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Control of the Stability, Electron-Transfer Kinetics, and pH-Dependent Energetics of Si/H_2O Interfaces through Methyl Termination of Si(111) Surfaces

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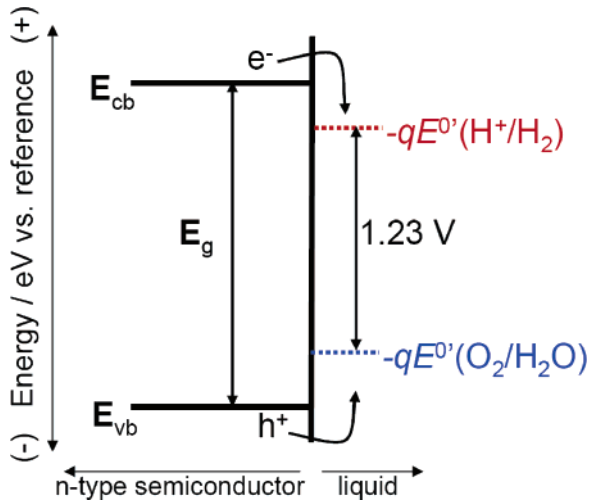
Methyl-terminated, n-type, (111)-oriented Si surfaces were prepared via a two-step chlorination-alkylation method. This surface modification passivated the Si surface toward electrochemical oxidation and thereby allowed measurements of interfacial electron-transfer processes in contact with aqueous solutions. The resulting semiconductor/liquid junctions exhibited interfacial kinetics behavior in accord with the ideal model of a semiconductor/liquid junction. In contrast to the behavior of H-terminated Si(111) surfaces, current density vs. potential measurements of CH_3-terminated Si(111) surfaces in contact with an electron acceptor having a pH-independent redox potential (methyl viologen$^{2+/+}$) were used to verify that the band edges of the modified Si electrode were fixed with respect to changes in solution pH. The results provide strong evidence that the energetics of chemically modified Si interfaces can be fixed with respect to pH and show that the band-edge energies of Si can be tuned independently of pH-derived variations in the electrochemical potential of the solution redox species.

I. Introduction

The positions of the band edges of photoelectrodes must be controlled to enable water splitting and other desirable photoelectrochemical reactions at semiconductor/liquid interfaces.[1,2] For water splitting, for example, the energies of the bottom of the conduction band and the top of the valence band, respectively, need to be positioned appropriately with respect to the electrochemical potentials of the H^+/H_2 and O_2/H_2O redox couples (Scheme 1).[1] The electrochemical potentials of the H^+/H_2 and O_2/H_2O systems can, of course, be manipulated by changing the pH of the solution.[3] It is well-documented, however, that such pH variation does not in general affect the energetics of the semiconductor/liquid interface, because the band-edge positions of the semiconductor surface are also sensitive to pH.[4−6] The need to manipulate the band-edge positions has prompted "band-edge engineering" approaches in which materials with different band gaps are layered onto desired photoactive materials, in attempts to shift the energetics of the semiconductor into the appropriate positions.[7] We describe herein another approach to control the interfacial energetics of photoelectrodes, in which covalent chemical modification of the surface is used to eliminate the pH dependence of the band edges, allowing pH control of the electrolyte to manipulate the energetics of the bands of the solid relative to the electrochemical potential of the solution.

Metal oxide photoelectrodes are well-known to display a Nernstian dependence of their flat-band potential, E_{fb}, on pH.[4−6,8] The 1.1 eV band-gap of Si is better matched to the solar spectrum than that of most metal oxides,[2] and Si could be used in a dual-junction or heterojunction type system for water splitting if its band-edge positions could be appropriately controlled. Si, however, readily oxidizes in the presence of mildly oxidizing redox species in water,[9] introducing both electrochemical instability and an oxide layer whose protonation/deprotonation equilibria impart pH sensitivity to the band-edge positions of Si/H_2O interfaces. For example, shifts of E_{fb} of −33

SCHEME 1. Energy vs Distance for an Idealized n-Type Semiconductor for Water Splitting in Contact with an Aqueous Solution[a]



[a] The conduction-band and valence-band edges, $\mathbf{E}_{cb}$ and $\mathbf{E}_{vb}$, respectively, separated by a band gap energy, $\mathbf{E}_g$, must straddle the formal potentials $E^{\circ\prime}(H^+/H_2)$ and $E^{\circ\prime}(O_2/H_2O)$ for the reduction (red) and oxidation (blue), respectively, of water.

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mV/pH unit,[10] −59 mV/pH unit,[11] as well as nonlinear shifts of E_{fb} with variations in pH,[9] have been reported for Si/H_2O interfaces.

In this work, we describe the covalent modification of Si surfaces via a two-step chlorination−methylation method[12] to introduce kinetically stable CH_3−Si bonds onto Si surfaces. This process eliminates the pH dependence of the Si band-edge positions, and additionally facilitates use of the Si under conditions in which it otherwise would be rapidly oxidized to produce pH-dependent surface potentials. This methylation process additionally allows for the experimental measurement of the interfacial electron-transfer kinetics in media which can not be probed at reactive, oxidizeable, H-terminated Si surfaces, and has produced a system which reveals "ideal" kinetics behavior at the semiconductor/liquid contact. The ability to control the band-edge positions, and to introduce, or eliminate, a pH-dependence of Si surfaces through molecular level control, without introducing deleterious levels of surface states, is of obvious relevance to Si chem-FETs (field-effect transistors),[13] light-addressable potentiometric sensor devices,[14] Si nanowire sensors used in chemical and biological applications,[15] and has implications in a variety of other applications of semiconductor/liquid interfaces.

II. Experimental Section

The (111)-oriented, n-type, Si single crystals (Crysteco Inc.) had a resistivity of 3.7 Ω cm, as determined from four-point probe measurements. The samples were H-terminated by etching for 20 min in an 11 M (40% by weight) NH_4F(aq) solution that was purged with Ar.[12,16,17] CH_3-terminated Si samples were prepared by chlorinating H−Si(111) samples with PCl_5 in chlorobenzene at 100 °C for 1 h, followed by heating at 70 °C for 14 − 18 h in a 1 M CH_3MgBr solution, as described previously.[12,16] Ga−In eutectic was used as an ohmic contact and silver print was used to connect the Ga−In to a tinned copper wire. Paraffin wax was used to seal the electrode assembly in a glass tube. The resulting electrode areas, typically 0.2−0.5 cm^2, were determined by digitizing photographs of a microruler and of the exposed Si surface.

Methyl viologen (MV^{2+}) dichloride was purchased from Aldrich and was used as received. Potassium chloride (pH = 1.4), phthalate (pH = 3.8), phosphate (pH = 6.8), borax (pH = 9.0), and phosphate (pH = 11.0) buffers were prepared by literature methods.[18] The ionic strength of all solutions was adjusted to 1.0 M by the addition of KCl. The pH was measured using a VWR Scientific model 8010 pH meter.

Electrochemical measurements were performed with a Schlumberger Instruments model SI1287 potentiostat. All potentials were referenced to a standard calomel electrode (SCE). All solutions were purged with Ar before each measurement, and measurements were performed under an Ar atmosphere in the dark. X-ray photoelectron spectroscopic (XPS) data were obtained using a 1487 eV Al Kα source, as described previously.[16]

III. Results andDiscussion

Figure 1 depicts the current density, *J*, vs. applied potential, *E*, data for CH_3−Si(111) and H−Si(111) electrodes, respectively, in the dark in contact with 10 mM MV^{2+}(aq). Si has a high overpotential for H_2 evolution, so H_2 production does not interefere with observation of the reduction of MV^{2+} in the potential range of interest (Figure 1).[19−22] The initial scan of the H-terminated electrode displayed in Figure 1 was very similar to that of the CH_3-terminated electrode, but the current density of the H−Si(111) surface decayed quite rapidly thereafter. In fact, most H-terminated Si electrodes studied initially displayed *J*−*E* curves with lower current densities at a given potential, being similar to the later scans of the *J*−*E* curve shown in Figure 1.

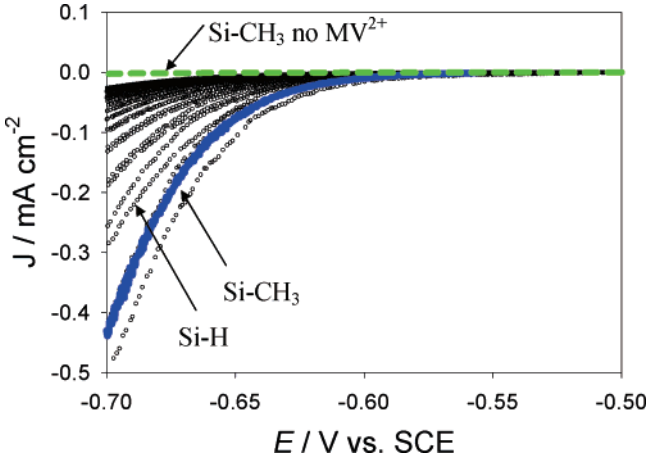

Figure 1. Plots of 20 scans of the current density (*J*) vs applied potential (*E*) at 10 mV s^{-1} for H-terminated Si(111) (black open circles) and CH_3-terminated Si(111) (solid line) electrodes in the dark in contact with a 10 mM MV^{2+} buffered at pH 11.0. Also shown is a *J*−*E* curve for CH_3-terminated Si(111) in contact with the aqueous solution but with no MV^{2+} present (green dashed line).

Figure 2a displays XPS data (1487 eV Al Kα excitation, ∼0.5 eV resolution)[23,24] in the Si 2p region of H−Si(111) samples before and after collection of the *J*−*E* data. Si oxide was clearly observed after the *J*−*E* measurements, even though extensive precautions were taken to prevent deliberate illumination of the electrode. The extent of oxidation was estimated by dividing the ratio of the SiO_x:Si 2p peak areas by the normalization constant 0.21, as described previously.[16] Values of oxide coverage of greater than one equivalent monolayer, typically 1.2−1.8 equivalent monolayers, were observed after two *J*−*E* scans at both 10 mM and 100 mM MV^{2+} in the solution. This growth of an oxide peak is in agreement with the decay of the current during successive *J*−*E* scans. Oxide was still formed even when the electrode was scanned only at relatively negative potentials (−0.5 to −0.75 V vs SCE). These results highlight the challenge of making reliable electrochemical measurements of H−Si(111) surfaces in contact with aqueous solutions. The pH dependence of Si electrodes reported previously[9−11] is then consistently ascribed to the presence of an oxide overlayer on the Si surface after it is initially used as an electrode in such aqueous solutions.

Figure 2b compares the high-resolution XPS data of the Si 2p region of CH_3−Si(111) samples with those of freshly prepared H−Si(111) surfaces. 0.2−0.5 monolayer equivalents of silicon oxide were observed following 2 to 10 *J*−*E* scans at [MV^{2+}] = 10 mM and [MV^{2+}] = 100 mM. The introduction of the methyl functionality onto the silicon surface clearly inhibited oxidation of the Si, in accord with the stability of the *J*−*E* curves for the CH_3−Si(111) surfaces displayed in Figure 1. This behavior is in accord with the stability toward oxidation of alkyl-terminated Si(111) photoanodes under illumination.[25,26]

The inhibition of oxidation enabled the measurement of interfacial electron-transfer processes that were in accord with the ideal model of electron transfer at the semiconductor/liquid interface. The current density for an electron-transfer process from the conduction band of an n-type semiconductor to an acceptor species, A, in solution, is given by

$$J(E) = -qk_{et}[A]n_s \quad (1)$$

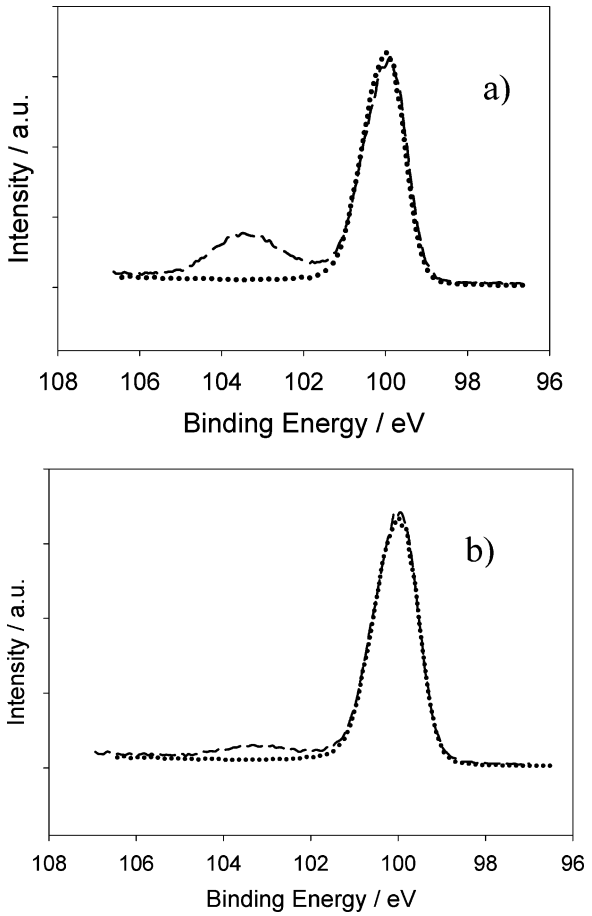

Figure 2. High-resolution XPS data (using 1487 eV Al Kα excitation) of the Si 2p region of: (a) a freshly etched H−Si(111) electrode (dotted line) and the electrode following $J-E$ measurements consisting of two scans at 10 mV s^{-1} (dashed line); (b) a freshly etched H−Si(111) electrode (dotted line) and a methyl-terminated Si(111) electrode following $J-E$ measurements consisting of 2 scans at 10 mV s^{-1} (dashed line).

where q is the charge of an electron (1.6022×10^{-19} C), k_{et} is the electron-transfer rate constant ($cm^4\ s^{-1}$), [A] is the acceptor concentration (cm^{-3}), and n_s is the electron concentration (cm^{-3}) at the surface of the semiconductor.[2] The rate law of eq 1 can be demonstrated to apply by verification of the first-order dependence of J on [A] and n_s.[27]

According to eq 1, an increase in [A] by a factor of 10 should produce a potential shift, ΔE, by $(k_BT/q)\ln(10)$ (with k_B being Boltzmann's constant), i.e., by 59 mV at room temperature, to produce a given value of J. Figure 3 displays a semilogarithmic plot of J vs. E for a CH_3-terminated Si(111) electrode in contact with solutions having $[MV^{2+}] = 10$ mM and $[MV^{2+}] = 100$ mM, respectively. The 10-fold increase in [A] resulted in a 50 mV shift of the $J-E$ curve, verifying the first-order dependence of J on [A].

All of the junctions showed rectifying behavior in accord with the diode equation:

$$J = -J_0\,(e^{(-qE)/\gamma k_B T} - 1) \qquad (2)$$

where J_0 is the exchange current density and γ is the diode quality factor. For CH_3-terminated Si(111) surfaces, the diode quality factors were typically 1.1−1.3 at low concentrations of acceptor, in accord with the expectation of $\gamma = 1$ for a process that is kinetically first order in the concentration of electrons at the surface of the semiconductor. In contrast, H−Si(111) electrodes either displayed, or quickly decayed to, a value of $\gamma \approx 2$.

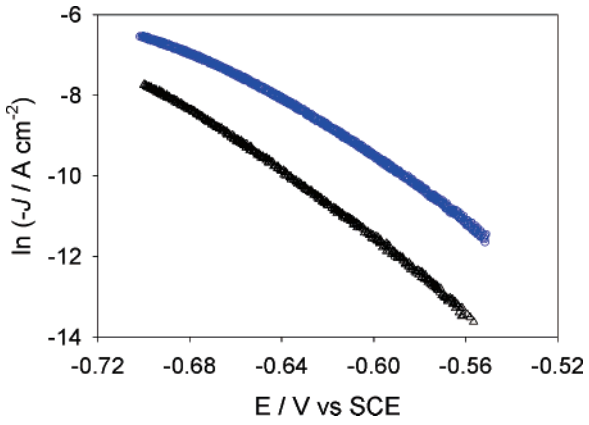

Figure 3. Semilogarithmic plots of J vs E for a methyl-terminated Si electrode at MV^{2+} concentrations of 10 mM (black triangles) and 100 mM (blue circles). As noted in the text, a 10-fold increase in [A] should result in a shift of the $J-E$ curve by approximately $\Delta E = 59$ mV.

Large MV^{2+} concentrations, while favoring direct electron transfer, typically produced higher diode quality factors on CH_3−Si(111) surfaces, indicating the presence of nonideal recombination pathways at high acceptor concentrations. This behavior is attributed to the small growth of oxide that could not be fully suppressed at high MV^{2+} concentrations. In addition, measurements of CH_3−Si(111) electrodes in contact with the stronger oxidant, $Ru(NH_3)_6^{3+/2+}$, exhibited $\gamma \approx 2$. A correlation between the value of the diode quality factor and Si oxide growth was thus observed, underscoring the necessity of using carefully prepared CH_3-terminated Si electrodes to probe the kinetics of interfacial electron transfer at n-type (111)-oriented Si electrodes in aqueous solution.

A Mott−Schottky (differential capacitance vs potential) analysis of the flat-band potential of CH_3−Si(111) surfaces was not possible because the necessary applied potentials led to oxidizing, anodic currents, even in the dark at all MV^{2+}/MV^{+} concentrations explored. This drawback precluded determination of the interfacial electron-transfer rate constant; however, the measured current densities (Figure 3) are consistent with a low barrier height contact for n-type CH_3−Si(111)/H_2O−$MV^{2+/+}$ contacts.

Because the kinetics of interfacial electron transfer are strongly dependent on the interfacial energetics,[8,28] the kinetics are a good, although indirect, probe of energetic variations. Figure 4 displays the $J-E$ data obtained at $[MV^{2+}] = 10$ mM for $1.5 \leq$ pH ≤ 11. If the band edges were to shift with pH, a corresponding change in the applied potential would be needed to produce a given value of the interfacial current density, as has been observed for n-ZnO electrodes in contact with outer-sphere redox couples.[8] The invariance of the $J-E$ curves relative to a fixed reference potential, despite the nearly 10 pH unit variation in the solution and in the formal potentials of the H^+/H_2 and O_2/H_2O redox couples, is strong evidence that the band edges of CH_3−Si(111) electrodes are fixed with respect to pH changes. This behavior is in contrast to the pH dependence of the band edges that is observed for metal oxides and for unmodified Si electrodes in aqueous solution. The data thus indicate that the energetics of the band-edge positions relative to a pH-dependent redox couple can be manipulated by pH changes at the CH_3−Si(111)/H_2O interface.

n-Type Si electrodes have previously been coated with metal films to achieve enhanced stability under illumination.[29−31]

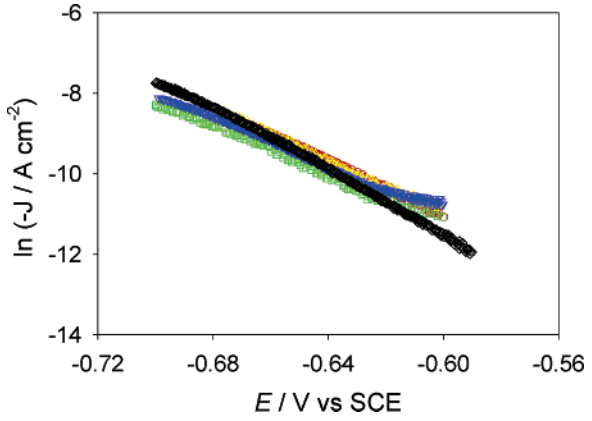

Figure 4. Semilogarithmic plots of J vs E for methyl-terminated Si electrodes in contact with 10 mM MV^{2+} at pH = 1.4 (blue upside down triangle), pH = 3.8 (green square), pH = 6.8 (yellow triangle), pH = 9.0 (red circle), and pH = 11.0 (black diamond).

Intimate contact of Si with a metal produces a floating junction in which the liquid does not control the energetics of the interface, and which suffers from majority-carrier-based thermionic emission type recombination at the regions having metal/Si contacts. In this work, control of the band-edge energies has instead been achieved by manipulation of the interfacial chemistry of the surface as well as the redox potential of the electrolyte. Functionalization of the Si to introduce Si−C bonds, along with further elaboration of the chemisty of such interfaces,[23,24,32] is therefore an interesting approach to control the properties of such semiconductor/liquid contacts.

IV. Conclusions

Methyl-terminated Si(111) electrodes have been demonstrated to effectively inhibit the oxidation of Si in contact with MV^{2+} dissolved in aqueous solutions. Such surface modification allowed for observation of current density vs applied potential behavior in accord with the ideal model of interfacial electron-transfer reactions at a semiconductor/liquid junction. The kinetics were observed to be independent of pH over approximately 10 pH units. Because the kinetics are dependent on the interfacial energetics, the invariance of the kinetics with respect to pH implies that the band-edge energetics of these modified Si surfaces are also independent of pH.

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