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Citation: *Applied Physics Letters* **101**, 053902 (2012); doi: 10.1063/1.4740079

View online: <http://dx.doi.org/10.1063/1.4740079>

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SiC photoelectrodes for a self-driven water-splitting cell

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(Received 30 May 2012; accepted 17 July 2012; published online 31 July 2012)

Photoelectrochemical properties of 4H-, 6H-, and 3C-SiC were characterized for a self-driven water-splitting cell. Correspondingly, the band edge potentials of SiC polytypes were estimated from the results of capacitance-voltage measurement in different electrolytes. The estimated potentials indicate that these polytypes were able to split water. The photocurrents of the epitaxially grown samples were found to be larger than the bulk samples. The solar-to-hydrogen conversion efficiency of p-type SiC was estimated for the first time for a self-driven two-electrode system. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4740079>]

Hydrogen attracts attention as an eco-friendly energy resource. It is usually produced from the fossil fuel, but, along with this, a greenhouse gas CO₂ is also generated during the production process. The water-splitting by light illumination of semiconductor materials can generate hydrogen without CO₂ emission. In general, water-splitting semiconductor materials should meet three criteria: (i) good material durability, (ii) suitable bandgap (1.6–2.2 eV), and (iii) band edges straddling H₂O redox potentials. Although many researches have been done for various semiconductors as possible water-splitting materials, the reported conversion efficiency or durability is not enough for practical use.^{1–3} For instance, metal oxides such as wide band gap TiO₂ are conventional water-splitting materials, which do not suffer from corrosion in electrolytes. However, the conversion efficiencies obtained from these materials are as low as 1%–2% owing to their wide bandgap.^{4,5} On the other hand, semiconductors other than metal oxides sometime show high conversion efficiencies, but they are weak against corrosion.⁶ Recently, new water-splitting materials, such as gallium nitride (GaN), have been studied to obtain a high conversion efficiency and resistance to corrosion.^{7–9} Silicon carbide (SiC) is chemically stable and can be made p-type with a high crystal quality. P-type materials are generally more stable than n-type materials in water-splitting and a high quality crystal could lead to a high conversion efficiency. In addition, one of polytypes, e.g., 3C-SiC ($E_g = 2.2$ eV at room temperature), can absorb visible light. Owing to these characteristics, SiC is attractive as a water-splitting material. Although many studies on the electrochemical properties of SiC have been reported,^{10–14} researches on SiC photoelectrode as a water-splitting material are rarely found.^{15–18} Moreover, to the best our knowledge, the self-driven system based on SiC electrode to photo-split water has never been reported. In this study, the band edge potentials of both n- and p-type SiC against H₂O redox potentials are evaluated and characterized. Furthermore, the solar-to-hydrogen conversion efficiencies are estimated in a self-driven two-electrode system based on p-type SiC for the first time.

Samples employed in this study were bulk grown and epitaxially grown SiC samples. The bulk samples are n- and

p-type 4H-, 6H-SiC, and n-type 3C-SiC. The epitaxial samples n- and p-type 4H-SiC were grown on (0001) Si-face with 4 and 8 degrees off 4H-SiC substrates, respectively. Thicknesses and doping densities for the samples estimated from capacitance-voltage (*C-V*) measurements are listed in Table I. Ohmic contacts were fabricated on the backside of the samples. The samples were then fixed by silicone resin on polycarbonate plates with only the sample surface exposed. A wire was bonded on the ohmic contact and connected to a potentiostat such that the sample could act as the working electrode. Platinum (Pt) sheet and saturated calomel electrode (SCE) were used as counter and reference electrodes in a three-electrode electrochemical cell, respectively. Capacitance-voltage (*C-V*) measurements were carried out in electrolytes at a frequency of 1 kHz to estimate the band edge potentials and net doping densities. Aqueous solutions of HCl (*pH* 1.5), Na₂SO₄ (*pH* 7), and NH₄OH (*pH* 12.2) were employed as electrolytes. Time dependence of photocurrent under illumination by a solar simulator with intensity of 1 W/cm² was measured in a 1 mol/l H₂SO₄ aqueous solution, which is a common electrolyte for water-splitting experiments,^{8,15,16} at a potential of 0 V vs SCE. The solar-to-hydrogen conversion efficiency was estimated from the photocurrent in a two-electrode system with a Ni counter electrode and without potential control (without electrical energy supply).

Figure 1 shows a Mott-Schottky plot for bulk n-type 4H-SiC obtained from a *C-V* measurement in an electrolyte of *pH* 7. In this figure, the intercept with the x-axis (−1.84 V) corresponds to a flat band potential, V_{fb} . Using V_{fb} and the Fermi level estimated from net doping densities, the band edge potentials were obtained in various *pH* for bulk samples as shown in Fig. 2 (the band edge potential for p-type 6H-SiC is not shown because the *C-V* measurement was not able to be performed for this sample due to high resistivity). In this figure, we also show the redox potentials of H⁺/H₂ and O₂/H₂O as the top and bottom of the gray band. If the edge of the conduction band is located above the redox potential of H⁺/H₂ and the edge of valence band is located below the redox potential of O₂/H₂O, the water-splitting is possible. The conduction band edge of 3C-SiC is near to the redox

TABLE I. Thicknesses and doping densities obtained from *C-V* measurements.

| (a) n-type samples | | | | |
|--------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| | n-4H bulk | n-4H epi | n-6H bulk | n-3C bulk |
| Thickness | 350 μm | 120 μm | 260 μm | 303 μm |
| Doping density | $1 \times 10^{19} \text{cm}^{-3}$ | $6 \times 10^{14} \text{cm}^{-3}$ | $4 \times 10^{19} \text{cm}^{-3}$ | $2 \times 10^{19} \text{cm}^{-3}$ |
| (b) p-type samples | | | | |
| | p-4H bulk | p-4H epi | p-6H bulk | |
| Thickness | 346 μm | 10 μm | 400 μm | |
| Doping density | $2 \times 10^{17} \text{cm}^{-3}$ | $3 \times 10^{16} \text{cm}^{-3}$ | | |

potential of H^+/H_2 , while other SiC polytypes clearly have band edge potentials capable of the water-splitting in all *pH*. Although, in principle, the band edge potential does not depend on the conduction type, the estimated band edge potential for n-type 4H-SiC is 1 eV above that of p-type 4H-SiC. The reason for conductivity type and *pH* dependence of the band edge potentials are still unclear, and hence further investigation is required.

Figure 3 shows the time dependence of photocurrents under light illumination for the n-type samples. The photocurrents were observed for all n-type samples including 3C-SiC. Among the n-type samples, epitaxial 4H-SiC exhibits the largest photocurrent. However, a gradual decrease of photocurrent is observed. It is known that when n-type SiC is oxidized by light illumination in an electrolyte,^{10,14} the resulting SiO_2 behaves as a resistant layer for photocurrent. It is confirmed in Auger electron spectroscopy (AES) result that an oxide layer was formed on the epitaxial n-type 4H-SiC. Hence, the observed gradual decrease in photocurrent could be caused by SiO_2 formation. Figure 4 shows the photocurrents for the p-type samples. As in the case of n-type samples, the photocurrent of epitaxial p-type 4H-SiC is larger than those of bulk samples. Interestingly, the observed photocurrents do not significantly decrease with time. No oxide formation or corrosion was observed for the p-type

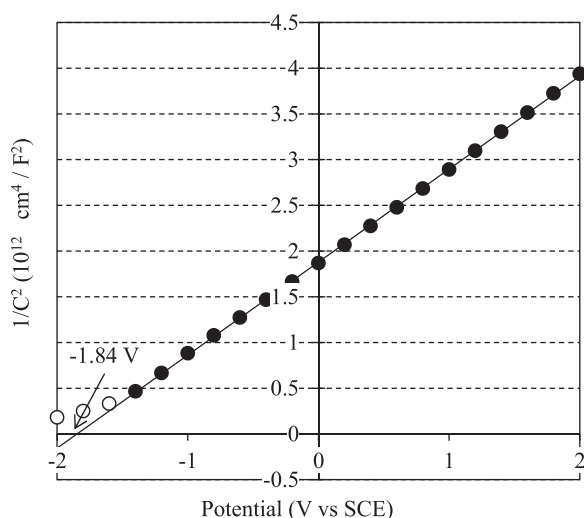


FIG. 1. Mott-Schottky plot for bulk n-type 4H-SiC (0.5 mol/l Na_2SO_4 aqueous solution). The intercept with the x-axis corresponds to the flat band potential.

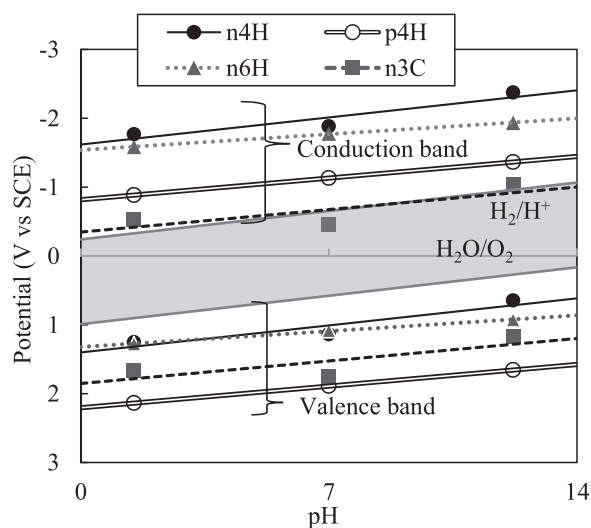


FIG. 2. Band edge potentials of SiC in various *pH* obtained from bulk samples. The redox potentials of H^+/H_2 and of $\text{O}_2/\text{H}_2\text{O}$ are also indicated by the top and bottom lines of the gray band.

samples after the photocurrent measurements in an optical micrograph and surface profile by a profilometer.

Large photocurrents are observed on the epitaxial 4H-SiC compared with the bulk samples for both n- and p-type. This could be due to the following reasons: the epitaxial samples have lower impurity concentrations, which introduce a wider depletion layer. 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 epitaxial samples. We may consider that since both the wide depletion layer and large carrier diffusion length lead to a thick light absorption layer, epitaxial 4H-SiC samples exhibit larger photocurrents than bulk samples.

The solar-to-hydrogen conversion efficiency was estimated in the two-electrode system for epitaxial p-type 4H-SiC, which showed the largest photocurrent among the samples. The obtained photocurrent was $\sim 830 \mu\text{A}/\text{cm}^2$ in the two-electrode system, as shown in Fig. 5. The solar-to-hydrogen conversion efficiency η can be obtained from

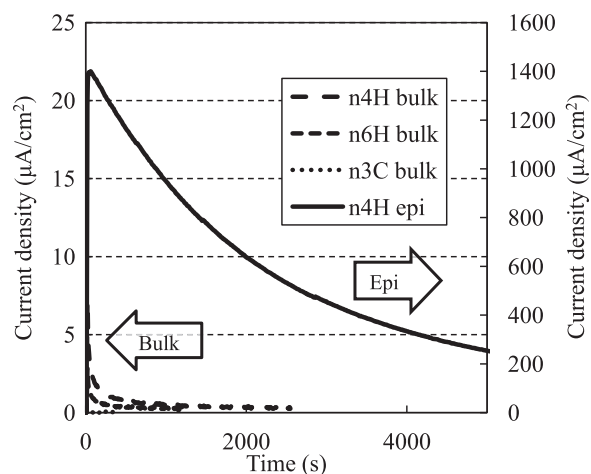


FIG. 3. Time dependence of photocurrents for the n-type samples under light illumination in the aqueous H_2SO_4 solution.

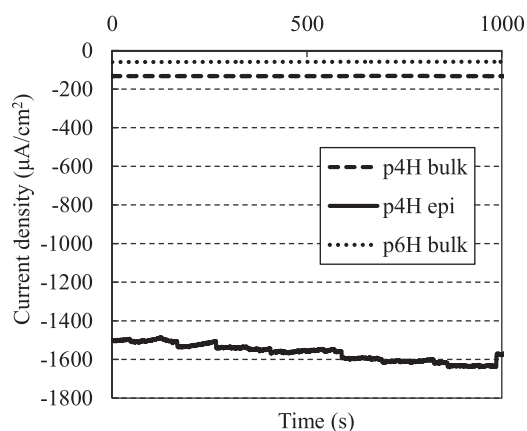


FIG. 4. Time dependence of photocurrents for the p-type samples under light illumination in the aqueous H_2SO_4 solution.

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

where I is the photocurrent, L is the light intensity, and 1.23 represents the redox potential width between H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$.^{7,8} The epitaxial p-type 4H-SiC showed an efficiency of 0.10%. Although the efficiency of 0.17% has been reported for p-type SiC by Akikusa and Khan,¹⁵ their photoelectrochemical cell was not self-driven and the efficiency was measured in a three-electrode system driven by a potentiostat. In contrast, our cell is self-driven and the efficiency was obtained in the two-electrode system without an external electrical power supply. It should be noted here that the self-driven water-splitting system based on SiC photoelectrodes has never been reported. In addition, this result suggests that higher efficiency could be expected if relatively small band gap epitaxial 3C-SiC or 6H-SiC is used instead of 4H-SiC.

In conclusion, the properties of SiC photoelectrodes for water-splitting were evaluated and characterized. Band edge potentials were estimated from C - V measurements for 4H-, 6H-SiC, and 3C-SiC, and all the polytypes seem to have band edge potentials capable to split water. Under light illumination, photocurrents were observed for all polytypes of SiC employed in this study. Moreover, the epitaxial 4H-SiC samples exhibited larger current than their bulk counterpart. The solar-to-hydrogen conversion efficiency of 0.10% was

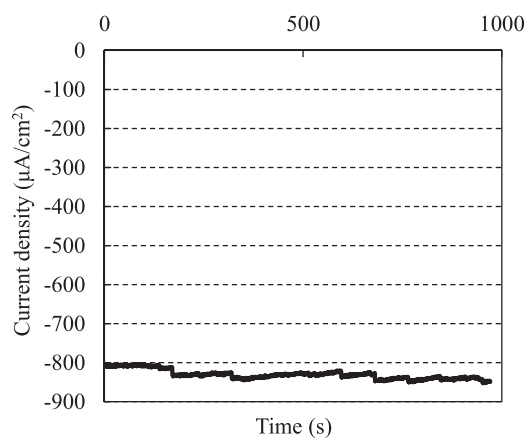


FIG. 5. Time dependence of photocurrents for the epitaxial p-type 4H-SiC under light illumination in the two electrode system.

estimated for epitaxial p-type 4H-SiC. These results suggest that SiC photoelectrodes are potential candidates for a self-driven water-splitting system.

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