Photoelectrochemical Properties of Wurtzite Gallium Phosphide Nanowires grown on GaP(111)B substrates

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Abstract

We have grown low-stacking-fault wurtzite GaP nanowires and tried some photoelectrochemical studies toward solar water splitting. We confirmed cathodic photocurrent for a p-type nanowire sample. Dispersed Au nanoparticles were found to be effective for reducing H_2O as cocatalyst. N-type GaP nanowires were subject to anodic dissolution under illumination. We expect that it will be improved by applying a proper coating method.

1. Introduction

Solar energy is an inexhaustible natural resource and many approaches to harvest energy directly from sunlight have been proposed and developed toward an ideal sustainable society. Since the first report by Fujishima et al. in 1972 [1], semiconductor photoelectrochemical (PEC) systems have been considered to be a promising option for direct photoconversion from H₂O to hydrogen and also from CO_2 to chemical fuels or organics. For a high efficiency solar-water-splitting device, it is necessary to consider the band structure so that the bandgap straddles the redox potentials of H₂O and has the proper energy to absorb photons within the wide range of the solar spectrum. It is also important to design and build the devices with stable materials to ensure long-term operation. III-V semiconductors are suitable for pursuing such ideal devices because we can use various combinations of heterostructure and p- and n-type materials.

So far, several Si and III-V semiconductor nanowires, such as GaP, InP, GaN, and GaInN, have been reported in regard to PEC studies in aqueous solution [2, 3]. The merits of III-V semiconductor nanowires include effective optical absorption with small volume, epitaxial growth for the heterostructure and p-n junction, capability to incorporate in a flexible film, and reduced recombination of carriers using a core-shell structure. Among the III-V semiconductor nanowires, GaP is composed of abundant and safer elements, has the proper bandgap for solar light absorption [2], and can be grown on Si [4] or graphene [5] in nanowire form.

Soon after GaP nanowires with a wurtzite crystal structure with a direct bandgap of 2.1 eV had been reported [6], an efficient p-GaP nanowire photocathode was demonstrated [2]. The study of PEC systems using wurtzite GaP nanowires has just started, and more experiments are needed to understand the fundamentals and their ability for solar water splitting. Here, we report on the PEC behavior of pand n-type wurtzite GaP nanowire electrodes with Au particles. The Au particles were expected to act as effective cocatalyst [7].

2. Experiments

Substrates used here were GaP(111)B. The carrier concentration of the p-type substrate was $2-8 \times 10^{18}$ cm⁻³ and that of n-type one was $3-6 \times 10^{17}$ cm⁻³. The growth was carried out in a low-pressure MOVPE reactor using all metalorganic sources [4, 5]. First, Au particles, which act as catalyst for nanowire growth, were dispersed on the substrates by using Au colloids with a diameter of 40 nm. Then the samples were loaded into the MOVPE chamber for nanowire growth. For PEC measurement, dense Au particles with a diameter of 5 nm were dispersed on the samples by using Au colloids (around 70 µm⁻²). The nanowire structures were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Dopant concentration was measured by secondary ion mass spectrometry (SIMS).

The PEC measurements were performed in a three-electrode electrochemical cell. The reaction area of samples was defined by an O-ring seal (1 cm² area) and samples were electrically contacted at their back side. The cell was placed inside a dark box to prevent the influence of stray light. A reversible hydrogen electrode (RHE) was employed as the reference electrode. The counter electrode was a Pt mesh. Optical illumination was performed by using a solar simulator of one sun energy with AM1.5G. The measurement was carried out by using a potentiostat. A solution of 0.5 M H₂SO₄ was prepared as the electrolyte.



Fig. 1 HAADF-STEM images and SEM images of GaP nanowires. The upper-left inset is the diffraction pattern, which shows the wurtzite structure.

3. Results and discussions

Figure 1 shows GaP nanowires with and without doping. The nanowire density was 0.4-0.9 μ m⁻². The undoped nanowires showed almost stacking-fault-free structures, while doped ones had several stacking faults. In particular, Zn-doped nanowires had many stacking faults at the bottom and a few layers of zincblende crystal were observed. SEM images revealed that they were tapered shape. Further growth optimization is necessary to obtain stacking-fault free structures for doped nanowires. Dopant concentration in nanowires, estimated from SIMS measurements, was 10^{18} - 10^{19} cm⁻³. Mott-Schottky plots confirmed S-doped and Zn-doped nanowires had n-type and p-type conductivity, respectively.

We performed linear sweep voltammetry under chopped illumination in acid aqueous solutions. We confirmed the cathodic photocurrent for a p-type GaP nanowire sample as shown in Fig. 2(a). The effect of dispersed Au particles could be compared for the substrate samples. The dispersed Au particles conducted as cocatalyst and enhanced the reaction of H₂O reduction. The p-type GaP nanowire sample also showed anodic photocurrent at the positive potential over 0.4 V. Because nanowires had the wurtzite structure, which has a lower band gap than zincblende GaP, there should be a certain height of the band offset at the interface. Because of the low nanowire density, most incoming photons reached the substrate and generated carriers. It is possible that some of the holes generated at the substrate drop to the valence band potential of the nanowire. For the p-type GaP nanowire sample, improving the efficiency of H₂O reduction will require a high nanowire density so that most of the incoming photons are absorbed at the nanowires. Moreover, we have to investigate the structural design for smooth carrier flow as well as for efficient photo-absorption. In the SEM image in Fig. 2(b), the side of the nanowires appears to be thinned, which indicates that the anodic photocurrent was consumed for nanowire dissolution.

For an n-type nanowire sample, at the anodic potential side, there was anodic photocurrent caused by illumination. After the linear sweep voltammetry as performed for the p-type samples described above, the n-type nanowire sample was apparently etched at the illuminated area and the bottom of the nanowires dissolved so much that they separated from the substrate, which is proof of the photo-induced dissolution of GaP [8]. In order to use n-type GaP nanowire samples as photoanodes, we have to investigate proper coating materials, such as previously reported amorphous TiO₂ [9].

4. Conclusions

We have investigated PEC properties of wurtzite GaP nanowires toward solar water splitting. We confirmed the cathodic photocurrent for a p-type nanowire sample. Dispersed Au nanoparticles were found to be effective for cathodic reaction of H_2O reduction. However, an n-type GaP nanowire sample was subject to anodic dissolution under illumination, which makes it difficult to use as photoanode for H_2O oxidation. By applying a proper coating method and a growth method for dense nanowires, we will be able to realize solar water splitting by using wurtzite GaP nanowires.



Fig. 2 (a) Linear sweep voltammograms for comparison of p-type nanowire with Au particles (red) and p-type substrate with (blue) and without (green) Au particles samples, performed under chopped illumination. The scan rate was 1 mV/s. Each ON/OFF time was 50 s. (b) A SEM image of nanowires after the voltammetry measurement observed from 30 degrees from the normal direction.

Acknowledgements

We thank Y. Uzumaki, T. Komatsu, G. Zhang, H. Gotoh, A. Yokoo, and M. Notomi for their fruitful discussions and continuous encouragement throughout this work. We also thank Drs. T. Mitate, A. Takano, and S. Mizuno of NTT Advanced Technology Corporation for their help in the TEM and SIMS analysis. This work was partly supported by KAKENHI (15H05735).

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