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PHOTOELECTROCHEMICAL CELL USING SiC FOR WATER SPLITTING

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Photoelectrochemical cell using silicon carbide and Pt electrodes can split water into H_2 and O_2 without any external bias. Maximum photovoltage was ca. 0.45 V for a $\langle$p-SiC/H_2O/Pt$\rangle$ photocell and 2.2 V for a $\langle$p-SiC/H_2O/n-SiC$\rangle$ photocell. Energy conversion efficiency to H_2 was ca. 0.4% for irradiation with a 500 W Xe lamp.

Photoelectrochemical processes at semiconductor electrodes have been intensively investigated in recent years concerning the solar energy conversion into electrical and/or chemical energy. Major interest is focussed upon the photoelectrochemical cells$^{1-5)}$ and the photoelectrosynthesis.$^{6-9)}$ Photoexcited semiconductors produce the electron and hole pairs which have high ability for the reduction and oxidation of solution species resulting from the charge transfer reaction across the semiconductor/liquid interface. Light-irradiated n- and p-type semiconductor electrodes show large photoinduced underpotentials for redox reactions.$^{10-12)}$

As for photoelectrochemical cells for water splitting into hydrogen and oxygen, various semiconductors such as n-type TiO_2,$^{1)}$ $SrTiO_3$,$^{4)}$ and p-type GaP$^{5)}$ have been employed from the viewpoint of the relationship between flatband potentials of semiconductors and redox potentials of water. Critical points for the photoelectrochemcial cell (PEC) construction are: 1) large photoinduced underpotential , 2) good matching to solar spectrum, 3) high stability, and 4) high quantum efficiency.

Silicon carbide (SiC) is recently employed in a stable electronic device, especially for the use in high temperature atmosphere, and is an interesting material for a photoelectrode in the photoelectrochemical system, because SiC has a high melting point ($>$2700 ^{o}C) and high chemical and mechanical stability.$^{12-14)}$ Gleria and Memming have employed SiC for the dye sensitization reaction where a hole injection process is promoted due to the shallow valence band potential of SiC.$^{15)}$ Bockris and Uosaki have reported a flatband potential of p-SiC for hydrogen generation.$^{16)}$ Krotova and Pleskov have reported the photoelectrode property of SiC, and have concluded that SiC is an unstable photoelectrode.$^{17)}$ Morisaki et al. have also reported on an anodic photocurrent at n-SiC.$^{18)}$ From these experimental reports SiC has a favorable photoinduced underpotential, but an electrode reaction would not be advantageous for the use in PEC because of the electrode surface corrosion and the low quantum efficiency of photocurrent. In this paper we show the characteristics of PECs employing n- and p-SiC, which can efficiently split water into hydrogen and oxygen for a long period without any external bias.

The materials employed here for semiconductor electrodes are single crystal SiC (α-type, hexagonal, c-axis, green n-SiC from Syouwa Denko Corporation and dark blue p-SiC from Mitsubishi Kinzoku Corporation). The n- and p-type were controlled by doping N and Al, respectively. Donor and acceptor densities obtained by impedance measurements are 1.2×10^{18} cm^{-3} and 3.3×10^{17} cm^{-3}, respectively. The crystal of 6x8 mm^2 and 1 mm thickness was etched by a 20% HF solution to remove surface layer (SiO_2) and rinsed with methanol and water. Ohmic contacts were ensured by the electrochemical deposition of Au/Ta alloy onto p-SiC and by painting of Ga/In alloy onto n-SiC. A Cu wire was connected to the alloy on SiC with Ag epoxy.

A flask-type Pyrex cell with a single compartment was used. A 100 W Hg lamp or a 500 W Xe lamp was used as a light source. Band gap energy Eg was determined from action spectra of photocurrents. Flatband potentials of semiconductors were obtained by Mott-Schottky plots. Photoelectrochemcial measurements of semiconductors were carried out by the method described elsewhere.[3,11] The evolved H_2 and O_2 which were collected as mixed gases in the closed cell, were determened by gas chromatography with a column of Carbosieve S.

Figure 1 shows the photocurrent-voltage curve of $\langle$p-SiC/0.5 $mol\cdot dm^{-3}$ (1 M = 1 $mol\cdot dm^{-3}$) H_2SO_4 aqueous solution/Pt$\rangle$ photocell. This cell gave an open circuit photovoltage of ca. 0.45 V, which is the largest value in the water splitting PECs ever reported. Table 1 summarizes the properties of various water-splitting photocells. Short circuit photocurrent I_{sc} was ca. 300 $\mu A\cdot cm^{-2}$.

The photocell reaction at the irradiated p-SiC cathode was mainly hydrogen evolution, while that at the Pt anode was oxygen evolution. In the dark, the p-SiC electrode showed a good rectifying property as shown in Fig. 2. Cathodic photocurrents appeared at the potentials more negative than 1.6 V vs. SCE in 0.5 M H_2SO_4 and 0.85 V in 1 M NaOH, respectively. Onset potentials of oxgen at the Pt anode were more negative than those of hydrogen at the p-SiC cathode. The flatband potential E_{fb} was found to change with solution pH of ca. -60 mV/pH. The relationship between E_{fb} and pH can be described as follows.

$$E_{fb}(\text{p-SiC}) = 1.66 - 0.06\ \text{pH} \quad (\text{V vs. SCE}) \tag{1}$$

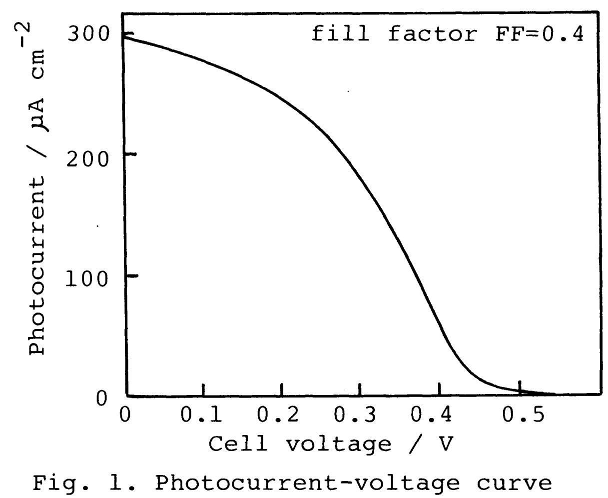

Fig. 1. Photocurrent-voltage curve of a $\langle$p-SiC/0.5 M H_2SO_4/Pt$\rangle$ photocell.

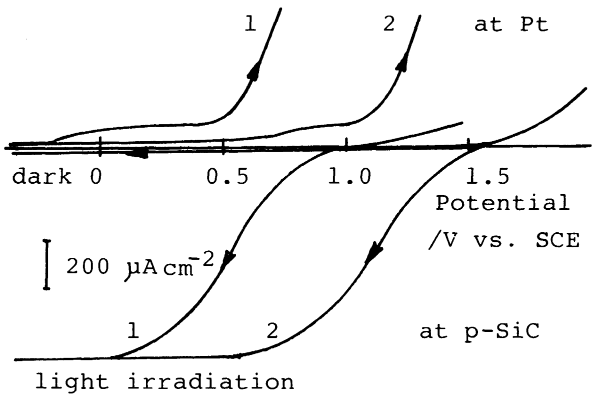

Fig. 2. Current-potential curves at Pt and p-SiC electrodes. 1: in 1 M NaOH, 2: in 0.5 M H_2SO_4.

Table 1. Properties of water-splitting photocells[a)]

Semi-conductor	Type	Band gap energy E_g/eV	Flatband potential E_{fb} /V vs. SCE[b)]	Under-potential $-\mu$/V[c)]	Value of ($\|\mu\|$-1.23) /V[d)]	Photovoltage V_{ph}/V[d)]
TiO_2	n	3.0	-0.34	1.24	0.01	ca. 0.0
$SrTiO_3$	n	3.2	-0.52	1.43	0.20	ca. 0.1
$BaTiO_3$	n	3.2	-0.51	1.42	0.19	ca. 0.1
SnO_2	n	3.8	+0.20	0.70	-0.53	-------
SiC	n	2.9	-0.70(-1.2)[f)]	1.61	0.38	ca. 0.3
GaP	p	2.4	+0.13(+0.9)[f)]	0.46	-0.77	-------
SiC	p	2.9	+1.6	1.90	0.67	ca. 0.45

a) The data shown in this table were obtained experimentally in our laboratory.
b) Measured in an aqueous solution at pH=1.
c) Negative overpotential for a photoelectrode reaction.
d) Water can be decomposed under the light irradiation when underpotential is larger than theoretical water splitting voltage (1.23 V).
e) This value shows the maximum open-circuit photovoltage in a PEC in 0.5 M H_2SO_4.
f) Onset potentials of photocurrents. E_{fb}s are shown in brackets.

Therefore, the photoinduced underpotential (μ) for p-SiC can be described with E_{fb} and redox potentials of water as follows,

$$\mu(\text{p-SiC}) = E_{fb}(\text{p-SiC}) - E_{H_2O/H_2} = \text{ca. } 1.9 \text{ V} \qquad (2)$$

The obtained μ value is larger than the theoretical decomposition energy of water (ΔE=1.23 V), and furthermore the value is large in comparison with $\mu(TiO_2)$ = 1.24 V and $\mu(SrTiO_3)$ = 1.43 V, so that the photoexcited SiC has large energy enough to overcome the activation overvoltage for the water splitting.

Current-potential curves of a Pt counter electrode are also shown in Fig. 2. Onset potentials of oxidation of water were 1.15 V vs. SCE in 0.5 M H_2SO_4 and 0.47 V in 1 M NaOH aqueous solutions. From the relationship between the onset potentials of cathodic photocurrent at p-SiC and anodic current at Pt, the combination of p-SiC and Pt in a homogeneous solution will give a photocell with a photovoltage of ca. 0.45 V. Diagonostic parameters of photocells are listed in Table 1.

Figure 3 shows the pH dependence of photovoltage V_{ph} for the photocell. V_{ph} was judged to be almost constant over pH=1 to 14, as expected from the same pH dependence of E_{fb} of SiC and E_{O_2/H_2O}.

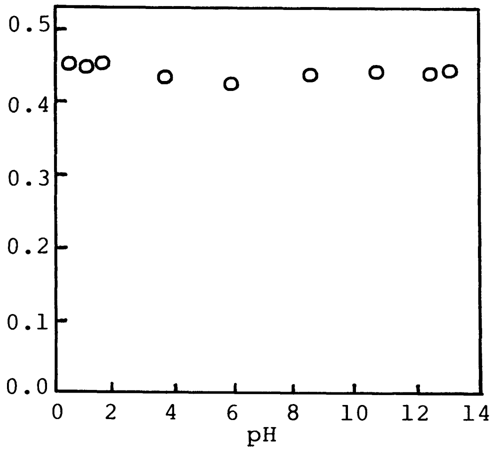

Fig. 3. pH dependence of open circuit photovoltage.

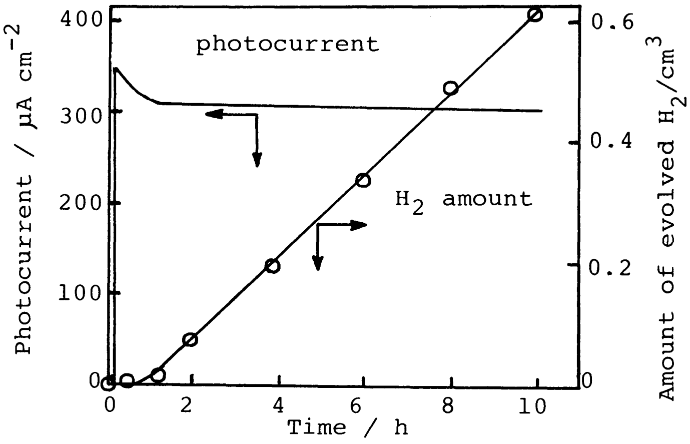

Fig. 4. Time dependence of photocurrent and hydrogen evolution in a PEC.

Figure 4 shows the time dependence of the photocurrent and the hydrogen evolution in the photocell ⟨p-SiC/H_2O/Pt⟩ . The magnitude of photocurrent was eventually invariable for a long duration of irradiation time. Hydrogen evolved with a linear time dependence but the amount of H_2 was less than a Faradaic equivalent presumably because of the reduction of dissolved oxygen.

When we used n-SiC instead of Pt in the photocell, the irradiation of both n- and p-SiC electrodes resulted in an increase of photovoltage to ca. 2.2 V, because the onset potentials of photocurrents at n- and p-SiC were ca. -0.7 vs. SCE and 1.6 V in 0.5 M H_2SO_4. As for the stability of a photocell, the decrease percentages of photocurrents after 10 h operation were 4% at p-SiC and 37% at n-SiC. The stability of n-SiC was a little lower than that of p-SiC.

From the point of view of the light energy conversion, the conversion efficiency to the hydrogen evolution of a photocell ⟨p-SiC/H_2O/Pt⟩ was found to be ca. 0.4% for irradiation with a 500 W Xe lamp. It should be remarked here that the photocathode used had a high resistance (ca. 1 kΩ), which might result in rather poor perfomance characteristics. Further investigations on the photoelectrochemical processes are required, because a large number of different crystal forms[13,14] are available in SiC as "polytypes" and many of their electronic and photoelectrochemical properties are still unknown.

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