Overall Water Splitting by RuO_2-dispersed Divalent-ion-doped GaN Photocatalysts with d^{10} Electronic Configuration

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Divalent-metal-ion (Zn^{2+} or Mg^{2+})-doped GaN with d^{10} electronic configuration was found to make a high and stable photocatalyst for overall water splitting when combined with RuO_2 as a promoter, whereas neither undoped nor tetravalent-metal-ion (Si^{4+} or Ge^{4+})-doped GaN showed photocatalytic activity upon loading of RuO_2. The present work clearly demonstrated the marked effects of dopants on photocatalytic performance of the metal nitride GaN for water splitting.

The development of photocatalysts for the overall splitting of water has been a key issue in the field of hydrogen energy, which is currently attracting great interest. Recent findings indicate that RuO_2-loaded typical metal oxides involving Ga^{3+}, In^{3+}, Ge^{4+}, Sn^{4+}, and Sb^{5+} ions with d^{10} electronic configuration form a new series of photocatalysts for overall water splitting,[1–5] as opposed to transition-metal oxides with d^0 electronic configuration. The conduction bands of d^{10} metal oxides are formed by hybridized sp orbitals with large band dispersion, indicative of high electron mobility, and, hence, high photocatalytic performance. This suggests that d^{10} electronic configuration is advantageous as photocatalysts. We have recently found that β-Ge_3N_4, a typical metal nitride, became a efficient photocatalyst for overall water splitting in the presence of a promoter, RuO_2, dispersed on the nitride surface.[6] This was the first discovery of a metal nitride capable of photocatalytically decomposing water into H_2 and O_2. More recently, we showed that a solid solution of GaN and ZnO, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, became photocatalytically active for the reaction when RuO_2 was dispersed on the surface.[7] Employing a solid solution is one method of activating GaN for water splitting. For the present approach to photocatalysis using d^{10} metal nitrides, it is desirable to develop another method to improve the photocatalytic properties of GaN. In the present study, divalent-metal-ion (Zn^{2+}or Mg^{2+})-doped GaN and tetravalent-metal-ion (Si^{4+} or Ge^{4+})-doped GaN were prepared using metal sulfides to avoid the formation of solid solutions with metal oxides. The photocatalytic activity with RuO_2 promoter was examined.

GaN was synthesized by the nitridation of Ga_2S_3 (High Purity Chemicals, 99.99%) in a NH_3 flow at 1273 K for 15 h. Zn^{2+}-doped GaN was prepared by the nitridation of a mixture of Ga_2S_3 and ZnS (molar ratio of Ga:Zn = 1:2 in the starting materials) under similar conditions. For Mg^{2+}-doped GaN, a mixture of Ga_2S_3 and MgS (molar ratio of Ga:Mg = 0.97:0.03), and, for the preparation of Si^{4+}- and Ge^{4+}-doped GaN, a mixture of Ga_2S_3 and Si_3N_4 or GeS_2 (molar ratio of Ga:Si or Ge = 0.97:0.03) were used, respectively. All prepared samples exhibited single-phase X-ray diffraction patterns belonging to a wurtzite crystal structure. The SEM image showed that the powdered GaN had round shapes with an average particle size of 1.2 µm. The morphology remained nearly unchanged upon doping. The XMA analysis showed that little sulfur and oxygen were present for Zn^{2+}-doped GaN. To deposit RuO_2 particles on the metal nitrides, the nitrides were impregnated up to incipient wetness with $Ru_3(CO)_{12}$ in THF solution, dried at 357 K, and calcined in air at 673 K to convert the carbonyl complex to RuO_2. The RuO_2 loading was 3.5 wt %. Photocatalytic water-splitting reaction was carried out in a gas-circulating closed system equipped with a Pyrex glass reaction cell and an on-line gas chromatograph. A photocatalyst (0.8 g) was dispersed in distilled and ion-exchanged water (700 mL) in the cell by a magnetic stirrer and irradiated with a 450-W high-pressure mercury lamp.

Figure 1 shows photocatalytic water decomposition on RuO_2-dispersed Mg^{2+}-doped GaN under UV irradiation. Both H_2 and O_2 evolved starting with the initial stage of the reaction. With each run, the production of both gases increased and leveled off after the 4th run. From the 5th through the 7th run, the ratio of H_2 to O_2 was nearly the stoichiometric value of 2. A small amount of nitrogen was produced until the 2nd run, after which no N_2 evolution occurred. The total amount of H_2 produced up to the 7th run was 12 mmol; this was 600 times higher than the estimated amount of Ga^{3+} ion present at the GaN surface. These results indicate that Mg^{2+}-doped GaN became a stable photocatalyst for the overall water splitting when combined with the RuO_2 promoter.

Figure 2 shows the photocatalytic activity of undoped, divalent-metal-ion (Zn^{2+},Mg^{2+})-doped, and tetravalent-metal-ion (Si^{4+},Ge^{4+})-doped GaN in the deposition of RuO_2 as a promoter. Undoped GaN produced only a small amount of hydrogen without oxygen. Zn^{2+}- and Mg^{2+}-doped GaN showed marked photocatalytic activity with nearly a stoichiometric production of H_2 and O_2. The tetravalent-metal-ion-doped GaN exhibited little production of H_2 and O_2. In all cases, N_2 evolution was ex-

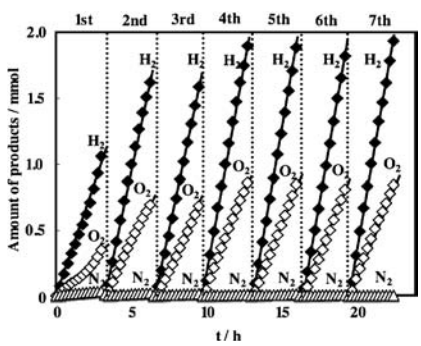

Figure 1. Water splitting into H_2 and O_2 on Mg^{2+}-doped GaN. 3.5 wt % RuO_2 loading: ◆, H_2; ◇, O_2; △, N_2.

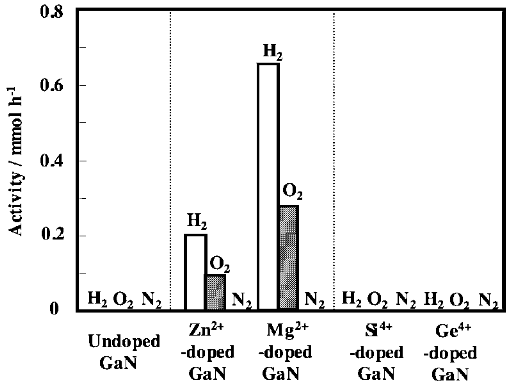

Figure 2. Photocatalytic activity for water splitting of undoped, divalent-metal-ion (Zn^{2+} or Mg^{2+})-doped and tetravalent-metal-ion (Si^{4+} or Ge^{4+})-doped GaN. 3.5 wt % RuO_2 loading.

tremely small. These results clearly indicate that only divalent-metal-ion-doped GaN became photocatalytically active when RuO_2 was used as a promoter.

UV–visible diffuse reflectance spectra showed that the absorption of undoped GaN occurred at around 370 nm, increasing sharply with decreasing wavelength. The absorption threshold of Zn^{2+}-doped GaN shifted to slightly longer wavelengths. Nearly the same characteristic absorption spectra were observed for Mg^{2+}-doped GaN. Figure 3 shows photoluminescence spectra of undoped and doped GaN. The undoped GaN exhibited emission at 373 nm, which was nearly the same as the band gap. The emission was assigned to electron transfer from the conduction to the valence band. The Zn^{2+}-doped GaN provided a broad emission spectrum that had a maximum at around 450 nm with tail extending toward longer wavelength up to 600 nm. The excitation spectra showed that the emission band at 450 nm appeared at an excitation wavelength of 400 nm and became the strongest at 350 nm. In the preparation of Zn^{2+}-doped GaN, a large amount of ZnS (Ga:Zn molar ratio = 1:2) was employed, but EPMA analysis showed that the Zn content of GaN was around 0.05 mol % since most of the excess Zn was removed by evaporation. This indicates that the impurity level of Zn^{2+} (0.05%) was capable of activating GaN enough to induce photocatalytic overall water splitting. The emission pattern of Mg^{2+}-doped GaN was similar to that of Zn^{2+}-doped GaN, although its intensity was half that of the latter. The doping of GaN by the divalent metal ions Zn^{2+} and Mg^{2+} was reported to produce

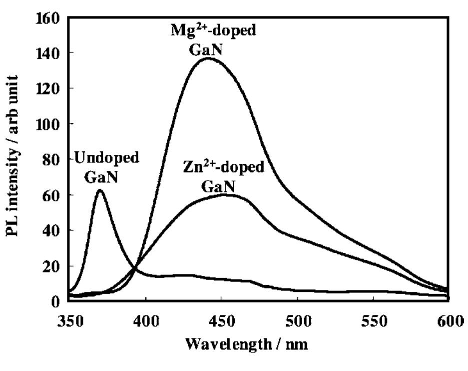

Figure 3. Photoluminescence of undoped and divalent-metal-ion (Zn^{2+} or Mg^{2+})-doped GaN measured at room temperature with a fixed excitation wavelength of 330 nm.

acceptor levels Zn_{Ga} and Mg_{Ga} at higher energy levels, 0.34 and 0.25 eV above the valence band, respectively. The radiation processes were explained in terms of a simple free to bound mechanism, i.e., transfer of free electrons to the acceptor levels Zn_{Ga} and Mg_{Ga}.[8] The observed emission peaks were close to these band emissions from the conduction band/donor levels to acceptor levels formed in the forbidden band. Thus, these results indicate that doping by the divalent ions yielded p-type GaN. For Si^{4+}- or Ge^{4+}-ion-doped GaN, photoemission was similar to that of undoped GaN, indicating that donor levels were located nearby at the conduction band. In GaN thin film photoelectrodes deposited on a sapphire substrate, H_2 and a trace amount of O_2, together with a considerable amount of N_2, were reported to be produced from H_2O by UV illumination under an applied voltage of $+1.0$ V.[9] In present study, RuO_2-dispersed powdered p-type GaN produced photocatalytically both H_2 and O_2 with the stoichiometric ratio without an any outer force. DFT calculation showed that the conduction bands of the active typical metal oxide photocatalysts with d^{10} electronic configuration consisted of hybridized sp orbitals with large dispersion, and it was proposed that the high photocatalytic performance was due to the formation of photoexcited electrons with high mobility.[1–5] Similarly, GaN with d^{10} configuration had a conduction band consisting of hybridized Ga4s4p orbitals with high dispersion, whereas the valence band was formed by the N2p orbital. This indicates that the electrons photoexcited to the conduction band of GaN had sufficiently large mobility to enable GaN to function as a photocatalyst. As shown in Figure 2, however, the activity of the Si^{4+}- or Ge^{4+}-doped GaN was negligible, which indicates the importance of hole control in photocatalytic water splitting by GaN. Thus, the high photocatalytic activity of divalent-metal-ion-doped GaN is considered to be associated with increases in the mobility and concentration of holes due to the formation of acceptor levels.

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