Photocathode for hydrogen generation using 3C-SiC grown on vicinal off-angle 4H-SiC

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We employed a 3C-SiC epilayer grown on a vicinal off-angle 4H-SiC substrate as a photocathode. Presence of 3C-SiC on the surface of this epilayer was confirmed by the optical micrograph and the Raman spectroscopy. Spectral responses of the photocathode show high quantum efficiencies in a wide wavelength range. By illumination of full-spectrum solar light with 1.1 W/cm^2 to the photocathode, the photocurrent was −13.5 mA/cm^2 with a Ni counter electrode. Generated hydrogen volumes were much larger than those reported previously for SiC photocathodes.

Recently, hydrogen attracts attention as a clean energy resource. Hydrogen is usually produced from fossil fuel, and thus CO_2 is generated during the production process. On the other hand, water splitting by solar light irradiation to semiconductor photoelectrodes generates hydrogen without CO_2 emission. Therefore, water splitting technologies and semiconductor materials for the photoelectrodes have been investigated to develop clean hydrogen generation technology. One of the typical photoelectrode materials is TiO_2, because this material does not suffer corrosion in electrolyte.[1-4] However, TiO_2 is difficult to absorb visible light because of the wide band gap. Although other materials have been studied as photoelectrodes, their characteristics are not sufficient for practical use.[5-9] Silicon carbide (SiC) is one of the durable photoelectrode materials because SiC is chemically stable and can be grown with p-type conductivity.[4,10-15] Furthermore, 3C-SiC is able to absorb a part of the visible light owing to the moderate band gap of 2.2 eV.[4,10-15] We have reported that the durability of SiC photocathodes and capability of hydrogen generation by 3C-SiC.[10-14] Furthermore, the photocathode using the 3C-SiC epilayer grown on the 6H-SiC substrate was the largest photocurrent among SiC photocathodes employed in our studies.[10,11] The photocurrent obtained from the 3C-SiC photocathode was ~3 mA/cm^2 with 1 W/cm^2 solar light illumination.[10,11] However, the photocurrent of 3 mA/cm^2 is much smaller than theoretical expectation of ~40 mA/cm^2 for 20 μm thick 3C-SiC.[10,11] Therefore, quality of the 3C-SiC photocathode should be improved to obtain the efficiency theoretically expected. In this study, we employed a 3C-SiC epitaxial layer grown on a vicinal off angle 4H-SiC substrate and characterized performance as the photocathode.

A sample employed was a 30 μm thick Al-doped p-type 3C-SiC epitaxial layer grown on a p^+-type 4H-SiC substrate with 0.7° inclined toward the <11 $\bar{2}$0> direction from the (0001) Si-face ("3C/4H"). Another sample "3C/6H" was p-type 3C-SiC epitaxial layer grown on a semi-insulating 6H-SiC substrate with the (0001) Si-face, which was employed in our previous study.[10,11,14] For the both samples, epitaxial growth was carried out by hot-wall chemical vapor deposition method with silane and propane as source gases. Table I lists sample conditions for "3C/4H" and "3C/6H". Surface structures of the samples were observed by the optical micrographs. Polytypes of the samples were identified by Raman spectroscopy using a 532.08 nm laser. For photoelectrochemical

experiments, Ti/Al/Ni ohmic contacts were fabricated by deposition and subsequent annealing in Ar. The annealing condition of Ti/Al/Ni ohmic contacts was 1000ºC for 5 min. For "3C/4H", the ohmic contact was fabricated on the substrate side due to p^+ conductivity of the 4H-SiC substrate. On the other hand, the ohmic contact for "3C/6H" was fabricated on the epilayer side because of low conductivity in the semi-insulating 6H-SiC substrate. We fabricated photoelectrodes using the samples fixed on polycarbonate plates by wax with only the the epilayer surface exposed (~0.2 cm^2). The current path between the exposed surface and the ohmic contact is short for "3C/4H" compared with "3C/6H", and thus series resistance in the "3C/4H" photoelectrode is smaller than that in the "3C/6H" photoelectrode. Then the photocathode was immersed to an aqueous 1.0 mol/L H_2SO_4 solution. For measurements of the spectral response, the photoelectrode, Pt and a saturated calomel electrode (SCE) were used as working (cathode), counter (anode) and reference electrodes, respectively. The exposed surface of the photocathode was illuminated with monochromatic light, and we measured photocurrents and then converted them to quantum efficiencies. For photocurrent measurements with full-spectrum solar light, the two-electrode system with Ni counter electrode was adopted, because, in the two-electrode system, Ni counter electrode is preferable to obtain photocurrent due to low oxygen overpotential compared with Pt.[10] The light source of the photocurrent measurements is a solar simulator (Abet Technologies model #10500) with a power density of ~1.1 W/cm^2. Then hydrogen volumes generated by the full-spectrum experiment was measured by gas chromatography. The photocurrent measurements were conducted at room temperature.

Figures 1(a) and 1(b) show optical micrographs for the surfaces of "3C/4H" and "3C/6H", respectively. For "3C/4H", the surface has macro steps parallel to the <1 $\bar{1}$00> direction with uniform yellowish color. For 3C/6H, there are domains with two colors: yellowish and white colors. Figure 2(a) shows Raman spectra for "3C/4H". "3C/4H" shows peaks at 774, 790 and 966 cm^{-1}. The wavenumbers of the two dominant peaks (790 and 966 cm^{-1}) are similar to those of the TO and LO modes for 3C-SiC.[16] Figure 2(b) show two spectra for "3C/6H" at point A and B in Fig. 1(b). Peaks are observed at 790 and 967 cm^{-1} for point A and at 763, 787, 962 cm^{-1} for point B. The peaks for point A are at almost the same wavenumber as the peaks for "3C/4H" and can be assigned to the TO

and LO modes for 3C-SiC.[16] On the other hand, the peaks for point B are at lower wavenumbers than those for point A and "3C/4H". It was reported that the intense FTO and FLO modes for 4H- and 6H-SiC are at slightly lower wavenumbers than TO and LO for 3C-SiC.[16] Therefore, "3C/4H" and point A of "3C/6H" correspond to 3C polytype, while point B of "3C/6H" is 6H-SiC considering that the substrate for "3C/6H" is 6H-SiC. This result indicates two different domains (3C-SiC and 6H-SiC) in "3C/6H". From observation of distribution of the domains by microscope, 58% of the surface area for "3C/6H" corresponds to 3C-SiC, while the entire surface of "3C/4H"can be identified as 3C polytype.

Figure 3 shows spectral responses for the "3C/4H" and "3C/6H" photocathodes.[14] Although the "3C/4H" photocathode shows lower quantum efficiencies in wavelengths of 300-340 nm compared with the "3C/6H" photocathode, it shows higher efficiencies in wavelengths of 340-500 nm. "3C/6H" has a smaller epilayer thickness of 20 μm than "3C/4H", while~~. However, the~~ a diffusion length of carriers in "3C/6H" ~~will be~~is smaller than 20 μm~~the epilayer thickness~~.[14] ~~since the quantum efficiency is much lower than the theoretical efficiency as discussed in Ref. 14~~. Thus the difference in efficiency between "3C/6H" and "3C/4H" is not caused by the thickness difference but by difference in defect concentrations In general, vicinal off-angle substrate induces epitaxial growth with the step-flow mechanism. As shown in Fig. 1(a), the surface of "3C/4H" shows macrosteps parallel to the <1 $\bar{1}$00> direction implying the step-flow growth.[17] On the other hand, the surface of "3C/6H" shows the domain structure originated from spiral growthof islands on the on-axis substrate. Therefore, 3C-SiC growth on the vicinal off-angle substrate induces large 3C-SiC area and low defect concentration in the epilayer resulting in the higher spectral responses at long wavelengths.

Figure 4 shows the time dependence of full-spectrum photocurrents for the "3C/4H" and "3C/6H" photocathodes.[10,11] For both the photocathodes, the photocurrents were constant with time, and this result indicates durability of the samples to chemical corrosion.[13] For the "3C/4H" photocathode, the photocurrent was −13.5 mA/cm^2 at 600 s. If we divided the photocurrent by the light power of 1.1 W/cm^2, we obtain −12 mA/W. The −12 mA/W is four times larger than the photocurrent of −3 mA/W for the "3C/6H" photocathode. This large photocurrent for the "3C/4H" photocathode is due to high quantum efficiency

at long wavelengths where irradiance is relatively large in the solar spectrum.

Figure 5 shows hydrogen volumes generated from the “3C/4H” and “3C/6H” photocathodes.[10)] The plots indicate hydrogen volumes measured by gas chromatography, whereas the lines indicate hydrogen volumes estimated from integration of the photocurrents. The measured hydrogen volumes are almost the same as the estimations, and hydrogen generated by the “3C/4H” photocathode is significantly larger than that generated by the “3C/6H” photoelecrtrode. The “3C/4H” photocathode shows better performance than any other SiC photocathodes reported so far.[10-14)]

In conclusion, we fabricated the photocathode using the p-type 3C-SiC epilayer grown on a vicinal off-angle 4H-SiC substrate. This photocathode shows the photocurrent of −12 mA/W owing to light absorption by large area 3C-SiC for a wide wavelength range. Volumes of generated hydrogen using this photocathode is much larger than those reported using SiC photocathodes so far. Photocathodes using 3C-SiC grown on a visinal off angle 4H-SiC substrate is promising for application to hydrogen generation technology by water splitting.

Acknowledgments

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Figure Captions

Fig. 1. Optical micrograph for the surfaces of (a) “3C/4H” and (b) “3C/6H”.

Fig. 2. Raman spectra for (a) “3C/4H” and (b) “3C/6H” for points A and B in Fig. 1(b).

Fig. 3. Spectral responses for the “3C/4H” and “3C/6H” photocathodes.[14)]

Fig. 4. Time dependence of photocurrents for “3C/4H” and “3C/6H” photocathodes with the two-electrode system.[10,11)]

Fig. 5. Hydrogen volumes generated by the “3C/4H” and “3C/6H” photocathodes. The plots indicate volumes obtained by gas chromatography (GC), and the lines indicate estimations from the photocurrents.[10)]

Table I. Sample conditions for "3C/4H" and "3C/6H"

Sample	3C/4H	3C/6H [10,11,14]
Substrate	p^+4H	6H (high resistance)
Epilayer thickness (μm)	30	20
Nominal Al doping density (cm^{-3})	$< 1\times10^{15}$	$1\text{-}4\times10^{16}$
Electrode fabrication	Substrate side	Epilayer side

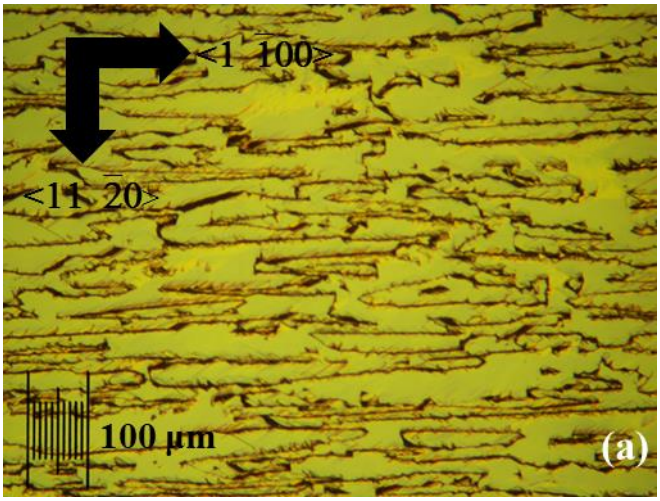

Fig. 1(a)

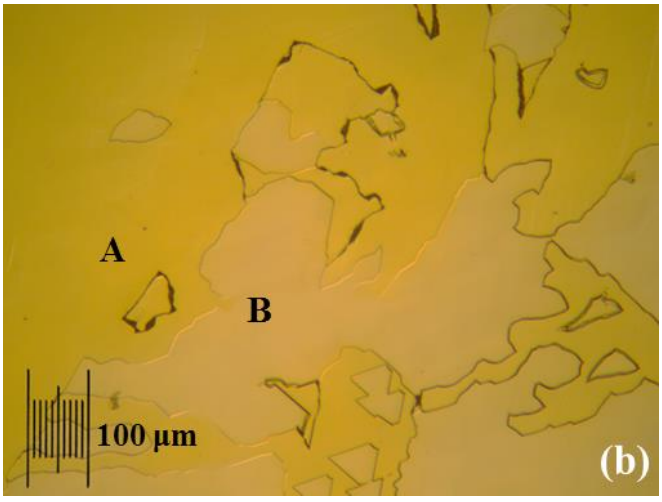

Fig. 1(b)

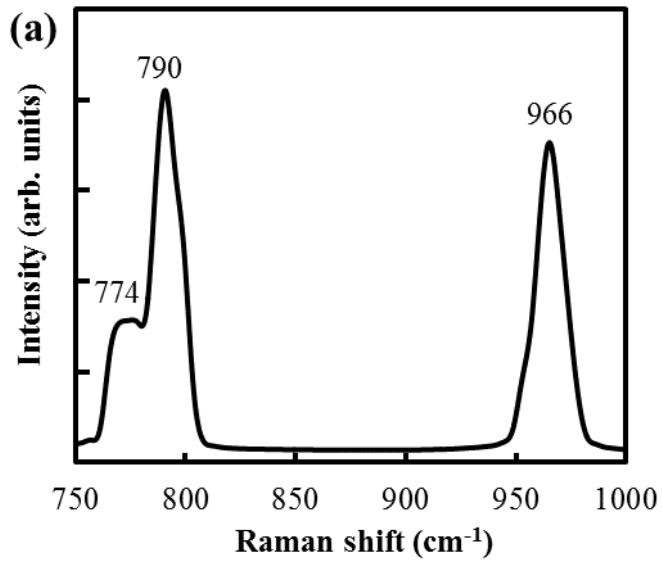
(a)
790
966
774
Intensity (arb. units)
750
800
850
900
950
1000
Raman shift (cm-1)

Fig. 2(a)

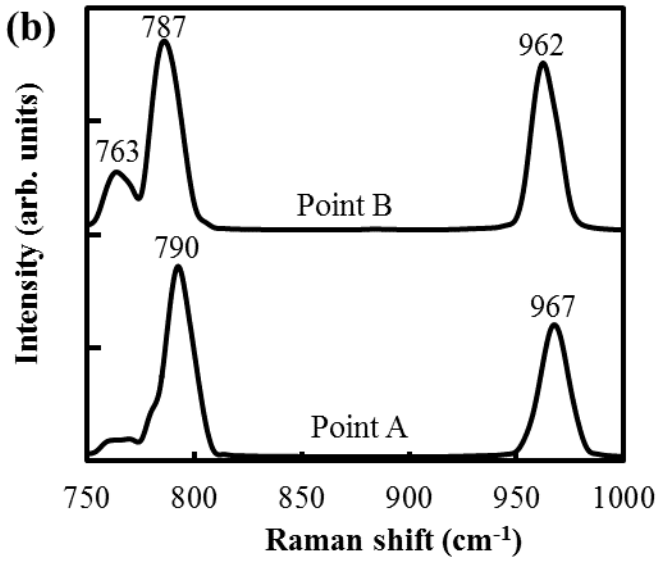
(b)
787
962
763
Point B
790
967
Point A
Intensity (arb. units)
750
800
850
900
950
1000
Raman shift (cm-1)

Fig. 2(b)

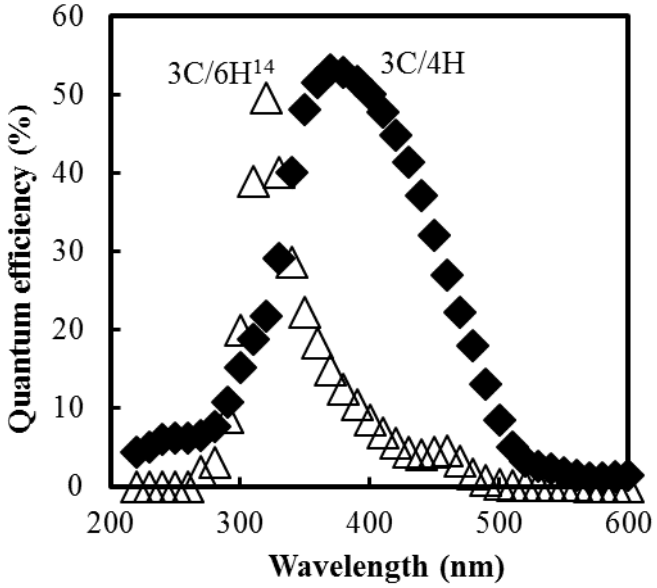
60
50
40
30
20
10
0
Quantum efficiency (%)
3C/6H14
3C/4H
200
300
400
500
600
Wavelength (nm)

Fig. 3

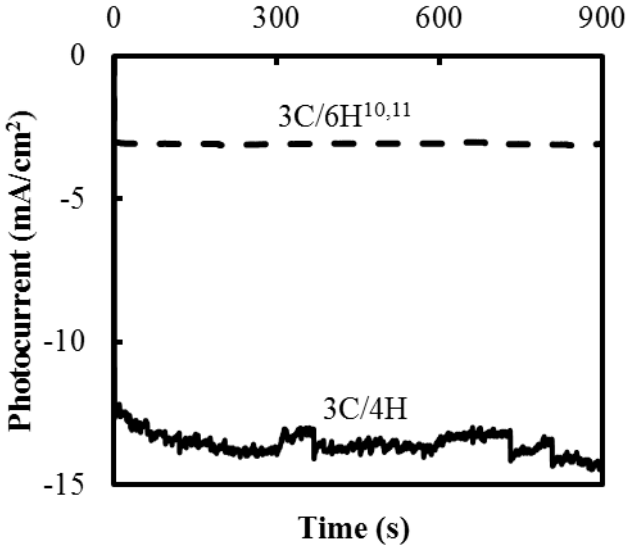
0
300
600
900
0
-5
-10
-15
Photocurrent (mA/cm2)
3C/6H10,11
3C/4H
Time (s)

Fig. 4

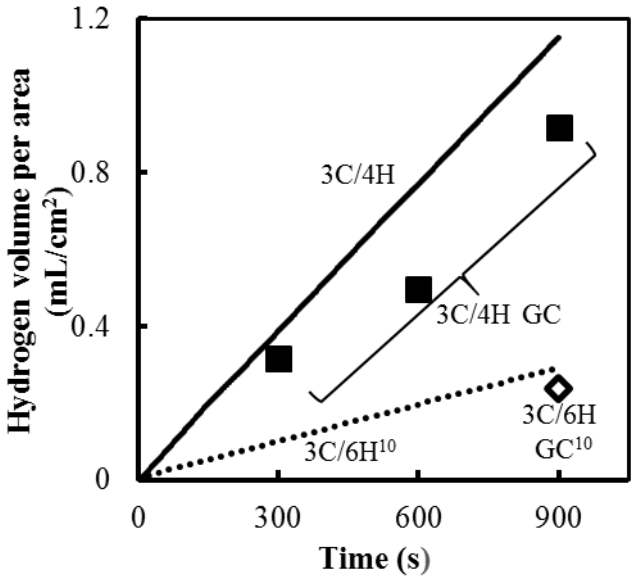
1.2
0.8
0.4
0
Hydrogen volume per area (mL/cm²)
3C/4H
3C/4H GC
3C/6H¹⁰
3C/6H GC¹⁰
0
300
600
900
Time (s)

Fig. 5