

## Reduction of Peroxodisulfate at Porous and Crystalline Silicon Electrodes: An Anomaly

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Electroluminescence from n-type porous silicon can be generated in solution by reduction of peroxodisulfate. It has been assumed that the  $\text{SO}_4^{\bullet-}$  radical ion, formed in the first reduction step, injects a hole into the valence band of the porous semiconductor. The hole should subsequently undergo radiative recombination with a conduction band electron. Using two techniques, viz., photocurrent quantum efficiency measurements with p-type porous and crystalline silicon electrodes and minority carrier injection studies with the “transistor technique”, we found that the reduction of peroxodisulfate is, however, not always accompanied by hole injection. The silicon results are compared with results obtained on GaAs electrodes.

### Introduction

The strongly oxidizing  $\text{SO}_4^{\bullet-}$  radical, which is formed in the reduction of  $\text{S}_2\text{O}_8^{2-}$ , has been employed to generate electroluminescence from porous silicon.<sup>1,2</sup> The emission from n-type porous silicon electrodes in contact with an acidic solution containing  $\text{S}_2\text{O}_8^{2-}$  is efficient and in the visible region of the spectrum. One of the interesting aspects of the luminescence is the shift of the emission maximum to higher energies as the potential is scanned to negative values.<sup>3,4</sup> This was explained by assuming a size distribution of the light-emitting particles; smaller particles become active at more negative potentials.<sup>5</sup> Nonradiative Auger recombination was suggested to play an important role in the quenching of both the electroluminescence and the photoluminescence.<sup>6</sup>

Memming concluded that a two-step mechanism was involved in the reduction of peroxodisulfate ( $\text{S}_2\text{O}_8^{2-}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at GaP electrodes.<sup>7</sup> In the first step an electron is captured from the conduction band of the semiconductor and a radical intermediate is formed. Owing to the strong oxidizing properties of this radical, which has unoccupied energy levels corresponding to the valence band, holes are injected into the semiconductor. With a p-type semiconductor it is necessary to illuminate the electrode as electrons are needed in the first reduction step of  $\text{S}_2\text{O}_8^{2-}$ . Since the second step leads to hole injection, the number of charge carriers contributing to the current in the external circuit should be twice the number of photons absorbed by the semiconductor; this is referred to as a “quantum efficiency” of 2. Cathodic photocurrent doubling at p-type electrodes has been observed with GaP,<sup>7</sup> GaAs,<sup>8</sup> and SiC<sup>9</sup> in solutions containing peroxodisulfate. Van den Meerakker has reported photocurrent doubling at passivated p-type silicon electrodes in alkaline  $\text{H}_2\text{O}_2$  solutions at 70 °C.<sup>10</sup>

As the second step of the reduction of  $\text{S}_2\text{O}_8^{2-}$  involves hole injection into the valence band, it is possible to generate electroluminescence from n-type electrodes. The injected holes recombine with the electrons and, if this recombination is radiative, emission characteristic of the semiconductor is observed. Electroluminescence has previously been reported for a wide range of n-type semiconductor electrodes in  $\text{S}_2\text{O}_8^{2-}$  solutions, including SiC,<sup>9</sup> ZnO, CdS, GaP,<sup>11</sup> GaAs, and InP.<sup>12</sup>

Peroxodisulfate is one of a class of strong two-electron oxidizing agents which cause photocurrent doubling at p-type III–V semiconductors; examples include  $\text{H}_2\text{O}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{OCl}^-$ , and  $\text{OBr}^-$ .<sup>13–17</sup> For the reduction of some of these oxidizing

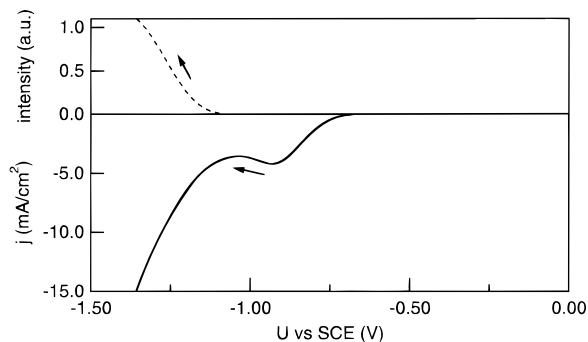
agents at p-type GaAs, a drop in quantum efficiency from 2 to 1 is observed as the surface electron concentration is increased at higher light intensity.<sup>18</sup> Since we suspected that a similar effect might be occurring with n-type silicon electrodes in peroxodisulfate solution and since such an effect could be important for the electroluminescence of n-type porous silicon, we decided to investigate the electrochemistry of silicon in acidic  $\text{S}_2\text{O}_8^{2-}$  solutions in detail. We compare the results with those obtained with GaAs. The photocurrent-doubling agents mentioned above also give rise to chemical etching of III–V semiconductors,<sup>13–17</sup> and a common reaction intermediate was postulated for both the reduction and etching reactions at GaAs. It therefore seemed interesting to compare the etching properties of silicon and GaAs in acidic  $\text{S}_2\text{O}_8^{2-}$  solutions. The outcome of both the current-doubling and etching experiments on silicon proved surprising.

### Experimental Section

Electrodes were made from phosphorus-doped n-type (1–10  $\Omega$  cm) and boron-doped p-type (1–15  $\Omega$  cm) single-crystal silicon wafers which had the (100) orientation. Crystalline silicon electrodes were dipped in a 1 M HF, 2 M  $\text{NH}_4\text{F}$  solution for 1 min before each measurement to remove surface oxides. Porous silicon electrodes were formed by anodic etching for 4 min at 35 mA  $\text{cm}^{-2}$  in a 1:1 mixture of 40% HF/ethanol, giving a 5  $\mu\text{m}$  thick porous layer. A two-electrode configuration with a Pt counter electrode was used. Anodization was performed under illumination at 0.4 V cell voltage for n-type and galvanostatically in the dark for p-type. The presence of the luminescent porous layer was checked by a photoluminescence measurement at an excitation wavelength of 354 nm. For the measurements on GaAs, p-type (100) samples with a doping density of  $10^{17}$   $\text{cm}^{-3}$  were used. Before each measurement the GaAs electrodes were etched for a few seconds in a 2%  $\text{Br}_2$  in methanol solution.

The electrochemical experiments were performed using a Bank POS273 Potentiostat in a conventional electrochemical cell containing a Pt counter electrode. A saturated calomel electrode (SCE) was taken as reference, except for the experiments involving HF solutions, where a Ag/AgCl electrode was used. All potentials are given with respect to SCE. The luminescence was measured with a Perkin-Elmer MPF-44B fluorescence spectrometer. For illumination of the electrodes a white light source (Schott KL1500) was used. The etch rate was determined by measuring the etched depth as a function of etching time using a Tencor Alpha-Step 500 surface profiler.

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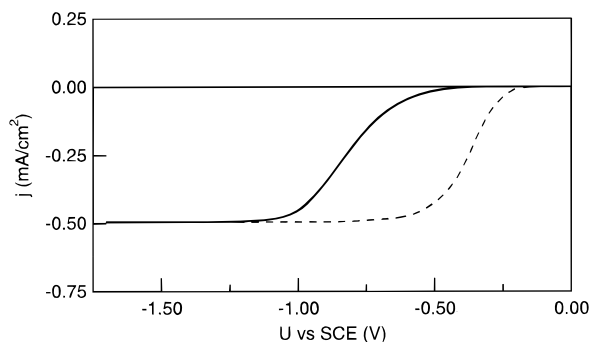
**Figure 1.** Potentiodynamic measurement of a stationary n-type porous silicon electrode in 0.1 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  aqueous solution. The current–potential curve is given by the solid line, while the dashed line represents the emission intensity at 650 nm as a function of the potential. The potential was scanned from  $-0.2$  to  $-1.5$  V at 50 mV/s.

We used the “transistor technique”<sup>19,20</sup> to determine whether the reduction of peroxodisulfate at n-type silicon electrodes proceeds via the conduction band (electron capture) or via the valence band (hole injection). The n-type surface of a silicon p–n junction was used as electrode; the junction was short-circuited. If the diffusion length is sufficiently long, holes injected into the valence band of the electrode will reach the p–n junction and a short-circuit current proportional to the hole injection current will be measured. Electron capture from the conduction band will not contribute to the short-circuit current.

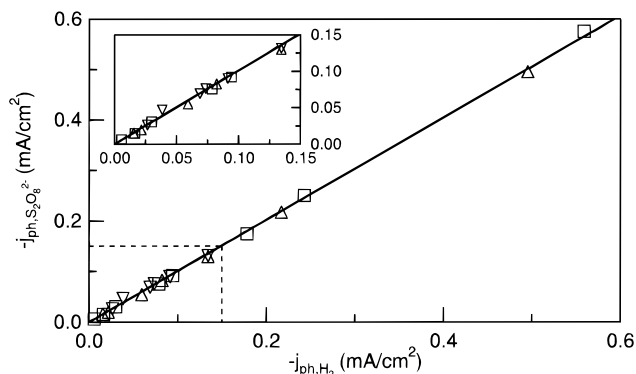
The samples we used in our experiments consisted of a 1  $\mu\text{m}$  thick silicon layer ( $10^{20}$   $\text{cm}^{-3}$  arsenic-doped) on a p-type silicon substrate ( $5 \times 10^{14}$   $\text{cm}^{-3}$  boron-doped) or a 1.6  $\mu\text{m}$  thick layer ( $2 \times 10^{19}$   $\text{cm}^{-3}$ ) on the same substrate. The p–n junction was made by arsenic diffusion into the substrate in a well-defined area masked by a 600 nm thick silicon dioxide layer. Both sides were contacted and insulated from the solution using adhesive PTFE (Teflon) tape. To calibrate the system, minority carriers were created near the surface by illuminating the sample from the n-type side using light with a large absorption coefficient. For 300 nm light (4.15 eV), the absorption coefficient is approximately  $1.8 \times 10^6$   $\text{cm}^{-1}$ ,<sup>21</sup> and holes are generated within 5.5 nm of the surface. Using such light, a considerable short-circuit current was measured, indicating that holes generated at the surface do indeed reach the p–n junction.

## Results

In Figure 1 the solid line gives the current–potential curve of a stationary n-type porous silicon electrode in 0.1 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  aqueous solution. The potential was scanned from  $-0.2$  to  $-1.5$  V at a rate of 50 mV/s. At potentials more negative than  $-0.7$  V a cathodic current is observed, which reaches a maximum at  $-0.9$  V. At potentials more negative than  $-1.1$  V the current increases sharply due to the evolution of hydrogen gas. During this potentiodynamic scan we also measured the electroluminescence at 650 nm from the porous silicon electrode as a function of the potential. The result is given by the dashed line in Figure 1. The emission intensity is very low at potentials more positive than  $-1.1$  V. Toward more negative values a strong increase of the light emission is observed. In this range the luminescence could be observed by the naked eye in broad daylight. For light of longer wavelength, the onset of emission was at slightly more positive potentials (e.g. at  $-1.0$  V for 800 nm light).<sup>3,6</sup> Current–potential characteristics similar to those described above for porous silicon electrodes were also found with crystalline silicon.



**Figure 2.** Potentiodynamic measurement of a stationary p-type porous silicon electrode under illumination in a 1 M  $\text{H}_2\text{SO}_4$  solution (solid line) and in a 0.05 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  solution (dashed line). The potential was scanned at 50 mV/s.

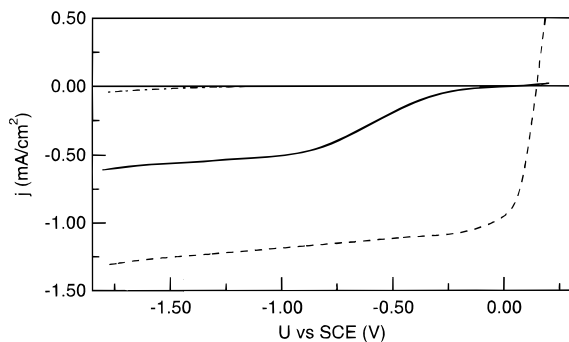


**Figure 3.** Limiting photocurrent for  $\text{S}_2\text{O}_8^{2-}$  reduction, measured at  $-1.5$  V in a 0.05 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  solution, as a function of the limiting photocurrent due to hydrogen evolution at p-type silicon electrodes at the same light intensity. In all cases the photon flux was smaller than the diffusion flux of  $\text{S}_2\text{O}_8^{2-}$ . Results were obtained using crystalline ( $\Delta$ ) and porous ( $\square$ ) electrodes in  $\text{H}_2\text{SO}_4$  solutions and in solutions containing 10 M HF ( $\nabla$ ). The inset is an enlargement of the indicated area.

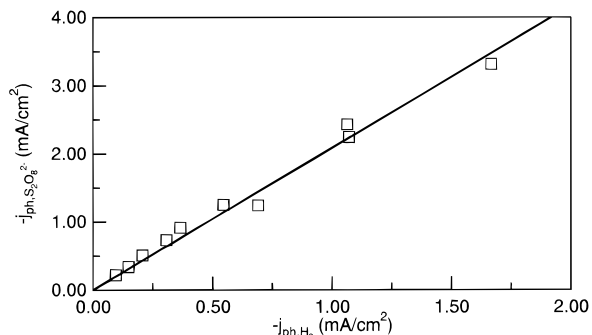
With these electrodes no visible emission could be detected, as expected.

Current–potential measurements using a p-type porous silicon electrode in 1 M  $\text{H}_2\text{SO}_4$  with and without  $\text{S}_2\text{O}_8^{2-}$  are shown in Figure 2. The potential was scanned from 0 to  $-1.7$  V at a rate of 50 mV/s. The dark current measured in both solutions was negligible. The solid line in Figure 2 was obtained under illumination in the  $\text{H}_2\text{SO}_4$  solution. At potentials more negative than  $-0.5$  V a cathodic photocurrent is observed due to the evolution of hydrogen gas. At potentials more negative than  $-1.1$  V the current reaches a limiting value, which is linearly dependent on the light intensity. The quantum efficiency, defined as the number of charge carriers measured in the external circuit per absorbed photon, is assumed to be 1 in this range. In the presence of 0.05 M  $\text{S}_2\text{O}_8^{2-}$  a limiting photocurrent was again observed. Although the onset of photocurrent is shifted considerably to more positive values, the limiting value is the same as when  $\text{S}_2\text{O}_8^{2-}$  is absent. The fact that no hydrogen evolution is observed indicates that the current is due to the reduction of  $\text{S}_2\text{O}_8^{2-}$ .

In Figure 3 the limiting photocurrent for the  $\text{S}_2\text{O}_8^{2-}$  reduction, measured at  $-1.5$  V, is plotted as a function of the limiting photocurrent due to hydrogen evolution at the same light intensity. Results were obtained using both crystalline ( $\Delta$ ) and porous ( $\square$ ) p-type silicon electrodes in 0.05 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  aqueous solution. During these measurements care was taken to ensure that the diffusion flux of  $\text{S}_2\text{O}_8^{2-}$  ions to the electrode surface always exceeded the photon flux. For this



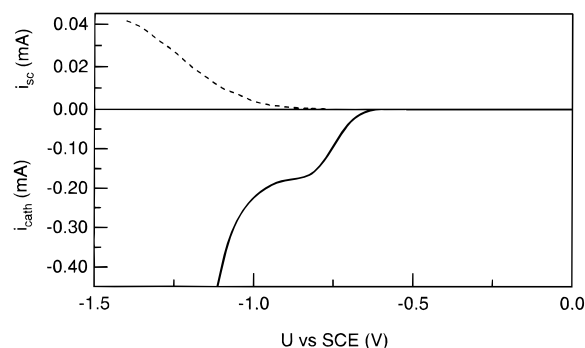
**Figure 4.** Potentiodynamic measurement of a rotating p-type GaAs electrode in the dark (dashed-dotted line) and under illumination in 1 M H<sub>2</sub>SO<sub>4</sub> (solid line) and 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> (dashed line). The electrode was rotated at 1000 rpm, and the potential was scanned at 50 mV/s.



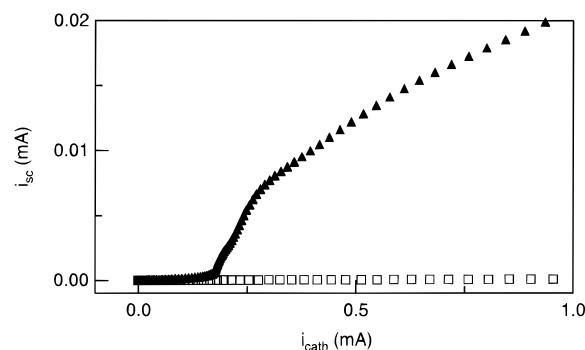
**Figure 5.** Limiting photocurrent for S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reduction, measured at -1.5 V in a 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution, as a function of the limiting photocurrent due to hydrogen evolution at a p-type GaAs electrode at the same light intensity. The electrode was rotated at 1000 rpm. The photon flux was smaller than the diffusion flux of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

purpose the electrode was rotated during measurements at higher photocurrent densities. To ensure that an oxide layer at the electrode surface was not influencing the photocurrent-potential characteristics, the same experiments were also performed in an S<sub>2</sub>O<sub>8</sub><sup>2-</sup> solution containing 10 M HF ( $\nabla$ ). A linear fit to all these points yields a straight line with a slope of 1, indicating that the quantum efficiency for the reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is 1, as for the hydrogen evolution.

For comparison we performed similar experiments using GaAs. In Figure 4 the current-potential curve of a p-type electrode is shown. The potential was scanned from 0.2 to -1.8 V at a rate of 50 mV/s, while the electrode was rotated at 1000 rpm. The rather small dark current in 1 M H<sub>2</sub>SO<sub>4</sub> is given by the dashed-dotted line. The current under illumination is given by the solid line. At potentials more negative than -0.25 V a cathodic current due to hydrogen evolution is observed. At -1.0 V the current reaches a limiting value which is directly proportional to the light intensity. As for p-type silicon, we assume that the quantum efficiency is 1 in this range. After addition of 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup> the dashed curve in Figure 4 is obtained. At 0.1 V the cathodic current increases rapidly to a limiting value, which is again proportional to the light intensity. The limiting photocurrent is approximately twice as high as in the absence of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at the same light intensity. It is clear that the cathodic current is due to the reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, as no hydrogen gas is evolved. Figure 5 shows the limiting photocurrent for reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at -1.5 V as a function of the hydrogen photocurrent at the same light intensity. In all cases the photon flux was smaller than the diffusion flux of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions to the electrode surface. The solid line is a linear fit to the data and has a slope close to 2, which indicates that the quantum efficiency for the reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is 2 over



**Figure 6.** Potentiodynamic measurements of an n-type silicon electrode with a short-circuited p-n junction in a 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution. The cathodic current and the short-circuit current are given by the solid line and the dashed line, respectively. The potential was scanned at 50 mV/s.



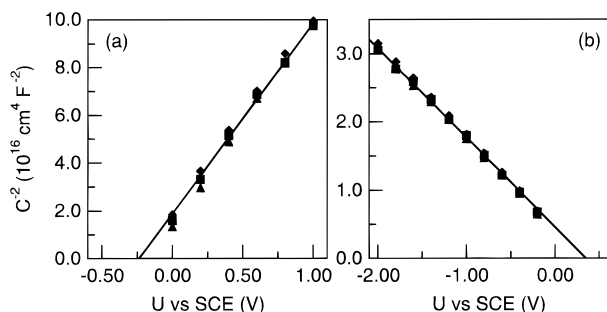
**Figure 7.** Short-circuit current as a function of the cathodic current in 1 M H<sub>2</sub>SO<sub>4</sub> ( $\square$ ) and in a 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution ( $\blacktriangle$ ).

the whole range of light intensity. Similar results were obtained in solutions containing 0.1 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and 10 M HF; we found a photocurrent enhancement factor of 2.

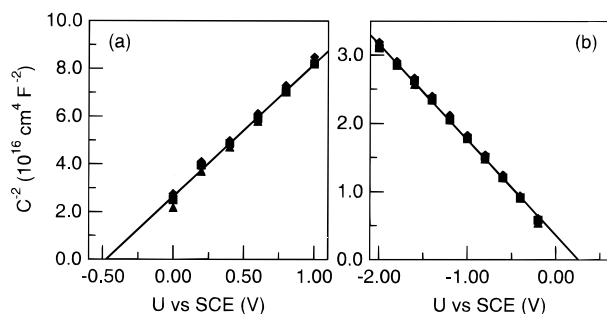
For the etching experiments part of the semiconductor wafer was masked and the etched depth was measured as a function of the etching time. The result for GaAs in a 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution yields an etch rate of approximately 44 nm/min, which is similar to that of GaAs in a 0.05 M H<sub>2</sub>O<sub>2</sub> solution. It is, perhaps, not strange that silicon does not dissolve in a 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution because of the insolubility of the dissolution products. However, to our surprise we found that even in a 10 M HF etchant the etch rate was only 0.2 nm/min, a value comparable to that of silicon in HF solutions without S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

When the electrode potential of the n-type face of the p-n junction in 1 M H<sub>2</sub>SO<sub>4</sub> is scanned toward negative values at which proton reduction takes place, a very low short-circuit current  $i_{sc}$  is found, as expected for conduction band processes. After addition of 0.05 M S<sub>2</sub>O<sub>8</sub><sup>2-</sup> we obtained the result shown in Figure 6. The current-potential curve has features similar to those shown in Figure 1. When the potential is scanned to negative values the reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> starts at -0.65 V, while at potentials more negative than -1.1 V proton reduction leads to a strongly increasing cathodic current. The corresponding short-circuit current is also given in Figure 6 by the dashed line. It is striking that, while S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is being reduced at a significant rate at potentials between -0.75 and -1.0 V, only a small short-circuit current is found of the same order of magnitude as the current through the diode in H<sub>2</sub>SO<sub>4</sub> solutions without S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. At more negative potentials a significant increase in  $i_{sc}$  is measured as the cathodic current increases rapidly due to hydrogen evolution.

In Figure 7  $i_{sc}$  is plotted as a function of the cathodic current  $i_{cath}$  measured at the same potential in solutions containing only



**Figure 8.** Mott–Schottky plots of n-type (a) and p-type (b) crystalline silicon in 1 M  $\text{H}_2\text{SO}_4$  solution. Measuring frequencies were 2.2 kHz (▲), 7.0 kHz (■), and 22.1 kHz (◆).



**Figure 9.** Mott–Schottky plots of n-type (a) and p-type (b) crystalline silicon in 0.1 M  $\text{S}_2\text{O}_8^{2-}$ , 1 M  $\text{H}_2\text{SO}_4$  solution. Measuring frequencies were 2.2 kHz (▲), 7.0 kHz (■), and 22.1 kHz (◆).

$\text{H}_2\text{SO}_4$  (□) and in solutions with  $\text{S}_2\text{O}_8^{2-}$  (▲). It is clear that at small values of  $i_{\text{cath}}$ , corresponding to the potential range between  $-0.2$  and  $-1.0$  V,  $i_{\text{sc}}$  is very small in both solutions. When hydrogen is evolved at more negative potentials, the cathodic current in both solutions increases. The short-circuit current in  $\text{H}_2\text{SO}_4$  solutions remains very small, while in  $\text{S}_2\text{O}_8^{2-}$  solutions it increases strongly as the cathodic current becomes larger. As mentioned above, the short-circuit current is a measure of the number of holes which are injected into the valence band of the n-type silicon. From Figure 7 we conclude that, in solutions containing  $\text{S}_2\text{O}_8^{2-}$ , a significant hole injection current is found only at more negative potentials.

To estimate the position of the silicon band edges with respect to the energy levels in solution, we performed Mott–Schottky measurements using both n-type and p-type crystalline silicon electrodes. The results obtained in 1 M  $\text{H}_2\text{SO}_4$  solution are given in Figure 8. The intercept of a linear fit through the data yields flat band potentials of  $-0.25$  and  $0.35$  V for n-type and p-type silicon, respectively. These values are in agreement with results obtained by Madou *et al.*<sup>22</sup> When  $\text{S}_2\text{O}_8^{2-}$  (0.1 M) was added to the solution, the results shown in Figure 9 were obtained. Flat band potentials of  $-0.45$  and  $0.25$  V for n-type and p-type silicon, respectively, indicate only a small shift of the band edges due to the presence of  $\text{S}_2\text{O}_8^{2-}$ . The band edges estimated from these results are  $E_{\text{CB}} = -0.60$  eV and  $E_{\text{VB}} = 0.55$  eV. If we consider the standard redox potential of the  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$  couple (1.72 V vs SCE<sup>23</sup>), a large overlap of the acceptor states in solution with the silicon valence band states can be expected.

## Discussion

As mentioned in the Introduction, the electrochemistry of semiconductor electrodes in the presence of oxidizing agents causing photocurrent multiplication has been studied extensively. In particular, the III–V materials have been investigated,<sup>7,24</sup> with p-type GaAs receiving most attention. For the oxidizing agents showing photocurrent doubling at p-type GaAs a distinction has

to be drawn between two classes.<sup>18</sup> For the first, of which  $\text{H}_2\text{O}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$  are representative, the dark current at the p-type electrode is low; hole injection is not important. Under illumination a quantum efficiency of 2 is observed up to high photon flux.<sup>14,15</sup> When the photon flux exceeds the diffusion flux of the oxidizing agent, hydrogen is evolved at negative potentials.<sup>18</sup> Our results show that the p-GaAs/ $\text{S}_2\text{O}_8^{2-}$  system pertains to this class.

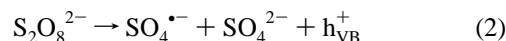
The oxidizing agents of the second class, which includes  $\text{OCl}^-$  and  $\text{OBr}^-$ ,<sup>16,17</sup> show some dark current, indicating that a limited hole injection occurs. When the photon flux exceeds the diffusion flux of the oxidizing agent in this case, hydrogen evolution is not observed at negative potentials. Instead the quantum efficiency for reduction of the oxidizing agent decreases from 2 to 1, before water begins to be reduced.<sup>18</sup> The reduction of  $\text{IO}_3^-$  in alkaline<sup>18</sup> and acidic<sup>25</sup> solutions is, in this respect, even more striking. At low light intensity a quantum efficiency close to 6 is observed, which drops to 1 as the photon flux is increased.

Such results involving variable quantum efficiencies and quantum efficiencies dependent on the photon flux have been interpreted in terms of electroactive species (reactants and intermediates), which are adsorbed on the semiconductor surface. These give rise to surface states with energy levels in the band gap. Such states can either capture an electron from the conduction band or inject a hole into the valence band. The rate of electron capture from the conduction band is determined by the rate constant  $k_n$  for electron capture and the surface electron concentration  $n_s$ . Hole injection from the surface state into the valence band is a thermally activated process, the rate of which depends on the rate constant  $k_p$ . If at low light intensities  $k_p$  is larger than the product  $k_n n_s$ , hole injection will prevail over electron capture. When the photon flux is increased,  $n_s$  becomes larger and electron capture from the conduction band may become the predominant process, leading to a decrease of the photocurrent quantum efficiency.

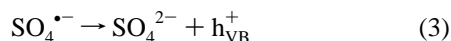
The measurements in both  $\text{H}_2\text{SO}_4$  and HF electrolytes show unequivocally that  $\text{S}_2\text{O}_8^{2-}$  does not inject holes into the valence band of porous and nonporous p-type silicon, either in the dark or under illumination (Figures 2 and 3). This is in clear contrast to what we find with p-type GaAs, which shows a quantum efficiency of 2 in a wide range of light intensity. Photocurrent doubling was also not observed with p-type silicon in  $\text{Br}_2/\text{HF}$  solutions.<sup>26</sup> In contrast to what van den Meerakker reported for passivated p-type silicon in alkaline solutions,<sup>10</sup> we have also found that  $\text{H}_2\text{O}_2$  does not cause photocurrent doubling in acidic ( $\text{H}_2\text{SO}_4$  or HF) medium. The results found with the n-type electrode of the p–n junction also show that the significant dark current observed before onset of hydrogen evolution does not involve hole injection from  $\text{S}_2\text{O}_8^{2-}$  (Figure 7). We must conclude that the reduction of  $\text{S}_2\text{O}_8^{2-}$ , like that of  $\text{Br}_2$ , occurs exclusively via the conduction band of the semiconductor:



This is very surprising. On the basis of the band edge positions estimated from flat band potentials (Figures 9 and 10) one might expect hole injection for the first step,



considering the strongly positive redox potential of the  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$  couple.<sup>23</sup> One would certainly expect hole injection for the second step,



since the  $\text{SO}_4^{\bullet-}$  radical anion is a powerful oxidizing agent. While oxide formation might hinder charge transfer in the case of  $\text{H}_2\text{SO}_4$  solutions, the results obtained with HF precludes such an effect; silicon oxides are highly soluble in HF solutions.<sup>27</sup> In addition, conduction band reactions are obviously not hindered in either solution. These results force us to conclude that both  $\text{S}_2\text{O}_8^{2-}$  and  $\text{SO}_4^{\bullet-}$  undergo a strong interaction with the silicon surface. The resulting surface species can obviously accept electrons from the conduction band but cannot inject holes into the valence band. While GaAs is chemically dissolved at a significant rate in acidic  $\text{S}_2\text{O}_8^{2-}$  solutions, silicon is not etched. The presence of a strongly adsorbed peroxodisulfate species on silicon might explain the absence of etching in such solutions. Since holes are not injected into silicon, electroless etching is not expected. If the surface is blocked by an adsorbed species, chemical etching by  $\text{S}_2\text{O}_8^{2-}$  is also prevented. In contrast to the present results, both (100) and (111) silicon surfaces are chemically etched in  $\text{Br}_2/\text{HF}$  solutions at a diffusion-controlled rate.<sup>26,28</sup> In addition, a considerable anodic current is observed with n-type silicon in  $\text{Br}_2/\text{HF}$  solution under etching conditions, indicating electron injection into the conduction band from surface state intermediates of the dissolution reaction. A similar result has been reported for GaAs.<sup>14,15</sup> The absence of both etching and electron injection in the silicon/ $\text{S}_2\text{O}_8^{2-}$  case indicates surface intermediates different from those formed on silicon in  $\text{Br}_2$  solution<sup>26</sup> and on GaAs with various photocurrent doubling agents.<sup>13-18</sup>

It is clear that considerable hole injection does occur at n-type electrodes at potentials at which hydrogen is evolved (see Figures 6 and 7). The observation of electroluminescence from porous n-type silicon in the same potential range also indicates hole injection from  $\text{S}_2\text{O}_8^{2-}$ . It is tempting to link the change in the mechanism of  $\text{S}_2\text{O}_8^{2-}$  reduction to the hydrogen reaction. One could envisage two possible effects. The adsorption of hydrogen formed in the reduction of protons might prevent the adsorption of  $\text{S}_2\text{O}_8^{2-}$  and/or its intermediate, thus allowing hole injection from nonadsorbed electroactive species. Alternatively, hydrogen (either atomic or molecular) might react with  $\text{S}_2\text{O}_8^{2-}$ , generating an  $\text{SO}_4^{\bullet-}$  radical, which could inject a hole into the valence band before it can adsorb. These suggestions are, of course, speculative.

## Conclusions

In contrast to what has been observed with other semiconductors, we found that the reduction of  $\text{S}_2\text{O}_8^{2-}$  at porous and crystalline silicon electrodes is not always accompanied by hole injection into the valence band. No enhancement of the photocurrent was found with p-type electrodes, indicating that hole injection does not take place. Using the transistor technique, we also did not observe significant hole injection at n-type electrodes in the potential range in which only peroxodisulfate is reduced. Considering the standard redox potential of the  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$  couple with respect to the band edges, this is surprising. In contrast to GaAs, silicon is not chemically etched by  $\text{S}_2\text{O}_8^{2-}$ , even in solutions containing 10 M HF. These results lead us to conclude that  $\text{S}_2\text{O}_8^{2-}$  and  $\text{SO}_4^{\bullet-}$  form on silicon

adsorbed species which can only accept electrons from the conduction band of the semiconductor. Such adsorbed species must block the surface, preventing chemical etching by  $\text{S}_2\text{O}_8^{2-}$ . At more negative potentials at which hydrogen is evolved, hole injection was found with n-type electrodes. The occurrence of electroluminescence from porous n-type silicon in this range also indicates hole injection. The reason for the change in the mechanism of reduction of  $\text{S}_2\text{O}_8^{2-}$  is not clear.

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