Water Splitting

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SiC: A Photocathode for Water Splitting and Hydrogen Storage**

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The report by Fujishima and Honda in 1971 that a TiO_2 photoanode, short-circuited to a Pt cathode, could be used to split water into hydrogen and oxygen caught the imagination of the scientific community.[1–3] Illumination of the n-type semiconductor creates electrons and holes. The minority carriers oxidize water to oxygen while the electrons reduce protons or water at the counter electrode to produce hydrogen. This discovery offered the prospect of using sunlight to produce environmentally friendly fuel. TiO_2 is chemically a very stable photoanode. However, the large band gap (3.2 eV) means that only the UV part of the solar spectrum is effective in water splitting. Subsequent work has concentrated on n-type semiconductors with a smaller band gap, such as WO_3[4] and Fe_2O_3.[5] Promising results based on the chemical modification of TiO_2 have recently been reported.[6–8] An alternative approach to splitting water is to generate hydrogen at a photocathode (a p-type semiconductor) and oxygen at the counter electrode. Turner and his group have shown that p-type $GaInP_2$, either coupled to a photovoltaic device (a GaAs p/n junction) or in combination with a photoanode (α-Fe_2O_3 or WO_3), offers interesting possibilities.[9–12] Recently, Mor et al. reported a similar approach[13] with a combination of a p-type Cu–Ti–O nanotube array and an n-type TiO_2 nanotube array. Hydrogen production at these photocathodes short-circuited to Pt has not been reported.

To produce hydrogen at a p-type electrode under short-circuit conditions, it is necessary to meet a number of requirements.[14] The conduction-band edge of the semiconductor should be located above the energy corresponding to the H_2O/H_2 redox couple, and the valence-band edge must be below the redox energy of the O_2/H_2O couple; this implies a band gap in excess of 1.23 eV. From literature values of flat-band potential,[15,16] it is clear that 4H and 6H-SiC readily meet these requirements. In addition, the kinetics of photocathodic reduction should be "favorable":[17] the potential range of this reaction must overlap with that of water oxidation at the metal electrode. Hydrogen evolution has been studied at p-type SiC by a number of groups.[15,18,19] On the basis of their results, one might expect water splitting for a p-type SiC/Pt galvanic cell. Herein we consider the hydrogen evolution reaction at p-type and n-type SiC electrodes. We show that SiC may be an interesting photocathode: illuminated p-type 4H-SiC, short-circuited to Pt, was found to split water. To our surprise, we also found that hydrogen, generated at both semiconductor types, is stored to a considerable extent in the solid. We consider the implications of these results, as well as the hydrogen transfer from the semiconductor to another medium.

Figure 1 presents electrochemical results for p-type 4H-SiC in 0.3 M KOH solution. Figure 1a shows the dark current as a function of potential for a scan from −0.5 to +2.8 V (versus SCE). In the vicinity of the flat-band potential, we see an anodic current due to dissolution of the semiconductor; this is followed by passivation.[20,21] These reactions depend on majority carriers: valence-band holes. The hysteresis in the return scan is due to oxide on the surface, which subsequently dissolves chemically. Cathodic reduction of water to give

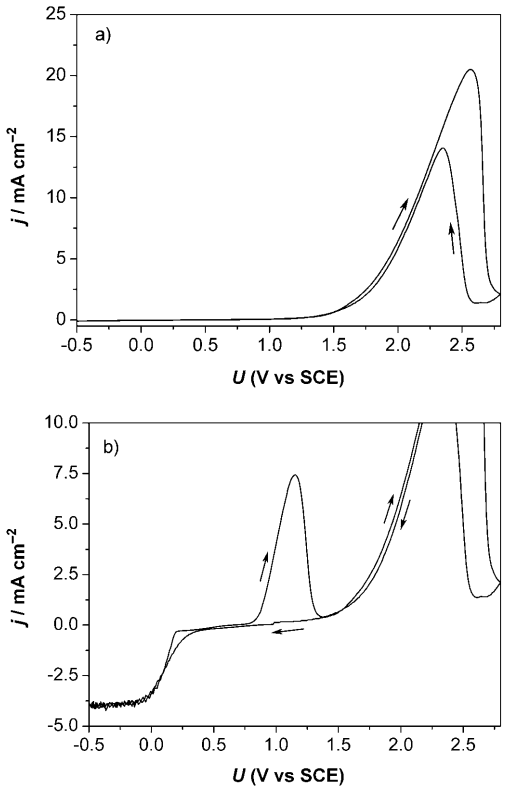

Figure 1. Current density versus potential plot for p-type 4H-SiC in 0.3 M KOH solution a) in the dark and b) under illumination. The potential was scanned from −0.5 to 2.8 V and back (at 10 $mV s^{-1}$).

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hydrogen is not observed, since this is a conduction-band (CB) reaction, which requires minority carriers [Eq. (1)].

$$2\,H_2O + 2\,e^-(CB) \rightarrow H_2(g) + 2\,OH^- \quad (1)$$

Conduction-band electrons can be generated by (supra)-band gap illumination ($E \geq 3.26$ eV). A cathodic photocurrent is measured at negative potential (Figure 1b) (its limiting value is directly proportional to the intensity of light). In the scan to positive potential, a second anodic peak is observed (also in the dark); this peak is absent in the return scan. The charge density obtained by integrating the current in the anodic peak (q_a) depends on the charge passed in the cathodic photocurrent range (q_c).

Figure 2 shows anodic current transients for a potential step from -1.0 V, at which hydrogen is evolved, to $+1.1$ V (the intensity of light in this experiment is lower than that of

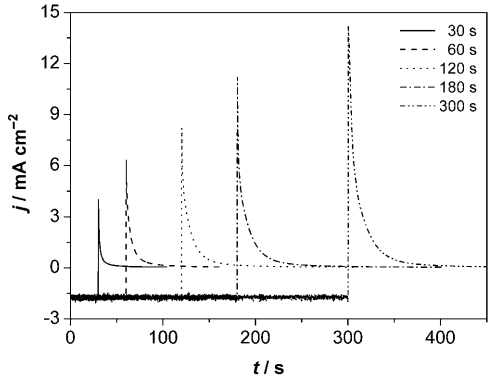

Figure 2. Potential step measurements for a p-type 4H-SiC electrode in 0.3 M KOH solution under illumination. After a fixed time at -1.0 V, the potential was stepped to $+1.1$ V and the anodic current was measured. Transients are shown for various "loading" times.

Figure 1b). As the time at negative potential is increased, the initial anodic current increases markedly, as does the total charge in the transient. The charge density deduced from the voltammogram of Figure 1b and the transients of Figure 2 (12–200 mC cm^{-2}) is much too large to be due to oxidation of a surface species. We must conclude that hydrogen, instead of being evolved as a gas [Eq. (1)], is (partly) absorbed by the electrode [Eq. (2)].

$$H_2O + e^-(CB) \rightarrow H^{\bullet}_{abs} + OH^- \quad (2)$$

Since illumination is not necessary for observation of the anodic peak, we conclude that reoxidation of the stored hydrogen requires valence-band (VB) holes [Eq. (3)].

$$H^{\bullet}_{abs} + OH^- + h^+(VB) \rightarrow H_2O \quad (3)$$

The kinetics of Equation (3) is clearly much more favorable than that of the anodic oxidation of the semiconductor, which starts at a considerably more positive potential. The results obtained with n-type 4H-SiC (and 6H-SiC) were in agreement with what one expects on the basis of the p-type results, which have already been described (see Figure 1 in the Supporting Information).

To determine how efficiently hydrogen was stored, the p-type electrode was illuminated for various times in the limiting photocurrent range, and the charged electrode was discharged in a scan to positive potential. The storage efficiency is defined as q_a/q_c: the ratio of the charge passed during hydrogen oxidation to that used for the photocathodic reduction of water. Figure 3 shows the storage efficiency as a

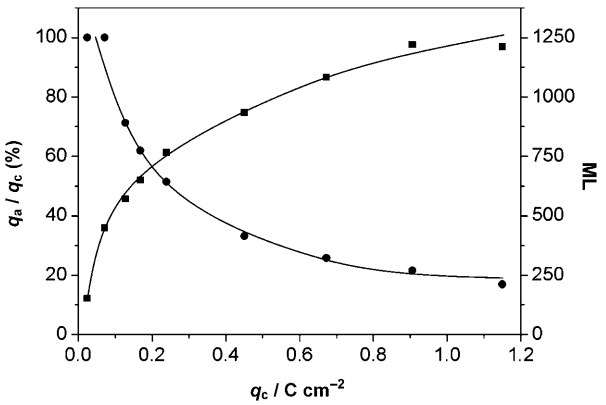

Figure 3. Efficiency of hydrogen storage (q_a/q_c) versus the loading charge (q_c) for illuminated p-type 4H-SiC in 0.3 M KOH solution (circles, left axis). On the right axis (squares), the number of monolayers (ML) of stored hydrogen is shown (1 ML is taken to be 1×10^{15} atoms cm^{-2}).

function of q_c. For low values of q_c, 100% efficiency is obtained, indicating that all the hydrogen generated is absorbed by the lattice. As q_c increases, the efficiency decreases to about 15%. On the right axis, the amount of hydrogen stored is expressed as the number of monolayers measured during oxidation (we take a monolayer to correspond to 10^{15} hydrogen atoms/cm^2). This increases quickly with increasing q_c and then more slowly up to a value of about 1250 monolayers. This trend is very likely due to a limitation in hydrogen diffusion into the lattice as the hydrogen content increases [Eq. (2)]. There is a competition between diffusion and gas evolution. Hydrogen absorption has been previously reported for p-type semiconductor electrodes (GaP[22] and Si[23]) under illumination. However, the amount of hydrogen stored was many orders of magnitude lower ($< 10^{14}$ cm^{-2}) than that found for SiC in the present study.

The results described in Figure 3 show the general trend for most samples from the p-type wafer. It is interesting to note that, while in some cases efficiencies were lower, in other cases efficiencies of almost 100% were observed for q_c values of 1.4 C cm^{-2} and 2.9 C cm^{-2}. Such large amounts of hydrogen could cause mechanical damage to the lattice, as was found for Si at much lower concentration.[23] However, for the experiments described herein, no changes in the electrode surface were observed either by SEM or by optical microscopy (on electropolished samples); this is very likely due to the superior chemical stability of SiC.

The onset of cathodic photocurrent at p-type SiC is at a potential strongly negative with respect to the flat-band value. In an attempt to improve the kinetics of the water reduction reaction [Eq. (1)], a palladium catalyst[24] was electrodeposited on the electrode. For the metalized electrode, the onset of the reduction current was sharper (see Figure 2 in the Supporting Information). Figure 4 shows a current density–

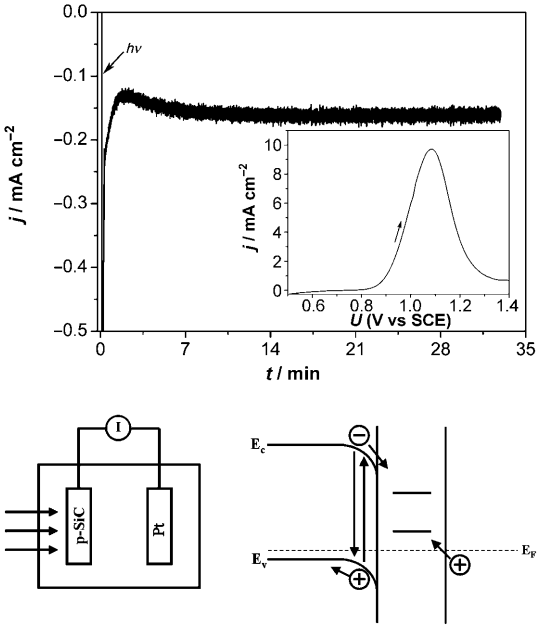

Figure 4. Top: Photocurrent–time plot recorded for a Pd-treated p-type SiC electrode in 0.3 M KOH solution. The light intensity was the same as for Figure 1. The stored hydrogen was subsequently oxidized by a potentiodynamic scan at 10 mV s^{-1} (inset). The limiting photocurrent for this measurement was 5.3 mA cm^{-2}. Bottom: Schematic representation of a galvanic cell (left) and the corresponding band-energy diagram (right).

time plot for a Pd-treated p-type SiC electrode short-circuited to a Pt counter electrode in 0.3 M KOH solution. The schematic representation of the experimental setup is also shown in Figure 4, together with the corresponding band-energy diagram. Upon illumination of the electrode, the current density peaks and stabilizes at a value of $-0.16\,\mathrm{mA\,cm^{-2}}$. The limiting photocurrent density under these conditions was $-5.3\,\mathrm{mA\,cm^{-2}}$. After 33 min, $315\,\mathrm{mC\,cm^{-2}}$ of charge had passed. The hydrogen was removed potentiodynamically (see inset of Figure 4). Hydrogen could be stored with an efficiency of 33 %. Similar results were found for the bare (nonmetalized) p-type SiC electrode. The short-circuit current density (j_{sc}) for the bare electrode was found to decrease with decreasing pH value on going to the acidic range. It is clear that the galvanic cell works best at high pH values.

Although these results are interesting in that they show the ability of SiC to split water, the band gap of 4H-SiC (E_g = 3.26 eV), like that of TiO_2, is too large to make the system practical for hydrogen production from solar radiation. In this respect, other polytypes should be considered. The absorption spectrum of 3C-SiC (E_g = 2.36 eV) corresponds much more favorably with the solar spectrum. Relatively little is known about the photoelectrochemical properties of this material. From the electrochemical experiments, it is clear that "bare" SiC is a poor catalyst for hydrogen evolution. The presence of a thin electrodeposited layer of Pd on p-type SiC was found to promote the hydrogen reaction. Results by Akikusa and Khan[19] indicate that Pt might be a better choice. They observed a positive shift of about 200 mV in the photocurrent onset potential with platinized p-type SiC. Effective catalysis of the hydrogen reaction will be essential for efficient water splitting at any type of SiC. The use of a two-compartment cell with electrolytes of different pH could, as in the case of TiO_2/Pt cell,[2] enhance quantum efficiency. The factors determining the efficiency with which hydrogen is stored in SiC are not well understood; further research is needed.

In galvanic cells used to split water, the hydrogen gas has to be collected. An attractive approach is to use a hydride-forming metal or alloy for this purpose.[25,26] Since such metals are generally very reactive, it is essential to "purify" the hydrogen beforehand by removing oxygen and water vapor, which are naturally present in an electrochemical environment. This is a tedious exercise. It would be very interesting if hydrogen, stored in SiC, could be transferred directly to such a metal or alloy. Provisional experiments have shown that hydrogen transfer may be possible. We have observed optical changes in a thin yttrium layer on p-type SiC when the semiconductor was loaded with hydrogen and also when the hydrogen was removed (see Figure 3 in the Supporting Information). Yttrium is one of a class of metals known as "switchable mirrors". The optical properties of the thin film, such as transparency, depend strongly on hydrogen content.[27]

Experimental Section

Single-crystal 4H-SiC (p- and n-type) and n-type 6H-SiC wafers with a polished Si-polar face were obtained from Cree (USA). The p-type wafer (4H) was oriented 8° off-axis, aluminum-doped, and had a resistivity of 3.86 Ω cm. The n-type wafers (4H and 6H) were oriented on-axis, nitrogen-doped, and had a resistivity in the range 0.06–0.07 Ω cm. Electrode preparation is described elsewhere.[20,21]

Electrochemical measurements were performed in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference.[20,21] UV light from a Hg arc-lamp (500W) was directed on to the sample using a dichroic mirror (280–400 nm) in combination with a planoconvex lens. The light intensity was varied with neutral-density filters.

It was essential to etch new samples anodically prior to use to remove the defect layer resulting from polishing and handling of the wafer. The details of electrochemical etching of n-type and p-type SiC are published elsewhere.[20,21,28]

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