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Improved Hydrogen Gas Generation Rate of n-GaN Photoelectrode with SiO_2 Protection Layer on the Ohmic Contacts from the Electrolyte

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Direct photoelectrolysis of water to generate hydrogen was performed using n-type GaN films with Cr/Au ohmic contacts to serve as working electrodes. To enhance the efficiency of electron collection in the GaN working electrode, meshed Cr/Au contacts with a SiO_2 protection layer were immersed in the NaCl electrolyte. With an external bias of 1 V, the typical photocurrent densities (gas generation rate) of the n-GaN working electrodes with and without the immersed ohmic contact layer were approximately 19.6 (9.4) and 9.9 A/cm^2 (3.6 mL/h), respectively, which corresponded to an enhancement in the photocurrent density (gas generation rate) of around 98% (160%). The marked enhancement in the gas generation rate could be attributed to the fact that the distance between the neighbor Cr/Au ohmic contacts is small enough to reduce the recombination probability of photogenerated electrons with holes or charged defects in the GaN layer before the electrons reach the ohmic contacts. In other words, the photogenerated electrons can be effectively collected by the Cr/Au ohmic contacts and thereby reach the Pt counter electrode to lead the generation of hydrogen.

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Using solar power to direct photoelectrolysis is a promising method of generating hydrogen from aqueous water.[1,2] There are many kinds of oxides serving as the photoelectrodes (working electrodes) that drive electrochemical reactions.[3-5] However, using these oxides as the working electrodes for water splitting has an insufficient solar-to-hydrogen conversion efficiency for practical application because of the limitation of the usable solar spectrum.[1] There are also many kinds of lower bandgap semiconductor materials that can absorb solar light more effectively, such as InP, GaAs, and CdSe. It has been reported, however, that these materials were easily corroded in acidic or alkaline solution.[6,7] Besides, to split aqueous water by using a photoelectrochemical cell, which is made of semiconductor materials, the conduction bandedge potential of the semiconductor material must be lower than that of the cathode-reduction half-reaction; furthermore, its valence band-edge potential must be higher than that of the anode-oxidation half-reaction.[1] Therefore, InGaN-based materials are promising candidates for direct photoelectrolysis of water not only because its band-edge potential could satisfy the condition to split water[8,9] but also because it is potentially resistant to the aqueous solutions.[10] Furthermore, the bandgap can vary from 3.4 to 0.7 eV by changing the content of In, making it possible for us to produce a photoelectrochemical cell that could fit the solar spectrum to enhance the light absorption.[10] Waki et al. reported that the patterned n-GaN epitaxial layer formed by the selective area regrowth with metal stripes was used to achieve the direct photoelectrolysis of water.[8] The metal stripes functioned to eliminate current crowding, thereby improving the photocurrent. However, the metal stripes they used were directly immersed in the electrolyte. The metal stripes were increasingly eroded away when the electrochemical reactions were under way. In this study, the n-GaN photoelectrode featuring a finger-type ohmic contact with a SiO_2 protection layer from the electrolyte was applied to improve the efficiency of hydrogen gas generation. This is the most important difference from the previous works of other groups. The relevant electrical and optical properties of the photoelectrochemical cells that were fabricated in our study are discussed subsequently in this paper.

To clarify whether the SiO_2 protection layer could enhance the current density and affect the gas generation rate or not, we designed two different n-type GaN photoelectrodes. One is the n-type GaN photoelectrochemical cells with a SiO_2 protection layer on the ohmic electrodes from the electrolyte, that is, the finger-type ohmic electrodes were immersed in the electrolyte, but the ohmic electrodes did not directly contact the electrolyte, owing to the SiO_2 protection layer on it (labeled as PEC1). For comparison, n-type GaN photoelectrochemical cells with ohmic electrodes aside from the working area (labeled as PEC2) were also prepared, that is, the ohmic electrodes were not immersed in the electrolyte and did not contact the electrolyte. The Si-doped n-GaN ($n \sim 1 \times 10^{19}/cm^3$) epitaxial layers with a thickness of 2 μm were grown on (0001) sapphire substrates. For sample PEC1, a Cr (50 nm)/Au (250 nm) bilayer metal was deposited on the n-type GaN epitaxial layers to form the metal stripes as the finger-type ohmic electrodes by the conventional photolithography. The width of the metal stripe was 20 μm, and the gap between stripes was 200 μm. The SiO_2 protection layer was deposited on sample PEC1 after the finger-type ohmic electrodes were formed. For the samples of PEC2, the Cr (50 nm)/Au (250 nm) bilayer metal was partly deposited on the n-type GaN epitaxial layers, as shown in Fig. 1c. Figure 1a and b shows the schematic diagram of the photoelectrochemical cell (PEC1) and the photograph of a local area on sample PEC1, respectively. The inset of Fig. 1b shows the schematic structure of the SiO_2-protected ohmic contact on the GaN layer. A potentiostat (Autolab-PGSTAT128N) was used to supply the external bias and measure the current density to evaluate the electrical properties of the experimental cells. A Ag/AgCl reference electrode and a platinum (Pt) wire counter electrode were used to measure potentials. A 300 W Xe lamp was used as the light source, and 1 mol/L NaCl was used as the electrolyte at room temperature. The effective light intensity, which was defined as the total light power measured at the n-GaN electrode to the working area, was 1.29 W/cm^2. n-GaN was stabilized against photodecomposition in Cl^--containing solutions as a result of the competing oxidation of Cl^- to Cl_2 via intrinsic surface states.[11] Using NaCl as the electrolyte, the photocurrent density did not decay as fast as the one using KOH or HCl as the electrolyte.[12] Moreover, NaCl is one of the main contents of seawater, which is safe and available, so we used 1 mol/L NaCl as the electrolyte. A gas chromatograph (Agilent-6850) was used to determine the composition of the generated gas. The schematic diagram of our setup is shown in Fig. 2.

Figure 3 shows the photocurrent density as a function of the external bias voltage (V_{ext}). It is clear that the photocurrent density

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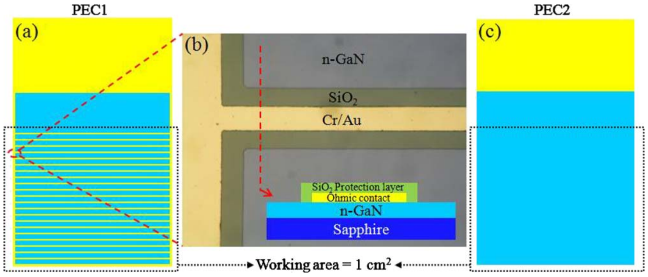

Figure 1. (Color online) Schematic diagram of the photoelectrochemical cells: (a) PEC1, (b) the picture taken at a local area of sample PEC1, and (c) PEC2. The inset of Fig. 1b shows the schematic structure of the SiO_2-protected ohmic contact on the GaN layer.

of PEC1 is markedly higher than the PEC2. We attribute this enhanced photocurrent density to the design of immersed finger-type ohmic contacts (IFOCs) in the PEC1. The marked enhancement of photocurrent density in PEC1 could be attributed to the fact that the distance between the neighbor Cr/Au ohmic contacts is small enough to reduce the recombination probability of photogenerated electrons with holes or charged defects in the GaN layer before the electrons reach the ohmic contacts. In contrast to the PEC1, the recombination of photogenerated carriers with each other or the charged defects occurs before the carriers reach the ohmic contact of the PEC2. In other words, the diffusion length of the photogenerated electrons is far shorter than the distance from the working area to the ohmic electrode, which is outside of the working area, as shown in Fig. 1c.

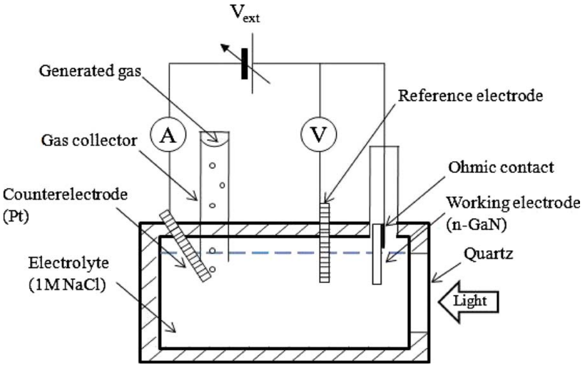

Figure 2. (Color online) Schematic setup of photoelectrolysis of water using an n-type GaN working electrode. The working electrode, reference electrode, and counter electrode were immersed in the electrolyte (1 M NaCl). The light source was 300 W Xe lamp. V_{ext} in this graph indicates the bias we applied to the n-type GaN working electrode vs Ag/AgCl reference electrode.

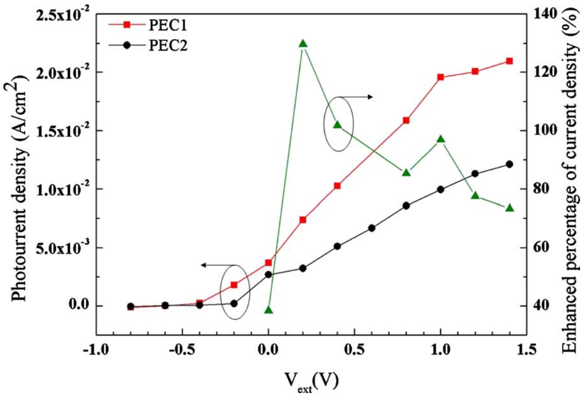

Figure 3. (Color online) Typical current–potential curves of PEC1 and PEC2. The enhanced percentage of the photocurrent density of the PEC1 compared with the PEC2 is also displayed.

As shown in Fig. 3, the enhancement of photocurrent density increased markedly with an increase in the applied external bias. This result indicates that the design of the IFOC could effectively enhance the photocurrent density, especially when the positive external bias exists because the applied electric field could effectively spread in the whole working area of PEC1 through the SiO_2-protected IFOC. In other words, the photogenerated electrons in PEC1 undergo less transit time compared with the PEC2 before they reach the ohmic electrodes, while the transit time is inversely proportional to the probability of electrons recombined with holes or charged defects. In PEC2, the applied fields (or electric force lines) are difficult to uniformly distribute over the whole working area, thereby leading to a longer transit time of electrons compared with the PEC1. As a result, the enhancements of photocurrent density with external bias were markedly higher than those of the zero-bias condition, as shown in Fig. 3. The enhanced percentage of photocurrent density tended to decay slowly when the applied bias became larger than 0.2 V, as shown in Fig. 3. The enhanced percentage of current density is defined as the difference in the photocurrent density between the PEC2 and PEC1 to the photocurrent density of PEC1. This enhancement could be attributed to the fact that the collection efficiency of photogenerated electrons in PEC2 increased markedly with an increase in positive bias (> 0.2 V) because the surface reaction of n-GaN in PEC1 leads to dense pores during water-splitting reactions especially for a positive bias applied to the PEC1. As a result, the n-GaN layer became resistive owing to the formation of these pores, thereby resulting in the decrease in the usable surface area for water-splitting reactions. In principle, the hydrogen gas generation occurs at the Pt electrode/electrolyte interface, while the photoelectrochemical reaction at the n-GaN/electrolyte interface leads to an etching reaction of the GaN layer and the generation of nitrogen. In other words, the etching reaction can cause dense pores on the GaN surface. Figure 4 shows the typical scanning electron microscopy (SEM) images taken from the n-GaN surface of PEC1 before and after the water-splitting reaction process. It is clear that the surface of n-GaN became rough by photodecomposition. However, this phenomenon was insignificant for the PEC2, implying that the gas generation rate in PEC1 is far higher than that of PEC2. The density of pores on the GaN surface of PEC1 increases markedly with the bias voltage because the applied field could effectively spread over the whole working area of PEC1, as mentioned above. However, in PEC2, the density of the pores has a slight increase with bias voltage. In other words, the decrease in the effective surface area in PEC2 was insignificant. Therefore, the decay rate of the photocurrent density of PEC2 was lower than that of PEC1 when the applied bias was increased. As a result, the enhanced percentage of the photocurrent density tended to decay slowly when the applied bias became larger than 0.2 V, as shown in Fig. 3. The lifetime of the experimental devices was estimated to be around 2 h, which was determined by the time to failure, i.e., zero or very low current output.[13]

Table I shows the gas generation rates at the counter electrode (Pt) when the PEC1 and PEC2 were used as the photoelectrochemical cells. This result is consistent with the current–potential curves, as shown in Fig. 3, indicating that the immersed ohmic electrode could effectively enhance the gas generation rate of the n-GaN photoelectrochemical cells. In this study, we used a gas chromatograph to analyze the gas composition. The experimental results indicated that the collected gas includes 67% of H_2 and 33% of N_2. The nitrogen gas was mainly from the etching reaction that occurred at the n-GaN/electrolyte interface during the photoelectrochemical process, thereby resulting in the formation of a surface texture on the n-GaN surface, as shown in Fig. 4b. Returning to Table I, one can conclude that with an external bias of 1 V, the typical photocurrent densities (or gas generation rate) of the n-GaN working electrodes with and without the SiO_2-protected IFOC were approximately 19.6

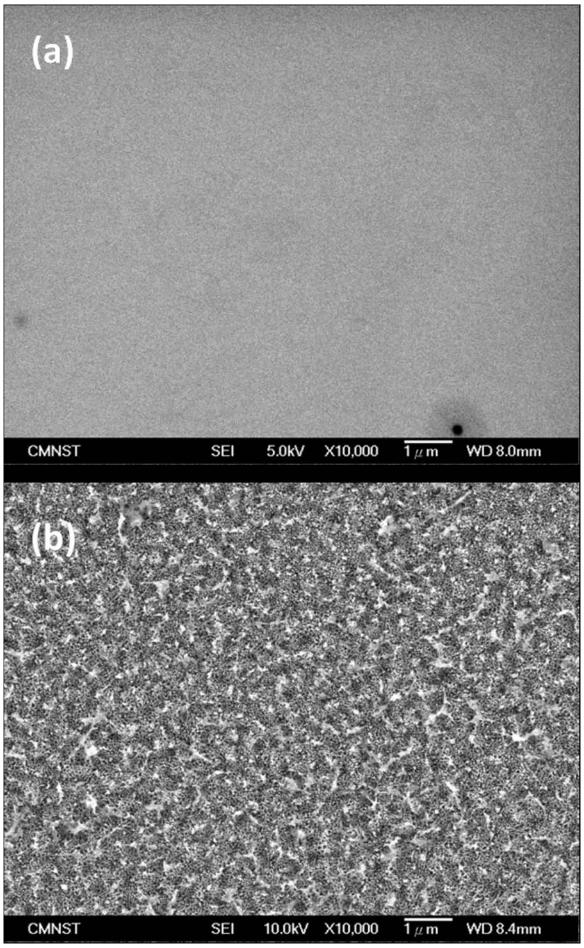

Figure 4. Typical SEM images taken from the n-GaN surface of PEC1 (a) before and (b) after the water-splitting reaction process.

(9.4) and 9.9 (3.6) mA/cm^2 (mL/h), respectively, which corresponded to an enhancement in photocurrent density (or gas generation rate) of around 98% (160%). On the basis of this result, one might question why an enhancement of 98% in photocurrent density could lead to an enhancement of 160% in the gas generation rate. In fact, this question could be answered if one considers the gas composition. However, related studies are underway to further clarify this point. The solar-to-hydrogen conversion efficiency (η) of PEC1 was 0.35% when at an external bias (V_{ext}) of 1 V. The solar-to-hydrogen conversion efficiency can be calculated from the equation[7]

$$\eta = j_p(1.23 - V_{ext})/I_0$$

where the j_p and the I_0 are the photocurrent density (A/cm^2) and the light intensity (W/cm^2), respectively.

To study the effect of different electrode designs on the photocurrent density, GaN PEC cells with different electrode schemes were also prepared. Samples used in this study were designed with distances between the metal stripes (L_d) of 120, 240, and 360 μm, and they were labeled as PEC-I, PEC-II, and PEC-III, respectively.

Table I. The rates of gas generation (mL/h) of PEC1 and PEC2 were measured under illumination.

Sample	V_{ext} = 0 V	V_{ext} = 1 V
PEC1	1.9	9.4
PEC2	1.1	3.6

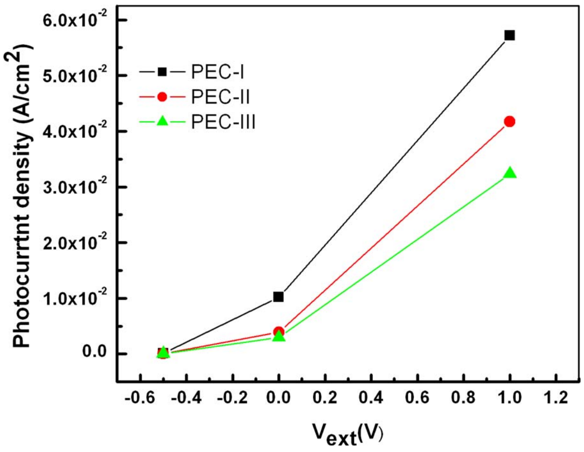

Figure 5. (Color online) Typical current–potential curves of GaN PEC cells with different spacings between metal electrode stripes.

Figure 5 shows the photocurrent density as a function of V_{ext}. It is clear that the j_p increased with a decrease in L_d when the PEC cells were biased at a given V_{ext}. This result can be attributed to the fact that the collection efficiency of photogenerated carriers was dominated by the carrier diffusion length rather than the shading effect of metal electrodes. In other words, most photogenerated carriers may recombine with charged states (i.e., defects) before they reached the metal electrodes, especially for the samples with large L_d.

In summary, we have measured the photocurrent density of two different n-type GaN photoelectrodes, with (PEC1) and without (PEC2) the SiO_2 protection layer on the ohmic electrodes from the electrolyte. As a result, distinct enhancements in photocurrent were achieved. The measured results indicate that the design of IFOC could enhance the photocurrent density, the rate of gas generation, and the solar-to-hydrogen conversion efficiency. The marked enhancement in the gas generation rate could be attributed to the fact that the distance between the neighbor Cr/Au ohmic contacts is small enough to reduce the recombination probability of photogenerated electrons with holes or charged defects in the GaN layer before the electrons reach the ohmic contacts. In addition to the enhancement of the generation rate of hydrogen gas, it is important to avoid the photodecomposition of the GaN photoelectrodes to extend the lifetime of the PEC device.

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References

1. A. J. Nozik and R. Memming, *J. Phys. Chem.*, **100**, 13061 (1996).
2. J. A. Turner, *Science*, **285**, 687 (1999).
3. A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972).
4. A. Heller and R. G. Vadimsky, *Phys. Rev. Lett.*, **46**, 1153 (1981).
5. S. U. M. Khan, M. Al-Shahry, and W. B. InglerJr., *Science*, **297**, 2243 (2002).
6. A. J. Nozik, *J. Cryst. Growth*, **39**, 200 (1977).
7. R. C. Kainthla, B. Zelenay, and J. O'M. Bockris, *J. Electrochem. Soc.*, **134**, 841 (1987).
8. I. Waki, D. Cohen, R. Lal, U. Mishra, S. P. DenBaars, and S. Nakamura, *Appl. Phys. Lett.*, **91**, 093519 (2007).
9. J. Li, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.*, **93**, 162107 (2008).
10. J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, and W. J. Schaff, *Appl. Phys. Lett.*, **80**, 4741 (2002).
11. I. M. Huygens, A. Theuwis, W. P. Gomes, and K. Strubbe, *Phys. Status Solidi C*, **0**, 448 (2002).
12. K. Fujii and K. Ohkawa, *Phys. Status Solidi C*, **3**, 2270 (2006).
13. N. A. Kelly and T. L. Gibson, *Int. J. Hydrogen Energy*, **31**, 1658 (2006).