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# Hole Injection at the Silicon/Aqueous Electrolyte Interface: A Possible Mechanism for Chemiluminescence from Porous Silicon

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## ABSTRACT

The reduction mechanism of oxidizing agents at silicon and porous silicon electrodes has been investigated in relation to light emission from the porous semiconductor. Oxidizing agents with a positive redox potential are shown to inject holes into HF-pretreated silicon. However, as the degree of oxide formation on the electrode surface increases, reduction by electron capture from the conduction band becomes important. Holes can be injected from  $H_2O_2$  when the intermediate  $OH^\bullet$  radical is formed chemically in solution; electrochemical reduction of  $H_2O_2$  generally does not involve the valence band. Hole injection at the open-circuit potential for certain oxidizing agents at porous silicon electrodes results in visible luminescence with characteristics similar to those of the emission observed during anodic oxidation in indifferent electrolyte. A mechanism similar to that proposed for anodic luminescence is suggested.

## Introduction

The open-circuit etching of silicon is of considerable technological importance. An interesting class of etchants is based on strong oxidizing agents in aqueous HF solution. The oxidizing agents may be reduced by extracting electrons from the valence band of silicon (injecting holes into the semiconductor); this is the case for "electroless" etchants with  $IrCl_6^{2-}$ ,  $MnO_4^-$ ,  $HNO_3$ ,  $^{2,5}$  and  $CrO_3$ .<sup>6,7</sup> Alternatively, a purely chemical reaction between the oxidizing agent and the silicon surface bonds may be responsible for dissolution of the semiconductor; the "chemical" etching of silicon in  $Br_2/HF$  solutions is an example.<sup>8,9</sup> It is clear that the mechanism of these reduction reactions is, in general, quite complex.

Little attention has been paid to the reduction reactions of oxidizing agents in HF-free aqueous solutions. The reason for this is obvious: hole injection leads to the formation of oxide on silicon, thus hampering kinetic studies. The current interest in visible luminescence from porous silicon electrodes has led to renewed interest in redox chemistry at silicon surfaces. Meulenkamp et al.<sup>10</sup> studied the electrochemistry of porous silicon in contact with various oxidizing agents. With n-type porous silicon in  $Ce^{4+}$  solutions the reduction current was diffusion controlled. With p-type electrodes, however, a much lower current was found in the dark. Two current plateaus were reported, one of which was sensitive to illumination. In  $S_2O_8^{2-}$  solutions similar current-potential curves were measured, although the reduction current at p-type porous silicon was considerably smaller than in the case of  $Ce^{4+}$ . The current-potential characteristics of porous silicon in  $H_2O_2$ ,  $NO_3^-$ , and  $MnO_4^-$  solutions resembled those obtained in indifferent electrolyte solutions. The importance of surface oxides was not considered.

Strong visible electroluminescence has been observed from n-type porous silicon in  $S_2O_8^{2-}$  and  $H_2O_2$  solution.<sup>10-12</sup> Radiative recombination of holes (minority carriers), injected during the reduction of these species, with electrons (majority carriers) was assumed to be responsible for the visible emission. Only weak electroluminescence was found in  $Ce^{4+}$ ,  $NO_3^-$ , and  $MnO_4^-$  solutions. Recently we described an anomaly in the reduction of peroxodisulfate and peroxide at crystalline and porous silicon electrodes; reduction

is generally not accompanied by hole injection into the valence band.<sup>13</sup> With p-type silicon, the absence of photocurrent enhancement indicated that the reduction of  $S_2O_8^{2-}$  and  $H_2O_2$  occurs exclusively by electron capture from the conduction band. With n-type electrodes no hole injection was observed in the potential range where only peroxodisulfate is reduced. However, at more negative potentials where hydrogen gas is evolved, a considerable valence band current was measured.

Meulenkamp et al.<sup>10</sup> showed that  $Ce^{4+}$  and  $MnO_4^-$  give rise to strong visible luminescence from porous silicon at open-circuit potential, while  $S_2O_8^{2-}$ ,  $H_2O_2$ , and  $HNO_3$  (0.1 M solution) give only very weak or no emission. In analogy with results of siloxene<sup>14-19</sup> the emission was attributed to chemiluminescence.<sup>10</sup> McCord et al.<sup>20</sup> had previously reported similar weak chemiluminescence from porous silicon in concentrated (4 M)  $HNO_3$  solution and in  $S_2O_8^{2-}$  solution.

In this work the redox chemistry at the silicon/aqueous electrolyte interface was studied with a view to elucidating the mechanism of chemiluminescence from porous silicon. First, the kinetics of simple one-electron oxidizing agents ( $IrCl_6^{2-}$ ,  $Ce^{4+}$ ,  $Fe(CN)_6^{3-}$ ,  $Fe^{3+}$ ) are considered. More complex redox systems such as  $MnO_4^-$  and  $HNO_3$  are then briefly described. We show that reduction of  $H_2O_2$  can lead to hole injection into p-type silicon when the  $OH^\bullet$  radical is formed in solution by a chemical reaction, but not by photoelectrochemical reduction of  $H_2O_2$ . The results are discussed in terms of the energetics of the redox system with respect to the position of the semiconductor band-edges. Strong visible chemiluminescence is observed from porous silicon in solutions containing  $IrCl_6^{2-}$ ,  $Ce^{4+}$ , and  $MnO_4^-$ . On the basis of the results obtained with  $Ce^{4+}$ , which show a strong similarity to those of anodic luminescence from porous silicon in indifferent electrolyte solution,<sup>21-24</sup> we propose a mechanism for chemiluminescence.

## Experimental

Electrodes were cut with a diamond saw from n-type (1–10  $\Omega$  cm) and p-type (1–15  $\Omega$  cm) single-crystal silicon wafers which had (100) orientation. Crystalline silicon electrodes were dipped in a 1 M HF/2 M  $NH_4F$  solution for 1 min before each measurement to remove surface oxides. Porous silicon electrodes were formed by anodic etching for 10 min at 35 mA/cm<sup>2</sup> in a 1:1 mixture of 40% HF:ethanol. A two-electrode configuration with a Pt counter

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electrode was used. Anodization was performed under illumination at 0.5 V cell voltage for n-type and galvanostatically in the dark for p-type samples. Before and after each measurement the presence of the luminescent porous layer was checked by a photoluminescence measurement at an excitation wavelength of 354 nm.

The surfaces of HF-pretreated crystalline and as-etched porous silicon are hydride terminated.<sup>25,26</sup> For most of the measurements performed in this work, very strong oxidizing agents were used. In these cases the surface hydride layer is very likely chemically oxidized, giving a superficial oxide layer. IR measurements on the n-type porous silicon/peroxodisulfate system confirm this.<sup>27</sup> When the oxidizing agent injects holes into the semiconductor and the surface hole concentration is large, thicker oxide layers are formed (see Results).

Electrochemical experiments were performed using an EG&G Princeton Applied Research 366A bipotentiostat in a conventional electrochemical cell containing a Pt counter electrode and a saturated calomel electrode (SCE) as reference. All potentials are given with respect to SCE. Unless otherwise stated the potential was scanned at 10 mV/s. The electrode surface was defined using an O-ring in a polychlorotrifluoroethylene (Kel-F) holder; the exposed area was 0.38 cm<sup>2</sup>. The luminescence was measured using an Oriel Instaspec IV CCD detection system. For illumination of the electrodes a white light source (Schott KL1500) was used. All measurements were carried out at room temperature. The chemicals were of p.a. grade (Merck).

## Results

**Hole injection into silicon.**—In Fig. 1 the limiting cathodic current of a p-type silicon electrode negatively biased in a 5 mM IrCl<sub>6</sub><sup>2-</sup>, 1 M KCl solution (pH 2–3) is shown as a function of the square root of the rotation rate. The current-potential curve is shown in the inset. From the linear relation between  $j$  and  $\omega^{1/2}$  it can be concluded that the reduction is diffusion controlled; the slope of the linear fit is proportional to the IrCl<sub>6</sub><sup>2-</sup> concentration in solution. The fact that a cathodic current is observed at a p-type semiconductor in the dark indicates that holes are injected into the valence band during the reduction of IrCl<sub>6</sub><sup>2-</sup>.

The rotation rate dependence of the limiting cathodic current of a p-type silicon electrode in a 10 mM Ce<sup>4+</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution is shown in Fig. 2. The inset shows the current-potential curve. Again, a considerable cathodic current is measured in the dark due to hole injection during the reduction of Ce<sup>4+</sup>. From the linear Koutecky-Levich plot ( $j^{-1}$  vs.  $\omega^{-1/2}$ ) it is clear that the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> is under mixed kinetic/diffusion control. When the electrode is first immersed in the solution at open circuit, the limiting kinetic current  $j_{\text{kin}}$ , obtained by extrapolating to  $\omega^{-1/2} = 0$ , decreases. Clearly, the surface becomes oxidized, which leads to a decrease in the rate constant for hole

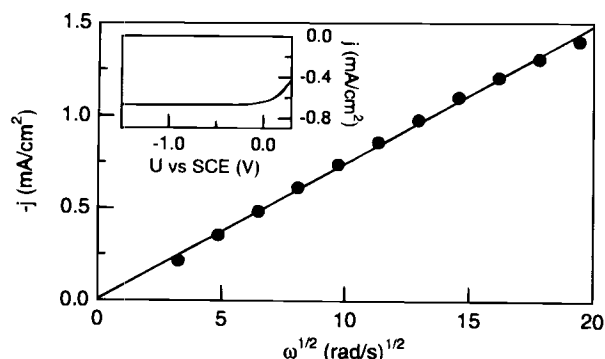


Fig. 1. Levich plot ( $j$  vs.  $\omega^{1/2}$ ) for p-type crystalline silicon in 5 mM IrCl<sub>6</sub><sup>2-</sup>, 1 M KCl (pH 2–3) solution ( $U_{\text{appl}} = -1.0$  V vs. SCE). The inset shows the dark current-potential curve at 900 rpm.

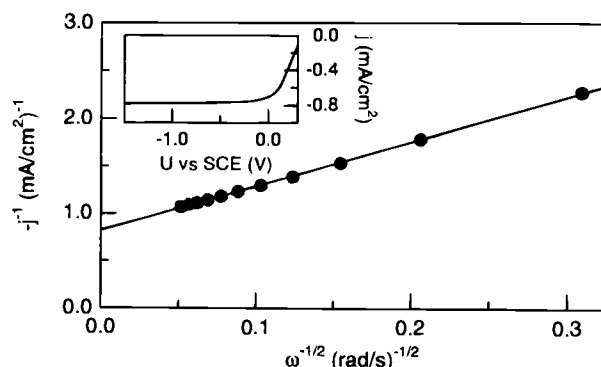


Fig. 2. Koutecky-Levich plot ( $j^{-1}$  vs.  $\omega^{-1/2}$ ) for p-type crystalline silicon in a 10 mM Ce<sup>4+</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution ( $U_{\text{appl}} = -1.0$  V vs. SCE). The inset shows the dark current-potential curve at 900 rpm.

injection. A similar effect, although less pronounced, was found with IrCl<sub>6</sub><sup>2-</sup>. Illumination of the silicon electrode, oxidized at the open-circuit potential, gives photocurrent. With increasing degree of oxidation the effect of illumination on the cathodic reduction current becomes more pronounced; electron capture from the conduction band becomes more important in the reduction reaction.

With Fe(CN)<sub>6</sub><sup>3-</sup> a small cathodic current is measured at negative potentials (Fig. 3). As shown in Fig. 3, illumination of the silicon electrode has a marked effect on the cathodic current, which indicates that the reduction of Fe(CN)<sub>6</sub><sup>3-</sup> involves electron capture from the conduction band. This can indeed be expected on the basis of the relative position of the bandedges and energy levels of the redox system (see Discussion). As in the case of Fe(CN)<sub>6</sub><sup>3-</sup>, a very small reduction current is also found with a p-type silicon electrode in the dark in a solution containing Fe<sup>3+</sup>; under illumination Fe<sup>3+</sup> is readily reduced.

With oxide-free p-type silicon electrodes a significant hole injection current is found in acidic solutions containing MnO<sub>4</sub><sup>-</sup> (0.25 mA/cm<sup>2</sup> for a stationary electrode in a 10 mM MnO<sub>4</sub><sup>-</sup>, 1 M H<sub>2</sub>SO<sub>4</sub> solution). The reduction of HNO<sub>3</sub>, on the other hand, gives a negligibly small current. With high HNO<sub>3</sub> concentration (>4 M) hole injection is found although the current is considerably smaller than in the case of MnO<sub>4</sub><sup>-</sup>.

One would expect photocathodic reduction of H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at p-type silicon to give strongly oxidizing radical intermediates (OH<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>). According to Memming<sup>28</sup> the redox potentials of the H<sub>2</sub>O<sub>2</sub>/OH<sup>•</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/SO<sub>4</sub><sup>•-</sup> couples are very positive ( $\geq 3.16$  V and  $\geq 2.66$  V vs. SCE, respectively). Nevertheless, the radical intermediates are not further reduced by hole injection into the valence band of the semiconductor.<sup>13</sup> This striking effect was attributed

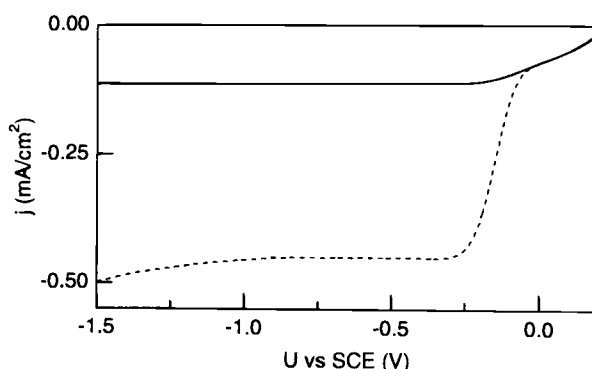
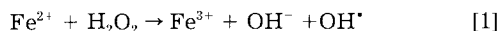


Fig. 3. Current-potential curve of a rotating p-type crystalline silicon electrode in 10 mM Fe(CN)<sub>6</sub><sup>3-</sup>, 1 M KCl (pH 2–3) solution (—) in the dark and (---) under illumination. The electrode was rotated at 900 rpm.

to a strong interaction of the  $\text{OH}^\bullet$  or  $\text{SO}_4^{\bullet-}$  intermediate with the silicon surface, giving rise to surface states in the bandgap. If this is the case, hole injection might be expected when the radical intermediate is formed in solution rather than electrochemically at the surface.

The hydroxyl radical can be generated chemically in solution via the Fenton reaction<sup>29,30</sup>



As mentioned above, reduction of  $\text{Fe}^{3+}$  at silicon electrodes takes place via electron capture from the conduction band



For p-type silicon this requires illumination of the semiconductor. With  $\text{Fe}^{3+}$  in solution, the photogenerated electron is consumed in the reduction reaction 2, while the hole contributes to the current measured in the external circuit; the photocurrent "quantum efficiency" is one. When  $\text{H}_2\text{O}_2$  is added to the solution the  $\text{Fe}^{2+}$ , electrochemically formed (reaction 2), may react with the peroxide. The "free" hydroxyl radical generated by reaction 1 could inject a hole into the valence band. When this happens more than one charge carrier is expected for each absorbed photon; this corresponds to a quantum efficiency higher than one. Of course, it is essential that the electrochemical reduction of  $\text{Fe}^{3+}$  is favored with respect to  $\text{H}_2\text{O}_2$  reduction. If this were not the case then peroxide would be reduced electrochemically and results similar to those without  $\text{Fe}^{3+}$ <sup>13</sup> would be expected. In Fig. 4 the photocurrent of a rotating p-type silicon electrode, polarized at  $-1.0$  V, in a  $10$  mM  $\text{Fe}^{3+}$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution with  $0.1$  M  $\text{H}_2\text{O}_2$  (filled circles) is shown as a function of the photocurrent at the same light intensity in a solution without  $\text{H}_2\text{O}_2$ . As a reference, results obtained with  $\text{H}_2\text{O}_2$  but without  $\text{Fe}^{3+}$  in solution are given by the open circles; the dashed line has a slope of 1. From the linear fit (the solid line in Fig. 4) a photocurrent quantum yield of 1.6 is obtained. Generally, quantum efficiencies between 1.2 and 1.6 were found, indicating that holes are indeed injected. Several reasons can be mentioned why values lower than 2 were found. There may be competition between reduction of  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ ; the direct, electrochemical reduction of  $\text{H}_2\text{O}_2$  will, as mentioned before, not lead to hole injection. It is also possible that the  $\text{OH}^\bullet$  radical is reduced chemically by  $\text{Fe}^{2+}$  before it injects a hole; this would again reduce the quantum yield. Finally, the  $\text{OH}^\bullet$  radical formed in solution may diffuse away from the electrode surface before injecting a hole.

**Chemiluminescence from porous silicon.**—When a porous silicon electrode is immersed in a solution containing the strong oxidizing agents  $\text{Ce}^{4+}$ ,  $\text{MnO}_4^-$ , or  $\text{IrCl}_6^{2-}$ , visible chemiluminescence is observed. The intensity of the emission is lower than what is generally observed during reduction of

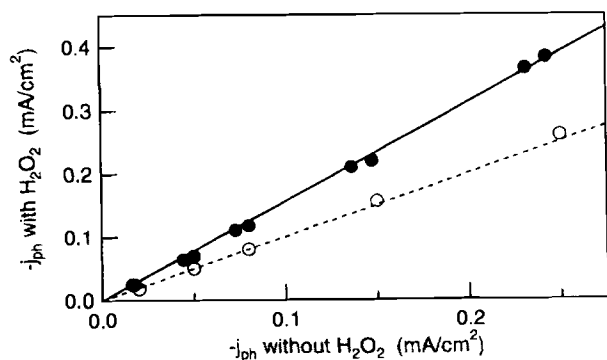


Fig. 4. Photocurrent of a rotating p-type crystalline silicon electrode in a  $10$  mM  $\text{Fe}^{3+}$ ,  $0.1$  M  $\text{H}_2\text{O}_2$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution as a function of the photocurrent of the same electrode in a  $10$  mM  $\text{Fe}^{3+}$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution measured at various light intensities. The open circles represent results obtained in a similar way without  $\text{Fe}^{3+}$  present in solution. The applied potential was  $-1.0$  V. The electrode was rotated at  $2500$  rpm.

peroxodisulfate or during anodic oxidation. However, the luminescence can still be observed by the naked eye in subdued light. The emission spectrum measured under open-circuit conditions in a  $0.1$  M  $\text{Ce}^{4+}$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution is given in Fig. 5a. Similar to the results of Meulenkamp et al.,<sup>10</sup> a broad emission peak is found with  $\lambda_{\text{max}}$  at around  $720$  nm.  $\lambda_{\text{max}}$  shifts to the blue with time. This is illustrated in Fig. 5b and c which shows the time dependence of the emission intensity on the flanks of the emission band. For low emission energy ( $790$  nm) the intensity passes through a maximum at shorter times than for the higher energy ( $650$  nm). Additionally, the emission intensity decreases to undetectable levels, typically within  $10$ – $15$  min. This is similar to what has been reported for emission during anodic oxidation of porous silicon in indifferent electrolyte solution.<sup>10,21–24</sup> In that case the transient nature of the emission was attributed to the fact that the surface gradually becomes oxidized to such an extent that current flow is hindered. The blue-shift was ascribed to the selective excitation of particles of different size. As the barrier for hole transfer is smallest for the largest, bulk-like regions which have an effective bandgap similar to bulk silicon, these regions will be oxidized first giving longer wavelength emission. As oxidation proceeds, current flow to such regions is hindered and holes are injected into smaller, more confined crystallites, which results in a blue-shift of the luminescence.

In Fig. 6 the current-potential and emission-potential curves of a p-type porous silicon electrode in a  $0.1$  M  $\text{Ce}^{4+}$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution are shown. The current-potential curve resembles that given in the insert of Fig. 2, which was obtained using crystalline silicon; at potentials below  $0$  V a constant cathodic current is measured in the dark. As the porous electrode was not rotated, the current density is lower in Fig. 6b, despite the higher  $\text{Ce}^{4+}$  concentration. Nevertheless, the fact that a considerable cathodic current is found with p-type material in the dark again indicates that holes are injected during the reduction of  $\text{Ce}^{4+}$ . At

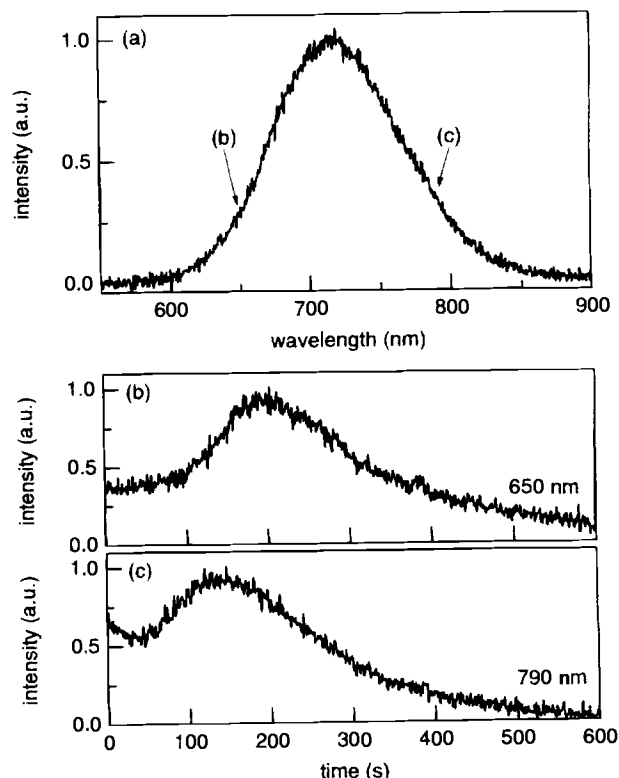


Fig. 5. (a) Emission spectrum of a p-type porous silicon electrode in a  $0.1$  M  $\text{Ce}^{4+}$ ,  $1$  M  $\text{H}_2\text{SO}_4$  solution at the open-circuit potential. (b,c) Time evolution of the emission intensity at  $650$  and  $790$  nm, respectively.

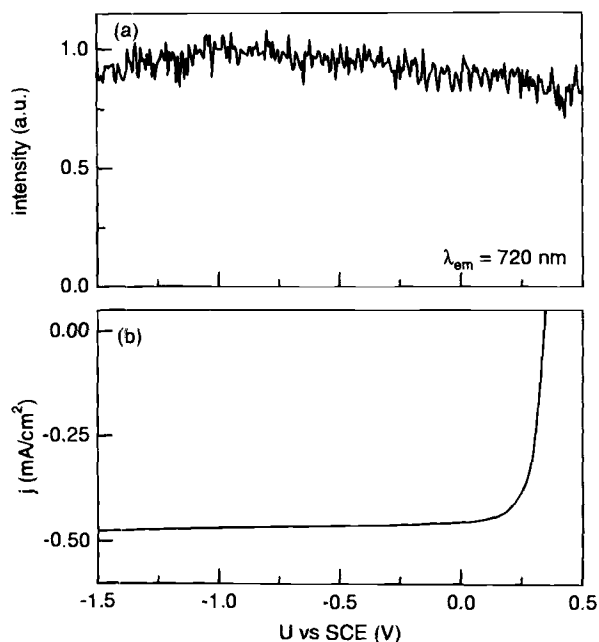


Fig. 6. (a) Emission-potential and (b) current-potential curves of a stationary p-type porous silicon electrode in a 0.1 M  $Ce^{4+}$ , 1 M  $H_2SO_4$  solution.

potentials more positive than 0.25 V the current becomes anodic due to oxidation of the silicon.<sup>24</sup> As shown in Fig. 6a the emission intensity does not depend on the applied potential because the rate of hole injection is potential-independent. When the potential is scanned to values more positive than 0.5 V an intense emission peak is observed due to anodic oxidation of the layer.<sup>24</sup>

The cell configuration did not allow rotation of the electrode. A variable flow rate of argon bubbled through the solution was used to enhance diffusion of species to the electrode surface. Upon increasing the flow rate the cathodic current measured with p-type porous silicon increased markedly. This indicates that the reduction of  $Ce^{4+}$  is, to some extent, diffusion limited. The emission intensity also increased. This is clear from Fig. 7 which shows the emission intensity from a p-type electrode in a  $Ce^{4+}$  solution polarized at -1.5 V as a function of the current density. At the open-circuit potential (no current) we also find that the luminescence intensity rises upon increasing the gas flow rate.

In Fig. 8 the results of measurements with n-type porous silicon in a 0.1 M  $Ce^{4+}$ , 1 M  $H_2SO_4$  solution are given. The potential was scanned from 0.5 to -1.5 V and back. At potentials more negative than 0.15 V a cathodic current

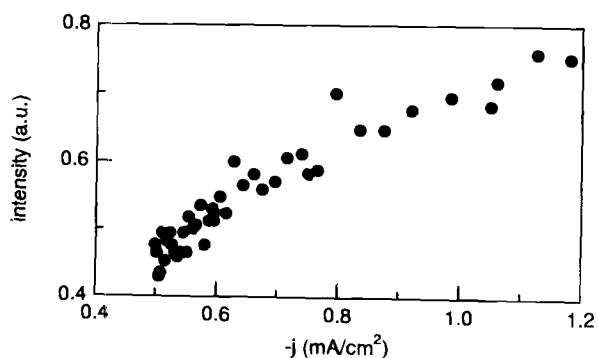


Fig. 7. Emission intensity (at 720 nm) as a function of the cathodic current of a stationary p-type porous silicon electrode in a 0.1 M  $Ce^{4+}$ , 1 M  $H_2SO_4$  solution at a constant applied potential of -1.5 V. The current was varied by bubbling Ar gas through the solution.

due to reduction of  $Ce^{4+}$  is observed. Between -0.1 and -0.65 V the current density is independent of the potential. At more negative potentials the cathodic current increases due to the hydrogen evolution. Some hysteresis is observed between the scan toward negative values and the return scan; between subsequent scans the current may vary to some extent.

Like Meulenkamp et al.<sup>10</sup> we found that, in contrast to the p-type case, the emission intensity of n-type porous silicon depends on the applied potential; this is shown in Fig. 8a. When the potential is scanned from the region in which no current is measured to more negative values corresponding to the current plateau, the emission intensity decreases, also to a constant value. When hydrogen is evolved, the luminescence is quenched almost completely. This is different from what Meulenkamp et al.<sup>10</sup> report. In their case the intensity also decreased with the onset of cathodic current, but upon further scanning to negative potentials increased again. This was attributed to electroluminescence which is generated by radiative recombination of electrons (majority carriers) with holes injected by  $Ce^{4+}$  ions in solution.

### Discussion

The trends observed in the present work for the reduction of one-electron oxidizing agents via the valence band of HF-pretreated silicon comply with what one expects on the basis of the energetics of these systems (see Table I). The rate of reduction of  $Ce^{4+}$  and  $IrCl_6^{2-}$ , with redox energy well below the valence bandedge of silicon, is high. Hole injection from  $Fe^{3+}$  and  $Fe(CN)_6^{3-}$  with redox energy close to or above the valence bandedge is weak; the overlap of the empty redox states with the filled valence band states is much less favorable. These oxidizing agents can be reduced via the conduction band, e.g., photocathodically at a p-type electrode. It is somewhat surprising that the  $Ce^{4+}$  reduction is not faster (i.e., diffusion controlled, as is  $IrCl_6^{2-}$ ) and that, as the electrode is oxidized, reduction via the conduction band becomes possible. The redox energy of  $Ce^{4+/3+}$  is 0.7 eV below the valence bandedge of crystalline silicon (see Table I). Effective hole injection from  $Ce^{4+}$  is therefore expected. A very significant downward shift of the bandedges could reduce the overlap of the acceptor levels of  $Ce^{4+}$  and the valence band states, and thus the injection rate. However, impedance measure-

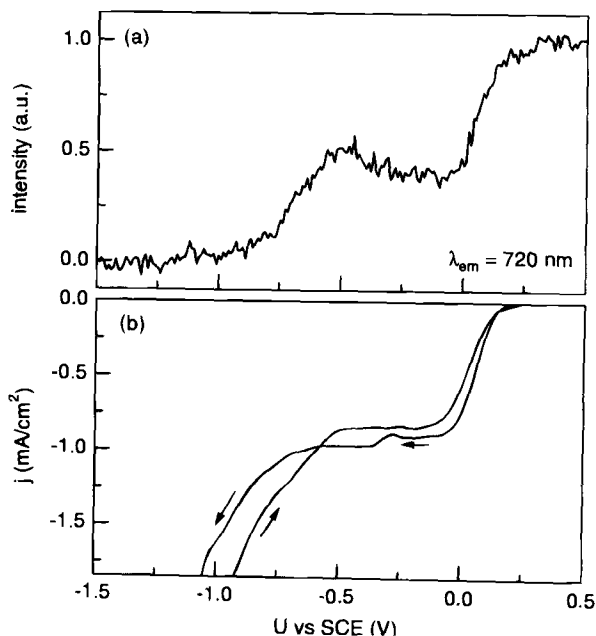


Fig. 8. (a) Emission-potential and (b) current-potential curves of a stationary n-type porous silicon electrode in a 0.1 M  $Ce^{4+}$ , 1 M  $H_2SO_4$  solution.

**Table I. Standard redox potentials of the four one-electron oxidizing agents considered in the present work. The positions of the valence band edge  $E_{VB}$  in solutions of the given pH were obtained from the flatband potentials  $U_{FB}$  of p-type silicon.<sup>13,31</sup>**

Redox couple	Redox potential (V vs. SCE) <sup>32</sup>	$U_{FB}$ (V vs. SCE)	$E_{VB}$ (eV)
Ce <sup>4+/3+</sup> (pH 0)	1.20	0.25	0.50
IrCl <sub>6</sub> <sup>2-/3-</sup> (pH 2-3)	0.75	0.15	0.40
Fe <sup>3+/2+</sup> (pH 0)	0.53	0.25	0.50
Fe(CN) <sub>6</sub> <sup>3-/4-</sup> (pH 2-3)	0.12	0.15	0.40

ments do not show a dramatic shift of the bandedges. The unfavorable kinetics could be due to adsorption of Ce<sup>4+</sup> at the (slightly) oxidized surface giving rise to acceptor states at higher energy. Recently it has been shown that Fe<sup>3+</sup> ions adsorb very effectively on silicon oxide.<sup>33</sup>

The idea that adsorption of the electron acceptor can drastically change the reduction mechanism seems to be confirmed by the results with S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub> and, in particular, by the enhancement of the quantum efficiency for H<sub>2</sub>O<sub>2</sub> reduction in the presence of Fe<sup>3+</sup> ions (Fig 4). Reaction mechanisms for reduction of the strong oxidizing agents MnO<sub>4</sub><sup>-</sup> and HNO<sub>3</sub> are known to be complicated and were not studied here in detail. It is clear, however, that MnO<sub>4</sub><sup>-</sup> gives a significant dark current at p-type silicon, indicating hole injection. The corresponding current for HNO<sub>3</sub> was considerably smaller.

With porous electrodes it is difficult to distinguish between charge transfer at the porous semiconductor/ solution interface and at the pore fronts. However, on the basis of energetics (Table I) hole injection into the valence band of porous silicon should be possible from IrCl<sub>6</sub><sup>3-</sup>, Ce<sup>4+</sup>, and MnO<sub>4</sub><sup>-</sup> (redox potential 1.5 V vs. SCE<sup>32</sup>). In Table II we summarize the chemiluminescence results of Meulenkamp et al.<sup>10</sup> for various oxidizing agents. The present IrCl<sub>6</sub><sup>2-</sup> result is also included. This table suggests a correlation between hole injection and chemiluminescence: strong emission is observed from oxidizing agents, which show a large cathodic dark current at p-type electrodes. Holes injected into (porous) silicon at the open-circuit potential are expected to oxidize the semiconductor. This points to a parallel between light emission due to an oxidizing agent at open-circuit potential and anodic luminescence in indifferent electrolyte solution (see Fig. 9).

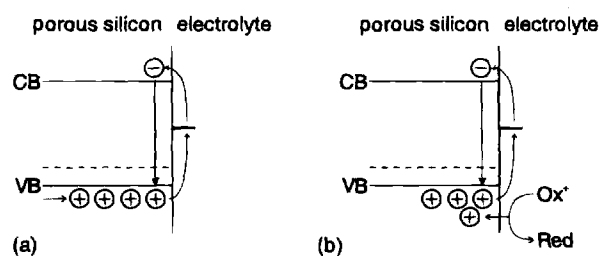
In previous work we have shown that during anodic oxidation of p-type porous silicon in the dark and n-type porous silicon illuminated with near-infrared light in indifferent electrolyte solutions, holes supplied from the bulk substrate are trapped in Si-Si surface bonds<sup>24</sup>

**Table II. Relative emission intensity of n-type and p-type porous silicon electrodes in solutions containing 0.1 M oxidizing agent, 1 M H<sub>2</sub>SO<sub>4</sub> at the open-circuit potential.<sup>a</sup>**

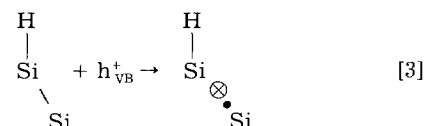
Oxidizing agent	Emission intensity		Hole injection
	n-type	p-type	
None	---	---	No
Ce <sup>4+</sup>	++	++	Strong
S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	-	--	Weak
HNO <sub>3</sub> <sup>b</sup>	---	---	Very weak
MnO <sub>4</sub> <sup>-</sup>	++	++	Strong
H <sub>2</sub> O <sub>2</sub>	---	---	Very weak
IrCl <sub>6</sub> <sup>2-</sup>	+	+	Strong

<sup>a</sup> (---) not detectable, (--) very weak, (-) weak, (+) moderate, (++) strong. Results (except those for IrCl<sub>6</sub><sup>2-</sup>) were taken from Ref. 10. An indication of the measured hole injection currents into p-type crystalline electrodes is also given.

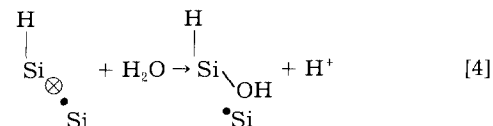
<sup>b</sup> At a concentration  $\geq 4$  M weak chemiluminescence is observed.<sup>20</sup>



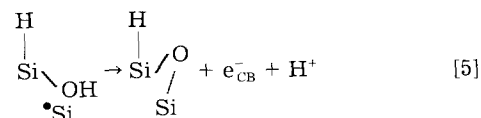
**Fig. 9. Schematic energy level diagrams of the porous silicon/electrolyte interface, illustrating (a) the mechanism of anodic luminescence in indifferent electrolyte solution with an externally applied potential and (b) the mechanism of chemiluminescence at open-circuit potential in solutions containing a strong oxidizing agent.**



A radical intermediate is formed. The electron-deficient surface bond can react with water to give Si-OH



The radical intermediate formed in this reaction very likely has energy levels in the bandgap. Such bandgap intermediates have been postulated to account for high quantum efficiencies observed during photoanodic dissolution of n-type crystalline silicon. Electrons in such levels can be thermally excited to the conduction band



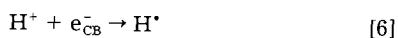
Radiative recombination of the injected electron with a hole gives rise to visible emission; this is schematically illustrated in Fig. 9a. Reaction 5 can also occur by hole capture from the valence band. Clearly, this will not lead to light emission.

In the case of chemiluminescence from porous silicon at the open-circuit potential in solutions containing a strong oxidizing agent, the holes are supplied from solution (Fig. 9b). The holes are injected either into the porous structure or into the substrate at the pore fronts, after which they may be transferred to the porous layer if the electric field is favorable. Similar oxidation reactions<sup>3-5</sup> are expected. The emission characteristics exhibit similar features. The spectrum of the chemiluminescence is centered at around 720 nm, while the anodic emission is found in the same region of the spectrum. The blue-shift and the transient nature of the luminescence (Fig. 5) in both cases support the idea of a common mechanism. We therefore conclude that light emission is due to an electroless oxidation of the silicon surface rather than a surface chemical reaction. The fact that strong oxidizing agents such as H<sub>2</sub>O<sub>2</sub> or S<sub>2</sub>O<sub>8</sub><sup>2-</sup> give only very limited or no luminescence at the open-circuit potential (Table II)<sup>10</sup> supports this conclusion. In the reduction of these two-electron redox systems, a conduction band electron is required in a first step to create a radical intermediate (OH<sup>\*</sup>, SO<sub>4</sub><sup>-\*</sup>) which then injects a hole in the second step. Only a small dark current is found at p-type silicon electrodes, indicating that hole injection occurs to a very limited extent. This explains the weak chemiluminescence observed with porous silicon in solutions containing these oxidizing agents.

Considering the proposed mechanism for chemiluminescence, the emission-potential curve of p-type porous silicon in Ce<sup>4+</sup>-containing solutions (Fig. 6) may seem surprising; the intensity is independent of potential even at strongly negative potentials. Holes are very likely injected both into the substrate at the pore fronts and into the confined regions within the porous layer. Under negative bias the holes injected at the pore fronts migrate from the surface due to the electric field at the interface, giving a cathodic current. The luminescent regions within porous silicon have dimensions which are much too small to support a depletion layer. Transport of the holes through the porous structure only occurs by diffusion and is therefore expected to be slow.<sup>34</sup> Therefore, holes injected into confined regions do not contribute to the current but give rise to oxidation of the semiconductor and to chemiluminescence via the mechanism described. This implies that "anodic" oxidation of the porous silicon occurs despite the strong cathodic polarization. The emission in Fig. 6 is constant because the intensity is determined by the constant flux of Ce<sup>4+</sup> ions to the electrode. When this flux is increased, as in the experiment of Fig. 7, both the cathodic current and the emission intensity increase.

The potential dependence of the emission intensity from n-type porous silicon shown in Fig. 8 is more complicated. A schematic energy level diagram of the interface between n-type bulk silicon and the porous structure under depletion conditions has been presented previously.<sup>24</sup> In the potential range more positive than 0.15 V no significant current is measured. The holes injected at the pore fronts are held at the surface by the electric field of the depletion layer. There they may oxidize silicon or be transferred by thermal excitation to the valence band of the porous layer where they cause oxidation and light emission. At potentials more negative than the open-circuit value, a cathodic current is measured and the emission intensity decreases. In this case the band bending at the bulk silicon/solution interface is reduced. The surface electron concentration is increased and holes injected at the pore fronts recombine with electrons, causing a cathodic current. There are two possibilities for holes injected directly into the porous layer. They may oxidize the semiconductor, thus generating chemiluminescence. That the level of light emission is lower than in the range positive with respect to the open-circuit potential can be attributed to the loss of holes by recombination at the pore fronts. Alternatively, if the electron (majority carrier) concentration in the porous layer is sufficiently high, electron-hole recombination in quantum confined structures can give light emission, as observed during cathodic reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The flatband potential under these conditions is at -0.35 V vs. SCE. A difference in efficiency between electroluminescence ( $U < 0.15$  V) and chemiluminescence ( $U > 0.15$  V) would in this case account for the decrease of the emission intensity. This implies that the onset of electroluminescence coincides with the onset of the cathodic current, different from what has been observed with S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sub>2</sub>O<sub>2</sub>. With these two-electron oxidizing agents the onset of electroluminescence is found at potentials significantly more negative than the onset of the reduction current.

The luminescence from n-type porous silicon is quenched at potentials at which hydrogen is evolved (Fig. 8). If this emission is due to chemiluminescence, hydrogen atoms from the electrochemical reduction of protons



could react with the Si<sup>\*</sup> radical, formed in reactions 3 or 4, to give an Si-H bond, thereby preventing the excitation of an electron to the conduction band. Consequently, emission would be quenched in the region where proton reduction occurs. In the case of electroluminescence, the quenching may be due to Auger recombination; as the potential is scanned toward more negative values the concentration of electrons within the porous structure becomes sufficiently large to give rise to this nonradiative decay. This is similar

to what has been proposed for n-type silicon under cathodic polarization in S<sub>2</sub>O<sub>8</sub><sup>2-</sup> solutions.<sup>35,36</sup>

## Conclusions

Simple one-electron oxidizing agents with a redox potential considerably more positive than the flatband potential of HF-pretreated silicon are shown to inject holes into the valence band of the semiconductor. However, as the degree of oxidation of the surface increases hole injection becomes kinetically limited, while electron capture proceeds unhindered. Adsorption of the oxidizing agent at the oxidized silicon surface is assumed to be responsible for charge transfer via the conduction band. Hydroxyl radicals, formed in solution by the Fenton reaction, also inject holes into p-type silicon; hole injection is not observed during photoelectrochemical reduction of H<sub>2</sub>O<sub>2</sub>.

These results suggest a relation between hole injection and chemiluminescence from porous silicon. On the basis of similarities in the luminescence characteristics we propose a mechanism for chemiluminescence which is similar to that for the emission observed during anodic oxidation in indifferent electrolyte. A hole is captured in an Si-Si surface bond which leads to an oxidation intermediate with an energy level in the bandgap. Electron injection from this level into the conduction band is followed by radiative recombination with valence band holes.

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# LiMn<sub>2-x</sub>Cu<sub>x</sub>O<sub>4</sub> Spinel (0.1 ≤ x ≤ 0.5): A new Class of 5 V Cathode Materials for Li Batteries

## I. Electrochemical, Structural, and Spectroscopic Studies

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### ABSTRACT

A series of electroactive spinel compounds, LiMn<sub>2-x</sub>Cu<sub>x</sub>O<sub>4</sub> (0.1 ≤ x ≤ 0.5), has been studied by crystallographic, spectroscopic, and electrochemical methods and by electron microscopy. These LiMn<sub>2-x</sub>Cu<sub>x</sub>O<sub>4</sub> spinels are nearly identical in structure to cubic LiMn<sub>2</sub>O<sub>4</sub> and successfully undergo reversible Li intercalation. The electrochemical data show a remarkable reversible electrochemical process at 4.9 V which is attributed to the oxidation of Cu<sup>2+</sup> to Cu<sup>3+</sup>. The inclusion of Cu in the spinel structure enhances the electrochemical stability of these materials upon cycling. The initial capacity of LiMn<sub>2-x</sub>Cu<sub>x</sub>O<sub>4</sub> spinels decreases with increasing x from 130 mAh/g in LiMn<sub>2</sub>O<sub>4</sub> (x = 0) to 70 mAh/g in "LiMn<sub>1.5</sub>Cu<sub>0.5</sub>O<sub>4</sub>" (x = 0.5). The data also show slight shifts to higher voltage for the delithiation reaction that normally occurs at 4.1 V in standard Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub> electrodes (1 ≥ x ≥ 0) corresponding to the oxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup>. Although the powder X-ray diffraction pattern of "LiMn<sub>1.5</sub>Cu<sub>0.5</sub>O<sub>4</sub>" shows a single-phase spinel product, neutron diffraction data show a small but significant quantity of an impurity phase, the composition and structure of which could not be identified. X-ray absorption spectroscopy was used to gather information about the oxidation states of the manganese and copper ions. The composition of the spinel component in the LiMn<sub>1.5</sub>Cu<sub>0.5</sub>O<sub>4</sub> was determined from X-ray diffraction and X-ray absorption near-edge spectroscopy to be Li<sub>1.01</sub>Mn<sub>1.67</sub>Cu<sub>0.32</sub>O<sub>4</sub>, suggesting to a best approximation that the impurity in the sample was a lithium-copper-oxide phase. The substitution of manganese by copper enhances the reactivity of the spinel structure toward hydrogen: the compounds are more easily reduced at moderate temperature (~200°C) than LiMn<sub>2</sub>O<sub>4</sub>.

### Introduction

Materials that reversibly intercalate lithium form the cornerstones of the emerging lithium-ion battery industry. Lithiated graphite and pyrolyzed carbons<sup>1,2</sup> and more recently, glassy tin oxides,<sup>3</sup> are the anodes of greatest interest as they offer a low potential vs. lithium, typically below 1 V. Layered rock-salt compounds such as LiCoO<sub>2</sub> and LiNiO<sub>2</sub><sup>4,5</sup> are proven 4 V cathode materials.<sup>6-8</sup> Currently, LiCoO<sub>2</sub> is the preferred electrode material for commercial lithium-ion batteries<sup>9</sup> which are now being manufactured at a rate of 250 million units/year.<sup>10</sup> Nonetheless, Co and Ni compounds have economic and environmental problems that leave the door open to exploit alternative materials.

The spinel LiMn<sub>2</sub>O<sub>4</sub> is an inexpensive, environmentally benign intercalation cathode that is the subject of intense development,<sup>11</sup> although it is not without faults. The achiev-

able electrode capacity (120 mAh/g) is 15-30% lower than that which can be obtained from Li(Co,Ni)O<sub>2</sub> cathodes. Moreover, an unmodified LiMn<sub>2</sub>O<sub>4</sub> electrode exhibits an unacceptably high capacity fade. Several researchers have stabilized the LiMn<sub>2</sub>O<sub>4</sub> electrode structure to lithium insertion/extraction reactions at ~4 V by substituting a small fraction (~2.5%) of the manganese ions with other metal cations.<sup>12-14</sup> Although these substitution techniques can successfully combat the capacity decline at 4 V, the initial reversible capacity is no better than 115 mAh/g.<sup>14</sup>

Extending the concept of Mn replacement in the spinel, Davidson et al.<sup>15</sup> and Amine et al.<sup>16</sup> have used Cr and Ni, respectively, to produce LiMn<sub>2-x</sub>M<sub>x</sub>O<sub>4</sub> electrodes (x ≈ 0.5) that provide improved stability to electrochemical cycling at 3 V. Guyomard and co-workers<sup>17</sup> showed that lithium extraction from the Cr-substituted spinel occurs at 4 and 4.9 V; these reactions were attributed to the oxidation of manganese and chromium, respectively. Gao et al.<sup>18</sup> dis-

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