Solar-to-hydrogen conversion efficiency of water photolysis with epitaxially grown p-type SiC

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Abstract. Solar-to-hydrogen conversion efficiencies of water photolysis with epitaxially grown p-type 4H-, 6H- and 3C-SiC were estimated in the two electrode system. For all the polytypes, the efficiency with a Pt counter electrode in the two electrode system was very low compared with those in the three electrode system. However, when Ni was used as a counter electrode in the two electrode system, photocurrents were as large as the three electrode system. The estimated efficiencies seem to depend on the bandgap of SiC polytypes, and the highest solar-to-hydrogen conversion efficiency was 0.38% with 3C-SiC.

Introduction

Hydrogen production by water photolysis attracts attention as a next generation energy technology [1-3], because water photolysis can generate hydrogen without CO_2 emission. However, the low conversion efficiency and corrosion of the water photolysis materials are obstacles for realization of this technology. For example, metal oxides are conventional water photolysis materials without corrosion in electrolytes. However, owing to their wide band gap, the conversion efficiencies for these materials are only 1-2% [4]. On the other hand, semiconductor materials other than metal oxides sometimes show high conversion efficiencies, but they are weak against corrosion [5]. Thus, new water photolysis materials, such as GaN, have been studied to obtain both high conversion efficiency and resistance to corrosion [6-8]. Although the reports on SiC as a water photolysis material have been rarely found [9], recently, we have reported capability and durability of p-type SiC for water photolysis [10,11]. In addition, 3C-SiC is expected to show a high efficiency, because it has a band gap of 2.2 eV and can absorb a part of visible light. Owing to these characteristics, SiC is attractive as a water photolysis material. So far, most of reports on water photolysis properties of SiC were investigated in a three electrode system [9,10]. We must use a two electrode system to estimate actual solar-to-hydrogen conversion efficiency, because in the three electrode system, an electrical power is supplied from a potentiostat to stabilize potential at SiC. In this study, we measured photocurrent of SiC in the two electrode system and estimated the solar-to-hydrogen conversion efficiencies for epitaxially grown p-type 4H-, 6H- and 3C-SiC.

Experiments

Samples employed in this study were epitaxially grown p-type 4H-, 6H- and 3C-SiC. 4H-SiC was grown on (0001) Si-face with an 8 degrees off 4H-SiC substrate. 6H- and 3C-SiC were grown on the (0001) Si-surface with 3.5 degrees off and on-axis 6H-SiC substrates, respectively. The epitaxial layer thicknesses are 10-20μm and doping densities estimated by capacitance-voltage measurements are of the order of 10^{16} cm^{-3}. The details for the sample properties are listed in Table 1.

Time dependence of photocurrents were observed in three electrode and two electrode systems. The experimental setups are shown in Fig.1. We fabricated ohmic contacts on the samples and the contacts were connected to a wire. Then the samples were fixed by electron wax on polycarbonate plates with only the sample surface exposed. The exposed surfaces were used as a working

electrode(W.E.). For the three electrode system, Pt was used as a counter electrode (C.E.) and a saturated calomel electrode (SCE) was used as a reference electrode (R.E.). The working electrode potential was adjusted to 0 V vs SCE during experiments. For the two electrode system, either Pt, Ni or Au was used as a counter electrode and no external power supply was connected. The light source was a solar simulator whose power was 1 W/cm^2 and the electrolyte was 1 mol/l H$_2$SO$_4$ aqueous solution at room temperature in all the experiments.
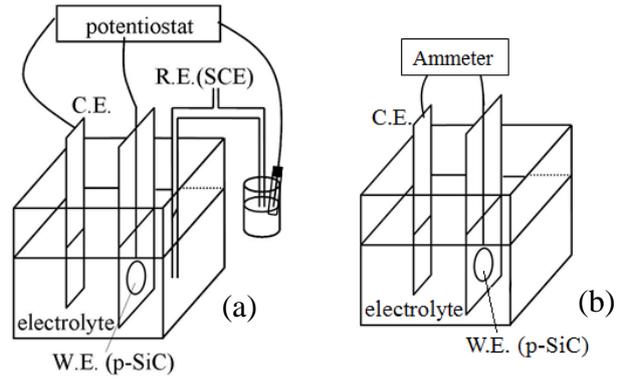
Fig.1 Schematics of experimental setups, (a) Three electrode system (b) Two electrode system.

Results and discussion

Figure 2 shows time dependence of photocurrents in the three electrode system. Photocurrents are constant and seems to depend on the bandgap of SiC polytypes. 3C-SiC has the smallest bandgap and shows the largest photocurrent among the samples. We have shown photocurrents of bulk grown SiC in ref.11, which were approximately 100 μA/cm^2, while the epitaxial samples show much larger photocurrents as shown in this figure. This could be due to the following reasons: the epitaxial samples have lower impurity concentrations, which introduce a wider depletion layer. In water photolysis, only the electrons reaching the electrolyte react with hydrogen ions. The electrons photo-generated in the depletion layer are accelerated to the electrolyte owing to the electric field there. Hence, a wider depletion layer can collect electrons from a wider region, leading to a larger photocurrent. In addition, the carrier lifetime in epitaxial samples should be longer than in the bulk sample. As a result, large carrier diffusion length could be expected in the epitaxial samples. We may consider that since both the wide depletion layer and large carrier diffusion length lead to a thick carrier-collection layer, epitaxial samples exhibit larger photocurrents than bulk samples.

Figure 3 shows time dependence of photocurrents in the two electrode system. When Pt was used as a counter electrode, the photocurrents were very small compared with those in the three electrode system. These results shows that the potential adjustment by a potentiostat enhanced photocurrent. On the other hand, in the case of a Ni counter electrode, the photocurrents are larger than those in the case of the Pt electrode and are as large as those in the three electrode system. We also measured photocurrent with a Au counter electrode, and in this case the photocurrent is smaller than in the case of the Pt counter electrode.

Table 2 shows conversion efficiencies calculated from photocurrents at 600 s after starting experiments in the two electrode system. The solar-to-hydrogen conversion efficiency η can be obtained from

$$\eta \, (\%) = \frac{I \times 1.23}{L} \times 100 \tag{1}$$

where I is the photocurrent, L is the light intensity, and 1.23 represents the redox potential width between H$^+$ / H$_2$ and O$_2$ / H$_2$O. The conversion efficiencies in the two electrode system strongly depend on the counter electrodes. The Ni counter electrode showed much higher efficiency than the other counter electrodes, and the efficiency of the Au electrode was the smallest. These results shows that the oxygen overpotential of metals may relate to performance of a counter electrode. An overpotential is a required potential for electrolysis over the theoretical value 1.23V. An oxygen overpotential is the overpotential at a cathode. The oxygen overpotential of Ni, Pt and Au at 5 mA/cm^2 are 0.461V, 0.80Vand 0.927V, respectively [12]. Therefore, we consider that when a metal with a low oxygen overpotntial was used, a high conversion efficiency was obtained.

For a counter electrode, durability is also important. We analyzed the Ni counter electrode by Auger electron spectroscopy (AES) and scanning electron microscope (SEM) after a photolysis experiment for 3 hours. It was found that Ni was seems to be oxidized from AES and the surface of

the Ni became rough in a SEM image, even though photocurrent was stable during photlysis for 3 hours. These results suggest oxidation of the Ni counter electrode during water photolysis , and we must investigate the durability of Ni for a longer period.

Then, we calculated the theoretical conversion efficiency for 3C-SiC using reported absorption coefficients and assuming that all photons absorbed in the epitaxial layer (20 μm) contribute hydrogen generation [13]. Estimated theoretical efficiency is more than 5% for 3C-SiC. The experimental conversion efficiency of 0.38% is still much smaller than this theoretical value. Therefore, if 3C-SiC with longer carrier lifetime is used in the water photolysis, the conversion efficiency of SiC will be improved.

Table 1. Thickness, net acceptor concentration and substrate of the samples

Sample	p4H	p6H	p3C
Thickness	10 μm	~20 μm	~20 μm
Net accetptor concentration	3×10^{16} cm^{-3}	1×10^{16} cm^{-3}	1×10^{16} cm^{-3}
Substrate	4H-SiC (0001) Si surface 8° off-axis	6H-SiC (0001) Si surface 3.5° off-axis	6H-SiC (0001) Si surface on-axis

Table 2. Conversion efficiencies in the two electrode system

	Ni electrode	Pt eletrode	Au electrode
p-4H	0.10 %	4.9×10^{-4} %	0 %
p-6H	0.26 %	9.6×10^{-4} %	1.8×10^{-4} %
p-3C	0.38 %	1.0×10^{-3} %	2.7×10^{-4} %
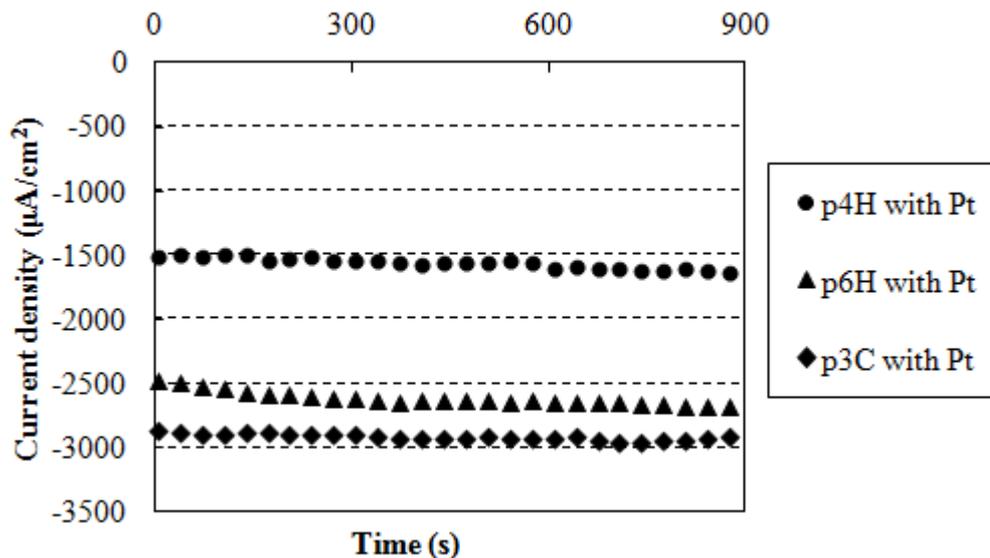
Fig.2. Time dependence of photocurrents in the three electrode system.
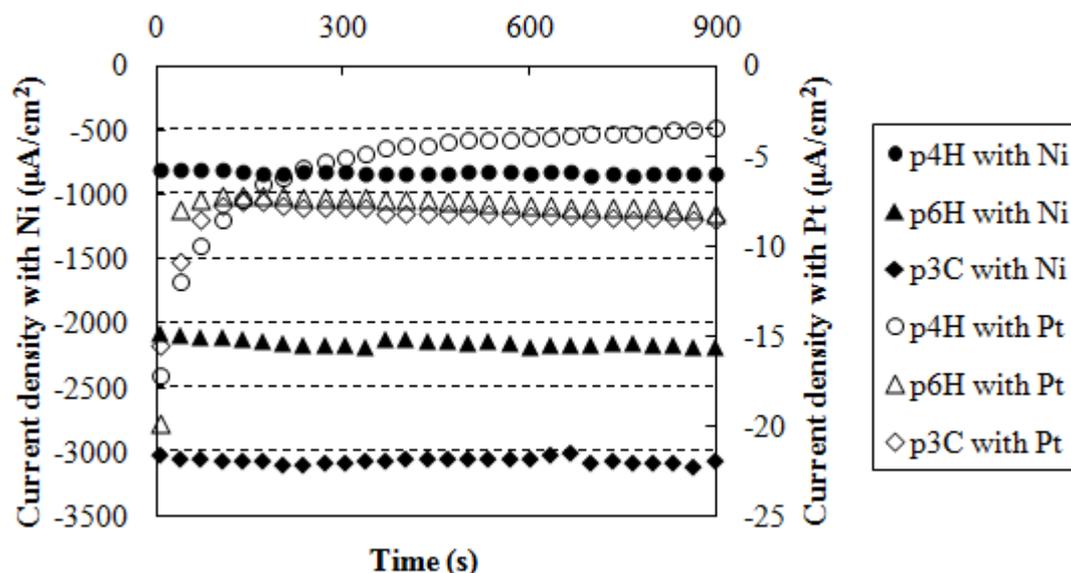
Fig.3. Time dependence of photocurrents in the two electrode system.

Conclusions

The water photolysis properties of SiC in the three and two electrode systems were characterized. When Ni was used as a counter electrode in the two electrode system, similar photocurrents to those obtained from the three electrode system were observed, and the estimated solar-to-hydrogen efficiencies were 0.10%, 0.26% and 0.38% for 4H-, 6H- and 3C-SiC, respectively. The efficiency 0.38% is the highest of all water photolysis with SiC reported so far, and it may be higher if we use 3C-SiC with a long carrier lifetime. Therefore, we consider that SiC is a potential candidate for a water photolysis material.

References

[1] K. Maeda and K. Domen: J. Phys. Chem. Lett. 1 (2010) 2655.

[2] D. A. Tryk, A. Fujishima, and K. Honda: Electrochimica Acta 45 (2000) 2363.

[3] A. J. Bard and M. A. Fox: Acc. Chem. Res. 28 (1995) 141.

[4] S. U. M. Khan, M. Al-shahry, and W. B. Ingler Jr.: Science 297 (2002) 2243.

[5] A. W. H. Mau, C. B. Huang, N. Kakuta, and A. J. Bard: J. Am. Chem. Soc. 106 (1984) 6537.

[6] K. Fujii, T. Karasawa, and K. Ohkawa: Jpn. J. Appl. Phys. 44 (2005) L543.

[7] K. Fujii and K. Ohkawa: J. Electrochem. Soc. 153 (2006) A468.

[8] K. Aryal, B. N. Pantha, J. Li, J. Y. Lin, and H. X. Jiang: Appl. Phys. Let. 96 (2010) 052110.

[9] J. Akikusa and S. U. M. Khan: Int. J. Hydrogen Energy 27 (2002) 863.

[10] T. Yasuda, M. Kato, and M. Ichimura: Mater. Sci. Forum, 717-720 (2012) 585

[11] T. Yasuda, M. Kato, M. Ichimura, and T. Hatayama: Appl. Phys. Lett. 101 (2012) 053902

[12] National Research Council, C. J. West: International critical tables of numerical data, physics, chemistry and technology vol.VI, McGraw-Hill Book Co., New York, 1926, p340.

[13] S. G. Sridhara, T. J. Eperjesi, R. P. Devaty, W. J. Choyke: Mater. Sci. Eng. B61-62 (1999) 229