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## Surface &amp; Coatings Technology

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# Effects of preparation condition on the photocatalytic activity of porphyrin-modified GaN:ZnO for water splitting

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## ARTICLE INFO

## Article history:

Received 31 May 2016

Revised 17 September 2016

Accepted in revised form 20 October 2016

Available online xxx

## Keywords:

Photocatalysis

Water splitting

Nitridation

Solid solution

Porphyrin

## ABSTRACT

Effects of nitridation condition on gallium–zinc oxynitride solid solution (GaN:ZnO) was investigated to optimize the composition of GaN:ZnO for dye-modified photocatalysts. Gallium nitride (GaN) formed from Ga<sub>2</sub>O<sub>3</sub> at 973 K, and GaN:ZnO was obtained over 1073 K under NH<sub>3</sub> gas flow. Nitrogen content in GaN:ZnO increased with increasing nitridation temperature and time, while zinc content decreased because of evaporation. Although UV–vis absorption spectra of GaN:ZnO powders were not significantly changed in different compositions, the water splitting activities of the dye-modified GaN:ZnO photocatalysts depended on the composition of GaN:ZnO. The highest formation rates of H<sub>2</sub> and O<sub>2</sub> were achieved by the GaN:ZnO containing 15% of zinc and 73% of nitrogen. Finally, the nitridation condition was optimized at 1123 K 15 h under NH<sub>3</sub> gas flow (200 ml/min) for preparation of the dye-modified GaN:ZnO powder as water splitting photocatalyst.

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## 1. Introduction

Hydrogen has been expected as an energy carrier in next generation owing to its environmental-friendliness. Photocatalytic water splitting can produce hydrogen from abundant sunlight and water without CO<sub>2</sub> emission, thus it is regarded as a promising process for hydrogen production [1,2]. In addition, Pinaud et al. reported that the photocatalytic water splitting has a potential for a cost-effective system for the renewable production of hydrogen fuel [3].

In the past decade, nitrides [4–6] or metal oxynitrides [7–10] have been studied as visible light-driven photocatalyst for solar energy conversion. Among them, GaN:ZnO is well-known photocatalyst, because it's highly active for overall water splitting under visible light irradiation [11–13]. Until now, crystal structure [14–16], band structure [17–20], preparation method [21–25] and surface modification [26–31] of GaN:ZnO have been actively investigated. We also reported the effect of surface modification by using porphyrin dyes for water splitting activity of the GaN:ZnO photocatalysts [32,33]. Although GaN:ZnO solid solution shows high photocatalytic activity under visible light irradiation, its low reproducibility in catalyst preparation is a major problem for further improvement. In general, GaN:ZnO is prepared by heating a mixture of Ga<sub>2</sub>O<sub>3</sub> and ZnO under NH<sub>3</sub> gas flow [11–13,26–28,32,33].

During this heating process, Ga<sub>2</sub>O<sub>3</sub> nitridation, zinc evaporation, and solid solution formation proceed simultaneously [34]. This complicated situation makes it difficult to control atomic compositions of GaN:ZnO. According to the previous reports, the photocatalytic activity of GaN:ZnO depended on the atomic composition [35]. Therefore, it is important to reveal the relationship between preparation condition and the atomic composition of GaN:ZnO.

In this study, we report the effect of nitridation conditions on the GaN:ZnO properties, such as crystal structures, photoabsorption properties, atomic compositions, and photocatalytic activities. GaN:ZnO samples were prepared in various nitridation conditions and investigated to find a reproducible preparation condition. Furthermore, the photocatalytic water splitting activities of GaN:ZnO samples modified with porphyrin dyes were evaluated to determine the optimized preparation condition.

## 2. Experimental

## 2.1. Preparation of GaN:ZnO powders

Preparation procedure of GaN:ZnO was reported previously [11]. Ga<sub>2</sub>O<sub>3</sub> (99.99%, Koujundo Chemical Lab. Co. Ltd., 1.35 g) and ZnO (99.99%, Koujundo Chemical Lab. Co. Ltd., 1.173 g) were mixed in alumina mortar for 5 min. The mixture of Ga<sub>2</sub>O<sub>3</sub> and ZnO was heated under NH<sub>3</sub> gas flow (99.8%, 200 ml/min) at 873–1143 K for 5–20 h on an alumina boat, as shown in Fig. 1.

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## 2.2. Characterization of GaN:ZnO powders

The crystal structure of the GaN:ZnO powder was analyzed by using X-ray diffractometer (RINT2500HLR, Rigaku, Japan) with CuK $\alpha$  radiation ( $\lambda = 0.1541$  nm) at 40 kV of tube voltage and 80 mA of tube current. The atomic composition of the GaN:ZnO was determined by using Energy Dispersive X-ray spectrometer (Genesis2000, EDAX Inc., USA), X-ray photoelectron spectrometer (XPS, AXIS165, Shimadzu Corp., Japan). The specific surface area of the GaN:ZnO powders measured by using BET surface area analyzer (BELLSORP-mini, Microtrac, USA). The K-edge extended X-ray absorption fine structure (EXAFS) of gallium and zinc in GaN:ZnO was measured in BL-12C beamline of Photon Factory (PF) at High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. PF has a 2.5 GeV synchrotron light source. Sample discs ( $\phi 10$  mm) were prepared by using a uniaxial pressing, and laminated with plastic bag for the measurement.

## 2.3. Preparation of dye-modified GaN:ZnO photocatalysts

The IrO $_2$  particle (0.1 wt%) was loaded on the GaN:ZnO powder as O $_2$  formation cocatalyst by using an evaporation to dryness method with a sodium hexachloroiridate(IV) hexahydrate (Na $_2$ IrCl $_6$ ·6H $_2$ O, 99%, Strem Chemicals Inc., USA) aqueous solution. After the evaporation to dryness, sample was calcined at 673 K for 1 h in air. The Cr(III)-tetraphenylporphyrin chloride (Cr-TPPCL) was used for GaN:ZnO surface modification in this study. Detail of the preparation of Cr-TPPCL was described in previous report [32]. The dye modification of GaN:ZnO was performed by an evaporation to dryness method with Cr-TPPCL-solved pyridine solution (0.5 mM) at 400 K. The Cr-TPPCL amount was 0.5 wt% on the amount of IrO $_2$ -GaN:ZnO. After the dye-modification, Rh (0.1 wt%) and NiO (0.1 wt%) were loaded as H $_2$  formation cocatalyst by using an evaporation to dryness method with an aqueous solution of sodium hexachlororhodate(III) *n*-hydrate (Na $_3$ RhCl $_6$ ·*n*H $_2$ O, Mitsuwa Chemicals, Japan) and Ni(NO $_3$ ) $_2$ ·6H $_2$ O (98%, Wako, Japan).

## 2.4. Photocatalytic water splitting reaction

The photocatalytic reaction was performed in a closed circulation type reactor with c.a. 450 ml in dead volume. The GaN:ZnO photocatalyst (50 mg) was dispersed in distilled water (30 ml), and the photocatalyst suspension was filled in a reaction cell with quartz glass window. A 300 W Xe lamp (620 mW, Cermax PE300BUV, Excelitas Technologies Corp., USA) was used for external light source for the photocatalytic water splitting. Argon gas (10.67 kPa) was used as a carrier gas in the closed circulation reactor. Gas formation amounts were measured by a gas chromatograph (GC-8A, Shimadzu Corp., Kyoto, Japan) with a thermal conductivity detector.

## 3. Results and discussions

### 3.1. Preparation condition and atomic composition of GaN:ZnO

To optimize the preparation condition of the GaN:ZnO, the precursor mixtures of Ga $_2$ O $_3$  and ZnO were calcined at different temperature. Fig.

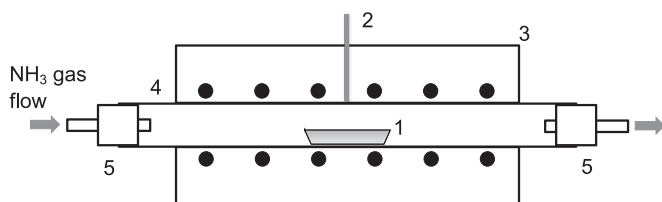


Fig. 1. Schematic image of the nitridation setup for GaN:ZnO preparation. 1: Alumina boat, 2: thermoelectric couple, 3: electric furnace, 4: alumina tube, 5: silicone rubber stopper with glass tube.

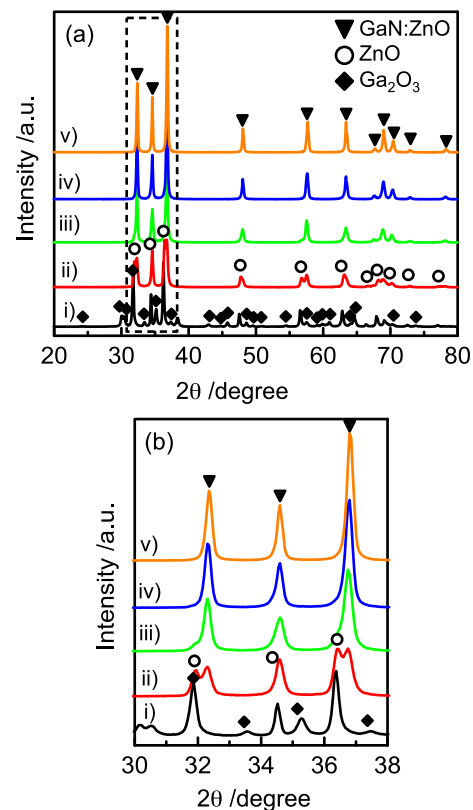
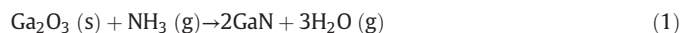


Fig. 2. (a) Powder XRD patterns of the samples calcined at i) 873 K, ii) 973 K, iii) 1073 K, iv) 1173 K, and v) 1143 K under NH $_3$  gas flow (200 ml/min) for 5 h. (b) Expanded image of (a).

2 shows XRD patterns of the GaN:ZnO powders calcined at 873–1143 K for 5 h. The diffraction peaks assigned to  $\beta$ -Ga $_2$ O $_3$  (JCPDS: 41-1103) and ZnO (JCPDS: 36-1451) were observed in the sample calcined at 873 K. The peaks of Ga $_2$ O $_3$  were disappeared after calcined at 973 K. Nitrogen content in GaN:ZnO increased with increasing nitridation temperature and time, whereas zinc content decreased because of evaporation. The ZnO peaks were still remained. These results indicate that the nitridation of Ga $_2$ O $_3$  [36] occurred at below 973 K under the NH $_3$  gas flow. The chemical reaction of the Ga $_2$ O $_3$  nitridation with NH $_3$  can be expressed as:



Furthermore, the intensity of ZnO peaks was decreased after calcination at 973 K. It has been reported that the formation of GaN:ZnO solid

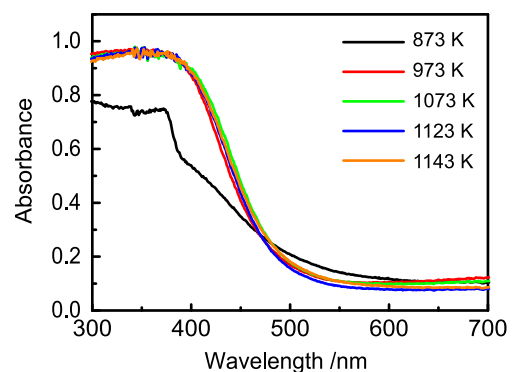


Fig. 3. UV-vis absorption spectra of the GaN:ZnO powders synthesized at different temperature for 5 h.

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