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Effect of Localized Surface Plasmon Resonance on Photoelectrochemical Water Splitting using Gallium Nitride Working electrodes

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Abstract

In this study, hydrogen gas (H_2) is generated through direct water photoelectrolysis using n-GaN as photoelectrodes. The production rate of H_2 can be improved by applying TiO_2-caped silver nanoparticles (NPs) on the n-GaN layer to absorb additional photons in the visible region. In addition to the absorption edge at 365 nm, transmission spectra obtained from the on the n-GaN layer with TiO_2-caped silver nanoparticles shows that a broad absorption band at around 550 nm due to localized surface plasmon resonance effect can contribute extra photocurrent and thereby improve the production rate of H_2 during the photoelectrochemical reaction.

1. Introduction

At present, the world's energy is mainly based on oil, natural gas, and coal. However, these energy sources are limited and development process will pollute the environment, such as the emission of greenhouse gas and air pollution, all of which lead to severe climate change. In fact, hydrogen has potential to replace fossil fuels because of its advantages over fossil fuels, such as high energy density and clean byproduct material. However, most of the used hydrogen is made by natural gas reforming, and it will cause carbon emission. Hydrogen can be generated through direct water photoelectrolysis from solar power, and typically produce only hydrogen and oxygen during the photoelectrochemical (PEC) reaction. PEC experiments were first developed in 1972. Fujishima and Honda et al. used titanium dioxide (TiO_2) semiconductors as working electrode and metal platinum (Pt) as the counter electrode [1]. Although some lower band-gap semiconductors, such as InP, GaAs, and CdSe can absorb solar light more effectively, it has been reported that these materials easily corrode in acidic or alkaline solution. III-nitride semiconductors are resistant to corrosion from acidic or alkaline solutions [2]. In this study, we used GaN epitaxial films as a working electrode to perform the PEC reaction to split water for generating H_2. The electrolyte is a mixture of NaCl and water which is friendly to environment.

It is a critical issue to extend the photon absorption from UV region to visible or infrared for enhancing the photocurrents when the working electrodes are made by GaN because the GaN cannot absorbs photons with energy less than 3.4 eV. Although the photocurrent density theoretically increases with an increase of In content in $In_xGa_{1-x}N$-based working electrodes due to the reduction of energy band gap, material quality of InGaN degrades markedly with the increase of In content and thereby results in a reduction of photocurrent. It has been shown that oxide-based working electrodes associated with metallic nanoparticles (NPs) exhibiting Localized Surface Plasmon Resonance (LSPR) effect could effectively enhance the solar to hydrogen generation efficiency [3]. We have demonstrated that photodetectors made of GaN films with SiO_2-caped Ag NPs could exhibit higher UV-to-visible rejection ratio due to the enhancement of photon absorption [4]. In this study, H_2 was generated through direct water photoelectrolysis using n-GaN as photoelectrodes. The production rate of H_2 could be improved by applying TiO_2-caped Ag NPs on the n-GaN layer to absorb additional photons in the visible region. As shown in Fig. 1, in addition to the absorption edge at 365 nm, transmission spectra obtained from the on the n-GaN layer with TiO_2-caped silver nanoparticles showed that a broad absorption band at around 550 nm due to the LSPR effect. This phenomenon was attributed to be the fact that Ag NPs on the GaN film could contribute extra photocurrent and thereby improve the production rate of H_2 during the photoelectrochemical reaction.

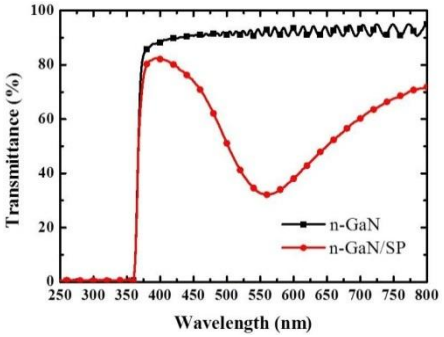

Fig. 1 Transmittance spectra of n-GaN and n-GaN/SP.

2. Experimental

GaN epitaxial films used in this study were grown on c-face (0001) sapphire substrates in a vertical metal-organic vapor-phase epitaxy system. As shown in Fig. 2(a), the layered structure of the GaN films comprised a 30 nm-thick

GaN nucleation layer grown at 550 ℃, a 2 μm-thick unintentionally doped GaN (u-GaN), a 2 μm-thick Si-doped GaN layer with a carrier concentration of $5 \times 10^{18}/cm^3$ (n^+-GaN). The u/n^+-GaN layers were sequentially grown at 1050 ℃. Next, the bilayer metal of Ti (30 nm)/Al (100 nm) was deposited on n^+-GaN to serve as ohmic contacts for the formation of the working electrodes, and they were labeled as *n-GaN*, as shown in Fig. 2(b). Ag NPs with TiO_2 cap layer formed on the n^+-GaN films were completed as follows: a Ag thin layer with a setting thickness of 10 nm was deposited by e-beam evaporator on the n^+-GaN layer followed by thermal annealing at 200 ℃ for 10 minutes, and then a 50 nm-thick TiO_2 over layer was deposited to passivate the formed Ag NPs, as shown in the Fig. 2(c), and they were labeled as *n-GaN/SP*. In addition, photolithography and wet etching process was performed on the TiO_2 over layer to create periodic stripes for mitigate the light absorption by the TiO_2 over layer, and they were labeled as *n-GaN/PS-SP*, as shown in Fig. 2(d). Fig. 2(e) shows the typical SEM images obtained from the surface of *n-GaN/SP* samples.

Fig. 3 shows the schematic of a PEC reactor. The electrolyte is 1M NaCl.

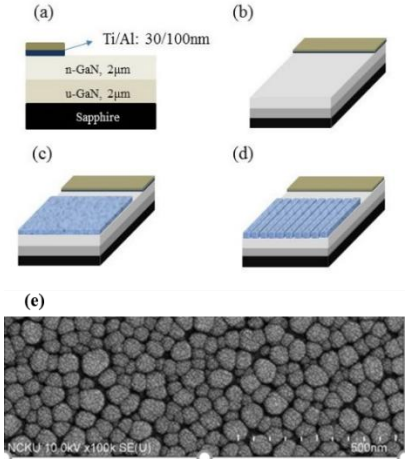

Fig. 2 Schematic layer structures of the working electrodes (a) cross section of n-GaN (b) top view of n-GaN (c) n-GaN/SP (d) n-GaN/PS-SP. (e) typical SEM images obtained from the surface of n-GaN/SP samples.

3. Results and Discussion

Although the transmission spectra indicated that the *n-GaN/SP* samples exhibited an extra absorption band at around 550 nm, as shown in the Fig. 1, the photocurrent density (J_{photo}) of PEC cell with *n-GaN/SP* working electrodes is lower than that of PEC cell with *n-GaN* working electrodes, as shown in the Fig. 4. Since the TiO_2 over layer prepared by RF sputtering without thermal annealing, it exhibits amorphous crystalline and high-resistivity properties. Therefore, low J_{photo} obtained from the *n-GaN/SP* working electrodes could be attributed to the fact that most of the UV photons are absorbed by the TiO_2 over layer before they reach the n-GaN layer and Ag NPs. To mitigate the negative effect of TiO_2 layer on the light absorption by the n-GaN and Ag NPs, the *n-GaN/PS-SP* working electrodes were used. As a result, the J_{photo} of PEC cell with *n-GaN/PS-SP* working electrodes is higher than those of PEC cells with *n-GaN* and *n-GaN/SP* working electrodes. This phenomenon means that the surface plasmonic effect does work in the PEC reaction. At a bias of 1V, the generation rate of hydrogen obtained from the PEC reactions were 98, 63 and 127 for *n-GaN*, *n-GaN/SP* and *n-GaN/PS-SP* working electrodes, respectively. These results were consistent with the trend of photocurrent density between the different working electrodes.

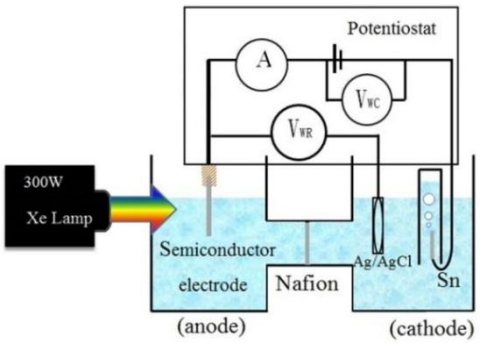

Fig. 3 Schematic of a PEC reactor for hydrogen generation.

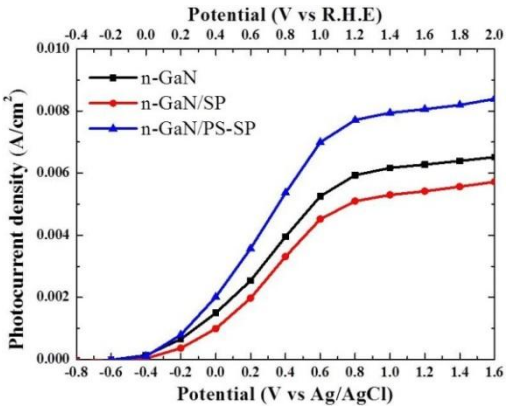

Fig. 4 Photocurrent density-potential curves of PEC cells with different working electrodes.

4. Conclusions

We have demonstrated that the Ag NPs with TiO_2 over layer on the n-GaN films could effectively enhance photon absorption to contribute extra photocurrent and thereby improve the production rates of hydrogen generated through direct water photoelectrolysis during the photoelectrochemical reaction.

References

[1] A. Fujishima, K. Honda, Nature, **238** (1972) 37.

[2] S. Y. Liu, Y. C. Lin, J. C. Ye, S. J. Tu, F. W. Huang, M. L. Lee, W. C. Lai, and J. K. Sheu, Opt. Express, **19** (2011) A1196, and references therein.

[3] Scott C. Warren and Elijah Thimsen, Energy Environ. Sci., **5** (2012) 5133.

[4] Jinn-Kong Sheu, Ming-Lun Lee, and Yu-Cheng Lin, IEEE J. Select. Topics Quantum Electrons, **20** (2014) 3801005.