PHOTOCATALYTIC ACTIVITY OF ZnO/GaP $_{1-x}$ N$_x$ FOR WATER SPLITTING REACTION

A collaborative work with Prof. Yoshinobu Inoue and Prof. Kazunori Domen of Tokyo University and group has been performed to rationalize the photocatalytic activity of ZnO/GaN matrix. The phosphidation of a ZnO/GaN solid solution photocatalyst enhanced significantly its activity for water splitting. Active phosphide ZnO/GaN provided a single GaP peak with diffraction angles higher than normal GaP by 2θ = 0.20 - 0.44°, indicative of the formation of a GaP $_{1-x}$ N$_x$ alloy system. The diffraction peaks were simulated using first principles *ab initio* calculations on molecular models of Ga$_{32}$P$_{32-y}$N$_y$. The comparison with experimental shifts showed that the highest activity was induced in an x range of 0.034–0.074 of GaP $_{1-x}$ N$_x$.[1]

INTRODUCTION

New visible-light activated photocatalysts for water splitting have been an important development. Among d^{10} electron configuration photocatalysts consisting of typical elements, GaN is one of the promising candidates; when combined with RuO2 it was active for water splitting [1]. GaP is a d^{10} phosphide. The band gap of this material is approximately 2.25 eV at 300 K and the threshold of light absorption is approximately 560 nm. However, there have so far been a few reports on its application as a photocatalyst for water splitting. Many reports have shown that incorporating small amounts of N into GaP induces a change in the fundamental optical transition from an indirect-gap (T_{15}-X$_1$) transition of GaP [2] to a direct-gap transition and lowering the band gap with increasing N concentration [3]. The N-induced decrease in the band gap is a result of an interaction between the nitrogen atoms and the GaP matrix, which forms a GaP $_{1-x}$ N$_x$ alloy system. [4] These results indicate that GaP $_{1-x}$ N$_x$ compounds, or at least GaP $_{1-x}$ N$_x$ layer formation on either GaN or GaP, efficiently produce visible-light-driven photoexcited carriers, and thus it is of interest to apply the GaP $_{1-x}$ N$_x$ system as a photocatalyst for water splitting.

This study is a combination of experiment and computer simulation [5]. In the following pages we will highlight the simulation results and refer to experiment whenever necessary. Please refer to the publication [1] for experimental details.

MODEL & METHOD

In the simulation of the crystal structure to compare with the experimental XRD pattern, we have used a supercell of 2x 4x 1 for a 64 atom structure with the composition Ga$_{32}$N$_{32}$. The model was chosen to give a symmetric substitution for the dopant phosphorus. The central strand was taken to minimize the interaction of the dopant arising from periodic boundary consideration. All the calculations were performed using the CASTEP (Cambridge Serial Total Energy Package) of BIOVIA Materials Studio (Dassault Systèmes) and the associated programs for symmetry analysis. This has been described in detail in the paper [5]. XRD simulations were carried out using the REFLEX module of BIOVIA Materials Studio (Dassault Systèmes).

AIM

Experimentally the challenge is to synthesize the right material. Once synthesized, the material needs to be characterized. Experimentally it has been observed that the photocatalytic activity is dependent on N to P ratio, but the location of P within GaN is very difficult to know from experiment. The position of P is very important for the photocatalytic activity of water in this case. We therefore used molecular modeling to rationalize the property and structure of the material.

(a)   (b)

(c)   (d)
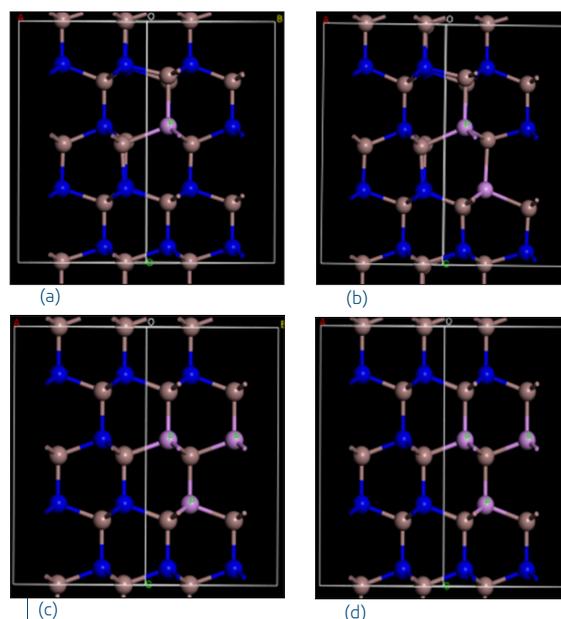
Figure 1: Structure model for GaP $_{1-x}$ N$_x$ with (a) P =1, (b) P=2, (c) P=3 and (d) P=4 within the Ga$_{32}$N$_{32}$ structure model

RESULTS

Several synthesis methods were applied to get the desired structure of GaN with P dope. The X-ray diffraction patterns of GaP nitrided between 873 and 1123 K consisted of strong GaP peaks, and no significant peak shifts were observed. Very small peaks attributed to GaN appeared. For RuO2-loading on the nitrided GaP, there was no significant production of H2 and O2, although a very small amount of H2 production occurred. Figure 2 shows the X-ray diffraction patterns of the $2\theta = 28$-$29°$ region for ZnO/GaN-P (873, x) as a function of x. Below the x = 0.01 region, no significant diffraction peaks were observed. A single peak appeared at $2\theta = 28.50°$ for x = 0.05, which shifted to $2\theta = 28.68°$ for x = 0.07. For x = 0.1, two
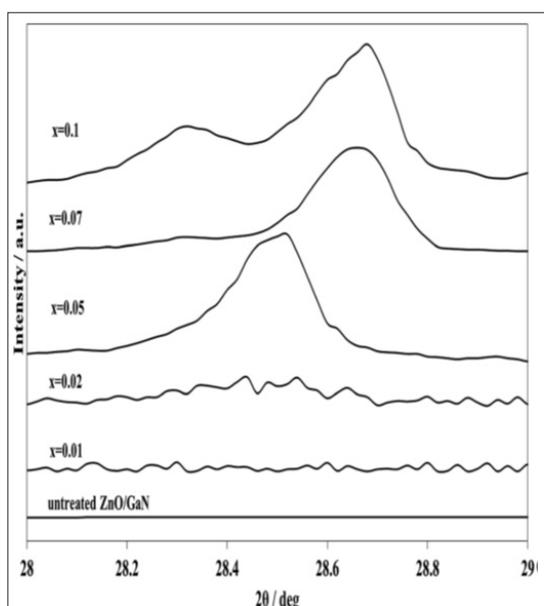
Figure 2: X-ray diffraction patterns in the range of $2\theta = 28$–$29°$ for ZnO/GaN-P (873, x) with an x value in the range of 0.01 to 0.1 and untreated ZnO/GaN

peaks appeared at $2\theta = 28.32°$ and $2\theta = 28.68°$. The peak shifts of GaP to a higher angle indicates that the N atoms are involved in a fundamental unit of the tetrahedral GaP4, producing $GaP_{1-x}N_x$, because the N^{3-} size is smaller than that of P^{3-}. Therefore, the shift of the GaP diffraction peak represents a change in the active site conformation induced by P introduction.

The photocatalytic activity at 823 K increased as the diffraction angle increased from $2\theta = 28.32°$ (GaP crystal), producing a maximum at approximately $2\theta=28.6°$, and decreased with further increase in the diffraction angle. A similar trend can be seen for 873 K phosphidation.

These correlations demonstrate that a high photocatalytic activity depends on the structures of $GaP_{1-x}N_x$ formed through the gas-solid reaction between vaporized P and GaN. To determine the active conformation, the diffraction peak shifts were simulated by taking the geometry-optimized model of the $Ga_nP_{n-y}N_y$ into account. Fig. 3 shows the GaP diffraction peaks calculated by the powder diffraction method as implemented in the REFLEX Module of the Dassault Systèmes BIOVIA method for n = 32 and y = 1, 3, 4, 6, 7 and 8. A 2θ range of 10 to 90° was used with a step size of 0.05. Peak position errors can result from an incorrect zero point or from errors in the placement or transparency of the sample. In this case, we have used Bragg-Brentano correction A peak because $Ga_{32}P_{32}$ appeared at $2\theta = 27.65°$, shifted to a higher angle with increasing N atom content, and attained at $2\theta = 28.44°$ for y= 4, 2θ= 28.75° for y = 6 and $2\theta = 29.03$ for y = 8. The diffraction angle shifts against the percentage of P atoms in the total of P and N atoms P/(P + N) x 100% showed a good linear relationship. In comparison with the experimental value which provides the greatest photocatalytic activity for shifts by $2\theta = 0.20$-$0.44°$ to a higher diffraction angle from GaP, the percentage of P atoms in the total of P and N atoms P/(P + N) x 100% showed a good linear relationship .
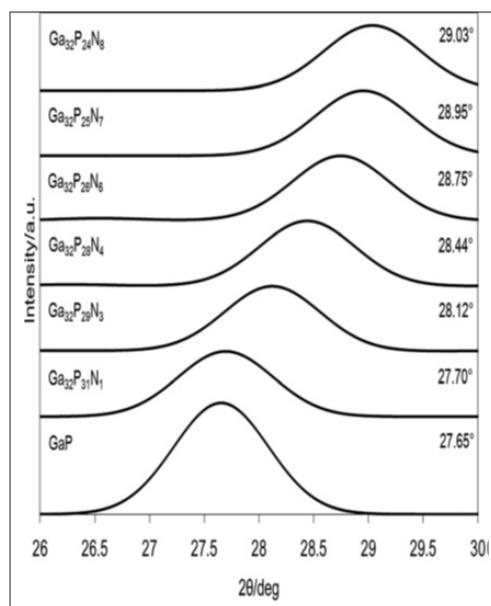
Figure 3: = Simulated X-ray diffraction peaks of GaP for $Ga_{32}P_{32-y}N_y$ (y=1–8)

The linear relationship provided the result that the optimal conditions for the highest activity are the involvement of N at the percentage of 3.4-7.4% in GaP.

The valence bands of ZnO/GaN-P consist of the hybridized Ga 4p + P 3p + N 2p AOs, which forms intermediate electronic band structures of GaP and GaN. Thus, the N atom inclusion to GaP lowers the valence band edge enough for the oxidation to proceed. This has positive effects on the oxidation of water, although the conduction band edge shifts to a lower energy level.

CONCLUSION

The phosphidation of active ZnO/GaN photocatalysts significantly enhances the photocatalytic activity for water splitting. The phosphidation of ZnO/GaN successfully permits the achievement of optimal nitrogen conditions in $GaP_{1-x}N_x$, which leads to the generation of high photocatalytic performance. The present approach shows promise for application to other metal nitride systems that will be advantageous for efficient photocatalysts for water splitting.

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