higher H_2 yield was observed when Na_2S was used with Na_2SO_3. This is due to the regeneration of S^{2-} by ${SO_3}^{2-}$ [19, 20]:

$$S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-} \quad (5)$$

As shown above, the present band energy scheme can well explain the reaction mechanism of the H_2 evolution over GaN under light irradiation, although it can be applied only to the Ga-polar faces of GaN powders.

3.3. Photoetching of GaN

The obtained results showed that the photocatalytic activity of GaN was improved by adding NaOH in the reaction solution containing electron donors. It has been reported that an alkaline solution can electrochemically etch GaN and remove the native oxide, Ga_2O_3, from the surface under UV illumination [16]. Because Ga_2O_3 has higher band gap (4.8 eV) and is less active than GaN, it is expected that the removal of the oxide from the surface is responsible for the improvement in the photocatalytic activity observed. In order to confirm the photoetching of GaN in an alkaline solution, GaN powder was treated with NaOH under UV irradiation, and then analyzed by XPS, XRD, and PL.

Fig. 5 shows Ga 3d, N 1 s, and O 1 s XPS spectra of GaN (a) before and (b) after the NaOH treatment. For bare GaN, the Ga 3d peak can be decomposed into two components at 20.1 eV and 21.5 eV, which are ascribable to Ga–N and Ga–O (or Ga–OH) bondings, respectively, though they slightly differed from the reported values for single crystalline GaN films (Ga–N : 19.7 eV and Ga–O : 20.7 eV) [21, 22]. After the NaOH treatment, a new peak appeared at 17.5 eV, which can be assigned as metallic Ga or Ga dangling bond [21, 22] and the intensity of the Ga 3d peak corresponding to the Ga-N bonding was decreased, suggesting the occurrence of photo-etching. The N 1 s peak is also decomposed into two components at 397.6 eV and 398.8 eV. The former is ascribable to Ga-N bonding, in good agreement with the reported value (397.4 eV) [21, 22] and the later may be due to N–O or N–N bonding. The intensity of the N 1 s peak corresponding to the Ga–N bonding was increased after the NaOH treatment, suggesting the exposure of GaN to the surface due to the removal of the oxide. The O 1 s peak for bare GaN is composed of two components corresponding to Ga–O bonding at 532.1 eV and O-H bonding at 533.5 eV [22]. The intensity of the O 1 s peak corresponding to the Ga-O bonding was decreased after the NaOH treatment, which may result directly from the removal of the oxide phase. We also studied the surface composition of the elements on GaN by comparing the Ga 3d, N 1 s, C 1 s, and the O 1 s peaks in the XPS spectra. As shown in Table I, the NaOH treatment decreased the oxygen and gallium percentage contents and furthermore the Ga/N ratio. Thus, as considered above, the XPS analyses revealed that the UV irradiation of GaN in the presence

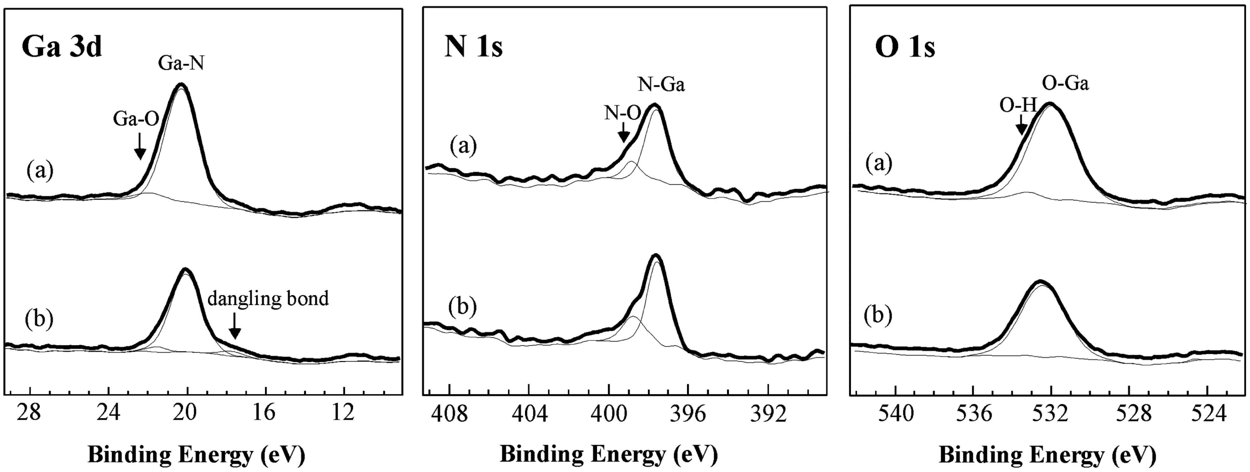

Figure 5. Ga 3d, *N* 1 s, and *O* 1s XPS spectra of GaN powders (a) before and (b) after the NaOH treatment under UV irradiation.

of hydroxyl ions resulted in the etching of GaN and the dissolution of the oxide from the surface.

Fig. 6 shows XRD patterns of GaN (a) before and (b) after the NaOH treatment. The reflections are indexed to hexagonal wurtzite GaN. There is no structural change observed after the NaOH treatment, but the peak intensities were slightly increased, suggesting the removal of the oxide or other amorphous phases from the surface. However, the relative intensity of the 0002 reflection was decreased after the treatment. This suggests the preferential etching of the (0001) surfaces in GaN. As mentioned earlier, wurtzite GaN has the two polar (0001) faces that have different surface atomic configuration, composition, and thus chemical activity from those of other non-polar faces. Such differences could account for the preferential etching of the (0001) surfaces observed. In addition, the full width at half maximum (FWHM) of the peaks almost remained unchanged, suggesting that no significant change in the crystallite size occurred. SEM analyses also showed no significant change in the particle size after the NaOH treatment (data not shown).

Photoluminescence (PL) is known to be sensitive to a change in surface state of semiconductor materials. Hence, we further analyzed the surface state of GaN after the photo-etching by PL measurements. Fig. 7 shows photoluminescence emission and excitation (inset) spectra of GaN (a) before and (b) after the NaOH treatment. The emission and excitation spectra were measured with excitation wavelength at 320 nm and emission wavelength at 550 nm, respectively. The excitation spectra show a single peak at 365 nm resulting from the band gap excitation of GaN. On the other hand, the emission spectra show two broad peaks centered at 390 nm and 550 nm. The peak at 550 nm, called yellow luminescence (YL), is ascribed to the defect related emission [23, 24]. It has been reported that the YL emission is caused by an elec-

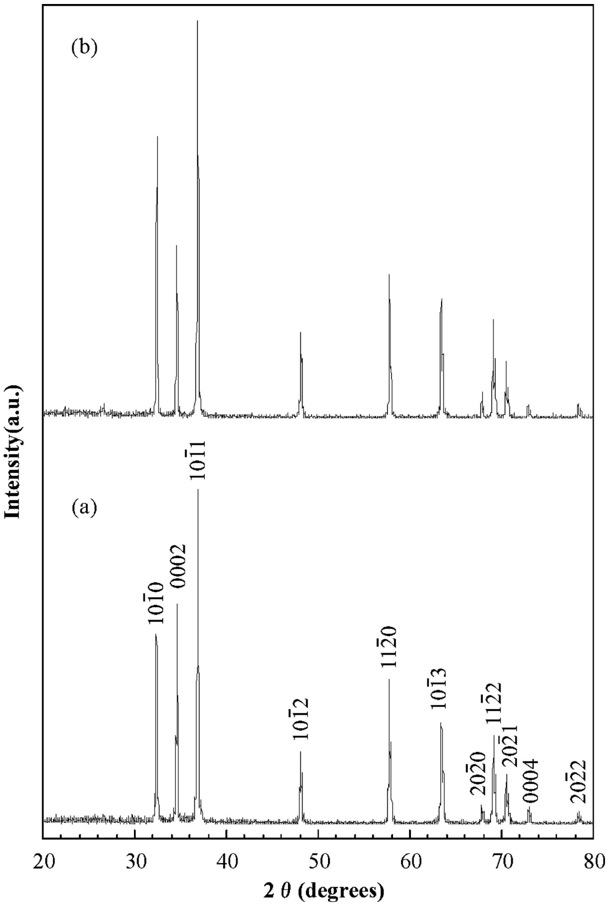

Figure 6. XRD patterns of GaN powders (a) before and (b) after the NaOH treatment under UV irradiation.

TABLE I Surface composition of GaN powder treated with NaOH under UV irradiation for 24 h

Composition	GaN	NaOH-treated GaN
Ga (%)	13.9	9.8
N (%)	4.7	6.3
C (%)	58.7	65.5
O (%)	22.7	18.4
Ga/N ratio	2.9	1.6

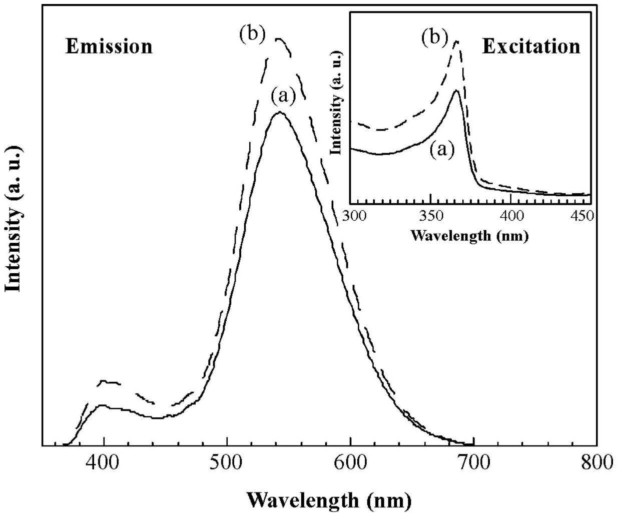

Figure 7. Photoluminescence emission and excitation (inset) spectra of GaN powders (a) before and (b) after the NaOH treatment under UV irradiation. The emission and excitation spectra were obtained with excitation wavelength at 320 nm and emission wavelength at 550 nm, respectively.

tronic transition between a shallow donor and a deep acceptor in GaN [25]. Although the origin of the YL is still under debate, the most probable acceptor is believed to be gallium vacancies, which are dominant native defects in GaN, whereas the donor levels are associated with nitrogen vacancies or oxygen impurities. The peak at 390 nm can be ascribed to the near band edge related emission. This emission is very broad and shifted to the red as compared to that observed for single crystalline GaN. This is presumably due to the presence of many defects of either interface or interior in powdered GaN, which create acceptor or donor levels within the band gap of GaN. Furthermore, the intensity of the near band edge emission is much lower than that of the YL emission for powdered GaN as compared to that reported for single crystalline GaN, which may also be due to the low crystal quality (high defect density) of powdered GaN. As shown in Fig. 6, the NaOH treatment increased the intensity of the two emissions, implying an increase in concentration of defects or impurities after the photo-etching of GaN by NaOH. The XPS analyses revealed that the gallium content on the surface was decreased after the photo-etching. Thus, it is possible that gallium vacancies were created concomitantly with the dissolution of the oxide from the surface as a result of the attack of hydroxyl ions. The creation of other defects should also be taken into consideration, because gallium vacancy may be associated with the YL emission, not the near band edge emission. However, the origin of the near band edge emission is unknown at present.

PL measurements have also been used to study photocatalytic reaction mechanisms, i.e., reaction pathways of photogenerated electrons and holes, on various systems such as TiO_2 [26] and ZnO [27], because PL results from the recombination between electrons and holes, which competes with the reaction of electrons (or holes) with adsorbed molecules. As discussed above, the observed increase in the emission intensity particularly for the YL after the photo-etching suggested an increase in gallium vacancy, which is reported to create a deep acceptor level positioned at 0.87 eV above the valence band edge [23]. Photogenerated holes in the valence band can be trapped at this acceptor level. The trapped electrons are still able to react with electron donors because the redox potentials of Na_2S and CH_3OH are higher than the acceptor level and the trapping of holes does not directly hinder the reaction of photogenerated electrons in the conduction band with water. Therefore, the observed increase in the concentration of gallium vacancy may not significantly contribute to the increase in the photocatalytic activity. However, it is difficult at present to directly correlate the photocatlytic activities with the photoluminescence properties of GaN because the reaction and emission pathways of photogenerated electrons and holes are not clear yet. Thus, further studies are necessarily to elucidate the reaction mechanism of photogenerated electron/hole pairs in GaN.

The XPS, XRD, and PL results confirmed that GaN was etched by NaOH under illumination. Therefore, it can be concluded that the enhancement of the activity by adding NaOH in the reaction solution is due to the removal of the oxide from the surface. The probable reaction of GaN with NaOH under UV illumination is considered to be as follows:

$$\mathrm{GaN} + 6\mathrm{OH}^- + 3\mathrm{h}^+ \rightarrow \mathrm{GaO}_3^{3-} + 3\mathrm{H}_2\mathrm{O} + 1/2\mathrm{N}_2(\mathrm{g}) \tag{6}$$

The oxide on the surface is removed concomitantly with the etching of GaN. In addition, this reaction scheme suggests that NaOH can also act as an electron donor and prevent the charge-recombination between the photogenerated electrons and holes. This effect may also contribute to the improvement in the photocatalytic activity.

3.4. Doping of foreign elements and loading of noble metals

This study found that GaN can split water to form H_2 in the presence of electron donors under light irradiation. However, it is expected that GaN has low activity under sunlight because of its wide band gap. To modify the band gap of photocatalysts, doping a foreign element into the photocatalysts has been tried for various systems [28–31]. Kudo et al. reported that for the $Ga_{2-x}In_xO_3$ solid solution system, the band gap and the photocatalytic activity for water splitting can be varied, depending on the In content [32]. In this study, indium was doped into GaN because it is reported that the bandgap of $In_xGa_{1-x}N$ can be varied from 2.0 to 3.4 eV by changing the indium content [33]. Fig. 2 b shows the diffuse reflectance spectrum (inset) and

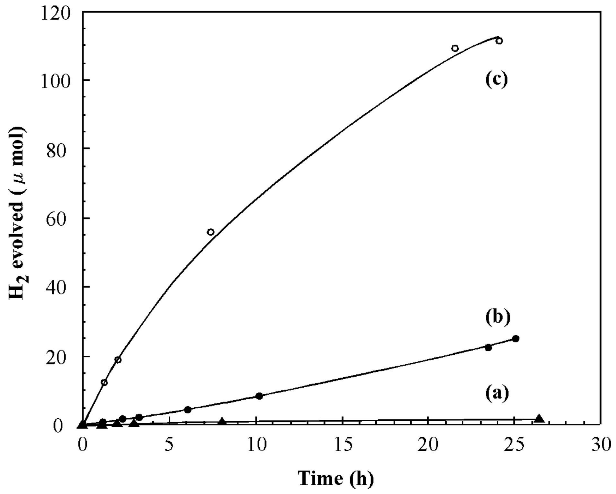

Figure 8. The amount of H_2 evolved over (a) $In_{0.1}Ga_{0.9}N$, (b) Pt (0.1 wt%)-$In_{0.1}Ga_{0.9}N$, and (c) GaN calcined at 873 K. The reactions were performed in the presence of Na_2S-Na_2SO_3-NaOH under Xe lamp irradiation.

Tauc plot of GaN doped with 0.1 mol% of In. The light absorption near the wavelength of visible light was obviously improved by the doping, which is probably due to the formation of a new energy level in the forbidden band of GaN. In addition, the doping decreased the band gap by ca. 0.1 eV. However, as shown in Fig. 8, the photocatalytic activity of GaN was significantly decreased by the doping as compared to that of undoped GaN (calcined at 873 K). This suggests that the newly created energy level is positioned at lower than the redox potential of H^+/H_2 in the forbidden band of GaN and/or the doping creates recombination centers for electron/hole pairs. Doping Ti and Ni also gave the same results. On the other hand, loading Pt onto the doped-GaN improved the activity, as shown in Fig. 8 c. It has frequently been reported that a loading of noble metals onto photocatalysts and/or a decrease of the particles size can upgrade the activity of the photocatalysts. Hence, such modifications may be more promising for increasing the H_2 yield over GaN under light irradiation.

4. Conclusion

We have investigated the photocatalytic activity of powdered GaN for producing H_2 from water in the presence of electron donors under Xe lamp irradiation. The amount of H_2 evolved over GaN from water containing Na_2S-Na_2SO_3 and the energy conversion efficiency were found to be 150 μmol and 0.12% for a 24 h-reaction, respectively. The hydrogen evolution rate was increased by adding NaOH in the reaction solution. XPS and XRD analyses revealed that GaN was photo-etched by NaOH and the native oxide layer was removed. This is responsible for the increase in the photocatalytic activity of GaN because the oxide layer has less photocatalytic activity. The intensity of photoluminescence (PL) of GaN was increased by the photo-etching, suggesting an increase in concentration of defects, i.e., gallium vacancies. However, they may have no significant effect on the photocatalytic activity for H_2 evolution from water in the presence of electron donors. On the other hand, doping foreign metals (In, Ti, and Ni) into GaN resulted in a decrease in the H_2 evolution yield, although the light absorption of GaN was improved. This study demonstrates that in spite of the low surface area (ca. 1.0 m^2/g) powdered GaN has activity for decomposing water into H_2 without a loading of noble metals.

References

1. M. A. FOX and M. T. DULAY, *Chem. Rev.* **93** (1993) 341.
2. K. HONDA and A. FUJISHIMA, *Nature* **238** (1972) 37.
3. K. DOMEN, J. N. KONDO, M. HARA and T. TANAKA, *Bull. Chem. Soc. Jpn.* **73** (2000) 1307.
4. A. KUDO, *J. Ceram. Soc. Jpn.* **109** (2001) 81.
5. Z. ZOU, J. YE, K. SAYAMA and H. ARAKAWA, *Nature* **414** (2001) 625.
6. J. SATO, N. SAITO, H. NISHIYAMA and Y. INOUE, *J. Phys. Chem.* **B105** (2001) 6061.
7. W. SHANGGUAN and A. YOSHIDA, *ibid.* **B106** (2002) 12227.
8. T. KIDA, G. GUAN, Y. MINAMI, T. MA and A. YOSHIDA, *J. Mater. Chem.* **13** (2003) 1186.
9. R. ASAHI, T. MORIKAWA, T. OHWAKI, K. AOKI and Y. TAGA, *Science.* **293** (2001) 269.
10. A. KASAHARA, K. NUKUMIZU, G. HITOKI, T. TAKATA, J. N. KONDO, M. HARA, H. KOBAYASHI and K. DOMEN, *J. Phys. Chem.* **A106** (2002) 6750.
11. G. HITOKI, T. TAKATA, J. N. KONDO, M. HARA, H. KOBAYASHI and K. DOMEN, *Chem. Comm.* (2002) 1698.
12. G. HITOKI, A. ISHIKAWA, T. TAKATA, J. N. KONDO, M. HARA and K. DOMEN, *Chem. Lett.* (2002) 736.
13. S. NAKAMURA, M. SENOH and T. MUKAI, *Jpn. J. Appl. Phys.* **32** (1993) L8.
14. S. S. KOCHA, M. W. PETERSON, D. J. ARENT, J. M. REDWING, M. A. TISCHLER and J. A. TURNER, *J. Electochem. Soc.* 142 (1995) L238.
15. H. P. MARUSAKA and J. J. TIETIJEN, *Appl. Phys. Lett.* **15** (1969) 327.
16. J. L. WEYHER, F. D. TICHELAAR, H. W. ZANDBERGEN, L. MACHT and P. R. HAGEMAN, *J. Appl. Phys.* **90** (2001) 6105.
17. G. NOWAK, X. H. XIA, J. J. KELLY, J. L. WEYHER and S. POROWSKI, *J. Crystal Growth* **222** (2001) 735.
18. K. SAYAMA and H. ARAKAWA, *Chem. Lett.* (1992) 253.
19. M. A. FOX and T. L. PETTIT, *Lamgmuir* **5** (1989) 1056.
20. K. HARA, K. SAYAMA and H. ARAKAWA, *Applied Catalysis A: General* **189** (1999) 127.
21. D. LI, M. SUMIYA, S. FUKE, D. YANG, D. QUE, Y. SUZUKI and Y. FUKUDA, *J. Appl. Phys.* **90** (2001) 4219.
22. T. S. LAY, Y. Y. LIAO, W. H. HUNG, M. HONG, J. KWO and J. P. MANNAERTS, *J. Crystal Crowth* **278** (2005) 624.
23. C. B. SOH, S. J. CHUA, H. F. LIM, D. Z. CHI, S. TRIPATHY and W. LIU, *J. Appl. Phys.* **96** (2004) 1341.
24. I. SHALISH, Y. SHAPIRA, L. BURSTEIN and J. SALZMAN, *ibid.* **89** (2001) 390.
25. T. OGINO and M. AOKI, Jpn.*ibid.* **69** (1980) 2395.
26. M. ANPO, M. TOMONARI and M. A. FOX, *J. Phys. Chem.* **93** (1989) 7300.
27. P. V. KAMAT and B. PATRICK, *ibid.* **96** (1992)) 6829.

28. M. ANPO, Y. ICHIHASHI, M. TAKEUCHI and H. YAMASHITA, *Res. Chem. Intermed.* **24** (1998) 143.
29. T. ISHIHARA, H. NISHIGUCHI, K. FUKAMACHI and Y. TAKITA, *J. Phys. Chem.* **103** (1999) 1.
30. S. IKEDA, N. SUGIYAMA, B. PAL, G. MARCI, L. PALMISANO, H. NOGUCHI, K. UOSAKI and B. OHTANI, *Phys. Chem. Chem. Phys.* **3** (2001) 267.
31. H. KATO and A. KUDO, *J. Phys. Chem.* **106** (2002) 5029.
32. A. KUDO and I. MIKAMI, *J. Chem. Soc., Faraday Trans.*, **94** (1998) 2929.
33. S. NAKAMURA, T. MUKAI and M. SENOH, *J. Appl. Phys.* **32** (1993) L16.

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