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Role of inversion layer formation in producing low effective surface recombination velocities at Si/liquid contacts

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(Received 27 June 2000; accepted for publication 23 August 2000)

Photoconductivity decay lifetimes have been obtained for NH₄F(ₐq)-etched Si(111) and for air-oxidized Si(111) surfaces in contact with solutions of CH₃OH or tetrahydrofuran (THF) containing either ferrocene (Fe(ₐq)), bis(pentamethycyclopentadienyl) Fe(ₐq), or I₂. Si surfaces in contact with electrolytes showing Nernstian potentials > 0 V versus the standard calomel electrode exhibited low effective surface recombination velocities regardless of the different surface chemistries, whereas those exposed only to N₂(ₐq) ambients or to electrolytes containing mild oxidants showed differing rf photoconductivity decay behavior depending on their different surface chemistry. The data reveal that formation of an inversion layer, and not a reduced density of electrical trap sites on the surface, is primarily responsible for the long charge-carrier lifetimes observed for Si surfaces in contact with CH₃OH or THF electrolytes containing I₂ or Fe(ₐq).

Low surface recombination velocities, S, of Si are important for passivation in electrical devices such as photovoltaics. In addition, low S values of Si/liquid contacts are desirable for monitoring the presence of contaminants in electrolyte solutions during Si etching and wet processing steps and for Si-based photoelectrochemical energy conversion devices. The Si/SiO₂ interface exhibits a low carrier recombination velocity, with S values as low as 3 cm/s observed under certain, nearly ideal conditions. The alkylated Si(111) surface obtained by a two-step wet chemical chlorination/alkylation procedure exhibits low S values (< 10 – 20 cm/s) that are stable in air for extended periods of time. H-terminated Si(111) exhibits a low surface recombination velocity in contact with aqueous acids, but the electrical properties of this system degrade rapidly upon exposure of the surface to an air ambient.

Silicon surfaces (1 cm²) were prepared from double-polished, float zone, (111)-oriented Si wafers having a long bulk lifetime and a resistivity of 3.8 ± 10³ Ω cm. Solutions were prepared in a N₂(ₐq)-purged glove box using anhydrous, oxygen-free solvents and dry reagents, and samples were exposed to air only briefly after etching and during rinsing steps. Surface recombination velocities were measured using a time-resolved rf conductivity apparatus. Typical incident light intensities at 1064 nm were 7 x 10⁻⁴ mJ cm⁻² pulse⁻¹, producing an injection level of 2 x 10¹⁴ carriers cm⁻³. NH₄F(ₐq)-etched samples typically displayed lifetimes in the range of 500 – 900 μs in contact with conc. H₂SO₄(ₐq), providing a lower bound on the bulk charge carrier lifetime for the Si wafers used in this work.

The mean decay for NH₄F(ₐq)-etched Si surfaces in contact with CH₃OH–0.05 M I₂ was very slow, with a lifetime of 600 ± 300 μs (Table I). Assuming an infinite bulk lifetime and a sample thickness of 195 μm, an upper bound on the surface recombination velocity for this type of sample was determined to be 16 ± 8 cm/s⁻¹. However, when the Si sample was removed from the CH₃OH–0.05 M I₂ solution and rinsed with methanol, the lifetime observed in a N₂(ₐq) ambient was significantly shorter, corresponding to S = 810 ± 70 cm/s⁻¹ (Table I). The effect was completely reversible in that reimmersion of the surface into the CH₃OH–0.05 M I₂ electrolyte again resulted in a long lifetime for the rf photoconductivity decay, and removal and rinsing again produced a short lifetime value in contact with N₂(ₐq).

Somewhat different behavior was observed for NH₄F(ₐq)-etched Si(111) surfaces that were immersed in CH₃OH–0.05 M Fe(ₐq) electrolyte solution. The carrier lifetime observed in contact with this electrolyte was 700 ± 200 μs, indicating an upper limit on the effective S value of 14 ± 4 cm/s⁻¹ (Table I). These observations are in accord with earlier measurements of the effective surface recombination velocity for silicon in contact with CH₃OH–Me₆Fe(ₐq) solutions which have a Nernstian potential within 100 mV of CH₃OH–Fe(ₐq). However, after rinsing with CH₃OH the value of S for this surface was only slightly higher in N₂(ₐq).
carrier lifetime for NH$_4$F (not shown), measured with different behavior observed, as expected, for the air-oxidized sample and then immersed into a THF–Fc$^+$ solution prior to contact with the THF–Me$_{10}$Fc$^{+}/0$ solution (Table I). Experiments were also performed with air-oxidized surfaces to investigate systems in which no chemical reaction is possible. These results can all be consistently explained through reference to the electrochemistry of Si/liquid contacts. The electrolytes that produced low Si surface recombination velocities all had electrochemical potentials >0 V versus the standard calomel electrode. In addition, the absence of such electrolytes, higher, and variable, S values were measured, with different behavior observed, as expected, for the various chemically different Si surfaces. This behavior can be readily understood from the Shockley–Read–Hall treatment for surface recombination. Redox couples that have very positive redox potentials are capable of extensive charge transfer from the Si into the electrolyte, thereby establishing an inversion layer at the surface of n-type Si. Simulations of the surface recombination...
tion rate using an extended Shockley–Read–Hall formalism, which incorporates the effects of band bending, have in fact shown that $S$ decreases significantly with increases in positive charge at the surface of $n$-type Si.\textsuperscript{11} Removal of the sample from the electrolyte will generally change the surface potential in a direction that reduces the band bending, so the observed value of $S$ should increase and the variations in the surface trap density, $N_t$, can then be reflected in the measurements of $S$ under these conditions. This expectation is in accord with the experimental observations that the surfaces investigated in this work all exhibited higher $S$ values in contact with $N_{2(9)}$ than they did in contact with the oxidizing electrolyte solutions.

Electrochemical data have located the conduction band edge of alkoxylyl Si surfaces at $\approx -0.83$ V versus the standard calomel electrode (SCE), in CH$_3$OH.\textsuperscript{14} This is consistent with the observation that, in air, in $N_2(9)$, or in electrolytes with moderately negative redox potentials (\textless 0 V vs SCE) such as THF–Me$_2$Fc$^{+/0}$, surfaces with significant $N_t$ values will exhibit a higher effective surface recombination velocity than they would under conditions that produce an inversion layer at the Si surface. In contrast, for electrolytes with redox potentials $\geq +0.2$ V vs SCE, such as I$_2$ or Br$_2$ in CH$_3$OH, C$_2$H$_5$OH, or THF, or Fe$^{+/0}$ in CH$_3$OH or THF, the steady-state rate of surface recombination will be suppressed due to the formation of a high concentration of minority carriers at the surfaces in contact with the electrolyte solutions. The observed effect should be rapid and reversible, because only electron exchange is required to produce the electrochemically induced change in surface carrier concentration that affects the effective $S$ value of the interface. This expectation is also in accord with the experimental observations. In our work, only etched surfaces that had been immersed in CH$_3$OH–0.05 M Fe$^{+/0}$ solutions showed low surface recombination velocities in $N_{2(9)}$, indicating that only these surfaces had low values of $N_{t,2}$ in contact with an ambient that did not produce an inversion layer at the Si surface.

Further evidence for charge-transfer control over the effective $S$ value in these oxidizing electrolytes can be obtained through reference to prior electrical and electrochemical measurements on Si/liquid contacts.\textsuperscript{12–14} Near-surface channel conductance measurements in $p^+–n–p^+$ Si structures exposed to electrolytes have clearly demonstrated the formation of an inversion layer at $n$-Si/CH$_3$OH–5.4 mM Me$_2$Fc–2.9 mM Me$_2$Fc$^+$ contacts but not at CH$_3$OH–Me$_{10}$Fc$^{+/0}$ electrolytes.\textsuperscript{12} Mott–Schottky measurements of the $n$-Si/CH$_3$OH–Me$_2$Fc$^{+/0}$ contact have indicated an equilib-rium barrier height of $\approx 1.03$ V,\textsuperscript{14–16} which is sufficient to drive the system into carrier inversion. The surface recombination velocity of Si/CH$_3$OH contacts after treatment with CH$_3$OH–Me$_2$Fc$^{+/0}$, deduced from current density versus potential data, is $< 100$ cm s$^{-1}$, whereas higher $S$ values were deduced for these Si samples in contact with redox systems such as CH$_3$OH–Me$_{10}$Fc$^{+/0}$ that cannot produce an inversion layer at the Si surface.\textsuperscript{10} Direct measurements of $S$ for the $n$-Si/CH$_3$OH interface as a function of the electrode potential have shown that at positive (and negative) potentials, where the surface is in inversion (accumulation), the effective surface recombination velocities are very low, whereas for surface potentials that produce moderate band bending in the semiconductor, much higher $S$ values are obtained.\textsuperscript{10} The formation of an electrochemically induced inversion layer has also been used to explain the unexpectedly large feedback currents observed in scanning electrochemical microscopy experiments at Si/CH$_3$OH–Fe$^{+/0}$ and Si/CH$_3$OH–Me$_2$Fc$^{+/0}$ contacts.\textsuperscript{13} Thus, the experimentally observed charge-carrier decay dynamics for a variety of chemically treated Si surfaces can be explained in the context of the known electrochemical behavior of Si/liquid contacts.

The authors acknowledge the National Science Foundation, Grant No. CHE-9974562, for support of this work.


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