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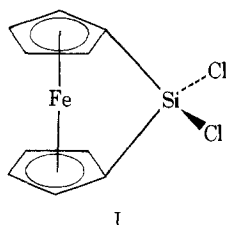
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Design and Study of a Photosensitive Interface: A Derivatized n-Type Silicon Photoelectrode

Sir:

We have found that the photoanodic decomposition of n-type Si can be suppressed by the competitive oxidation of ferrocene in EtOH solution with $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ as the supporting electrolyte.¹ Such studies¹⁻⁴ have led us to suspect a strong interaction of the stabilized photoanode with the reductant added to the solution. We now report the covalent attachment of a photoelectrochemically active ferrocene derivative to the surface of n-type Si which passivates the electrode to decomposition (SiO_2 formation). This study opens a new avenue for the stabilization of semiconductor/liquid junction photo-cells.

A number of interesting papers have been published recently concerning derivatized electrodes,⁵⁻¹⁶ and attachment of electroactive groups to electrodes via surface oxide and hydroxide groups has proven fruitful. We have carried out initial derivatization of n-type Si with the ferrocene derivative (1,1'-ferrocenediyl)dichlorosilane (**1**) prepared by slow addition



of 1,1'-dilithioferrocene to neat SiCl_4 . The red-orange solid **1** is purified by sublimation. The mass spectrum shows a parent peak region characteristic of a molecule bearing two Cl atoms.

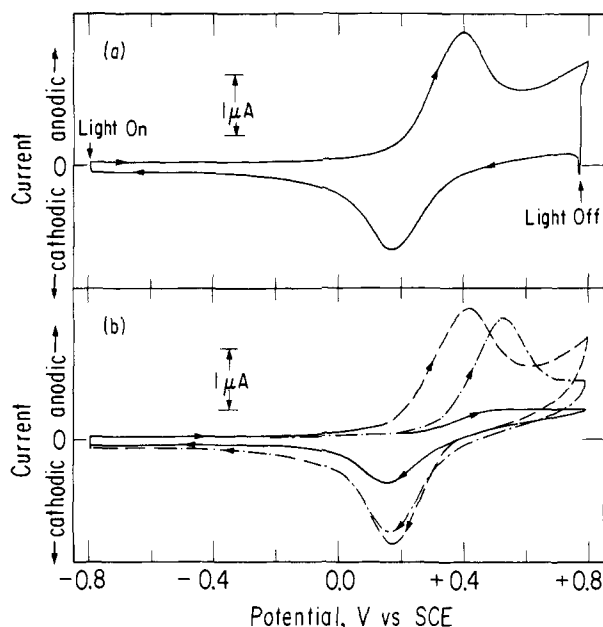


Figure 1. Cyclic voltammograms (100 mV/s) of derivatized n-type Si electrode in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ in CH_3CN under Ar at 298 K. (a) Scan begins at -0.8 V with 632.8-nm He-Ne laser irradiation (3 mW, 6X beam expanded); at the anodic limit the light is switched off. (b) Scans with 632.8-nm He-Ne laser irradiation (---), room light irradiation (-.-.-), and in the dark (—).

The ^1H NMR shows a pair of multiplets centered at δ 4.02 and 4.29, respectively, in dry C_6D_6 , characteristic of a disubstituted ferrocene.^{17,18} The elemental analysis (Galbraith) is satisfactory [calcd (found): C, 42.43 (42.44); H, 2.83 (2.90); Cl, 25.07 (25.30); Si, 9.93 (10.22)]. Such a complex has precedence from the reaction of Ph_2SiCl_2 with 1,1'-dilithioferrocene which yields the diphenyl analogue of **1**.¹⁸ Complex **1** is hydrolytically unstable (fumes in moist air), and this is the basis of its attachment to the Si surface.

n-Type Si (3–5 Ω cm) electrode material was single-crystal with ~ 0.1 cm^2 of a 100 face exposed. Contact was made by rubbing Ga–In eutectic onto the back of the Si, and a copper wire lead was attached with Ag-epoxy. The assembly was encased in a glass tube for secure mounting and insulated with ordinary epoxy to expose only the Si surface. The electrode was etched for 10 s at 298 K in concentrated HF immediately prior to use. The electrode surface was pretreated by dipping into 10 M NaOH for 60 s at 298 K, presumably introducing surface groups which could react with **1** to form SiOSi bonds. The electrode was washed with H_2O and with acetone and dried in air at 298 K. Attachment of **1** was accomplished by dipping the electrode into a dry isooctane solution of **1** under Ar. The reaction was carried out at 298 K for a typical time of 45 min. The electrode was washed with isooctane and finally with CH_3CN .

Derivatized n-type Si was characterized by cyclic voltammetry in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ in CH_3CN solvent at 298 K under Ar. The electrolyte solution contained no deliberately added electroactive species. Figure 1 shows the cyclic voltammograms for derivatized n-type Si. The first noteworthy point is that we find cyclic waves at all. Integration of the cyclic waves typically shows $\sim 2 \times 10^{-10}$ mol/ cm^2 of surface attached electroactive material. Nonderivatized electrodes show a photoanodic current which corresponds to the buildup of SiO_2 , but there is no reduction peak in the potential range scanned; with such cycling the oxide layer builds and the current declines to essentially nothing after 4–10 scans. By way of contrast, the derivatized electrodes show persistent cyclic waves (oxidation and reduction); e.g., the data shown in Figure 1 are after ~ 50 scans.

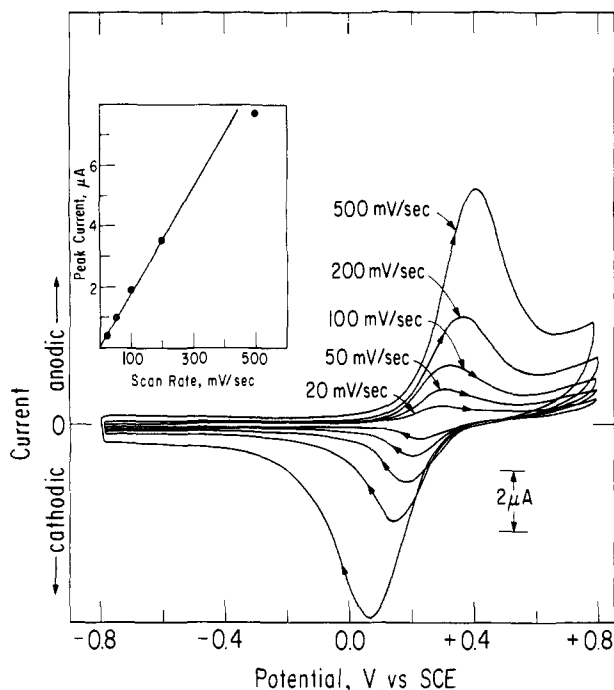


Figure 2. Cyclic voltammograms of derivatized n-type Si as a function of scan rate in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ in CH_3CN under Ar at 298 K. The electrode is exposed to 632.8-nm He-Ne laser irradiation (3 mW, 6X beam expanded). The inset shows a plot of peak photoanodic current against scan rate.

The oxidation wave for the derivatized electrode is strongly dependent on the incident irradiation, whereas the cathodic peak is relatively independent of whether the light is on or off. In the dark there is just a hint of what appears to be a background anodic current, but the return scan shows a well-defined cathodic peak. A larger anodic excursion produces more oxidation and a well-defined peak appears at $\sim +1.2$ V vs. SCE. If the anodic scan is carried out with the light on but the return scan is with the light off, both an anodic and cathodic wave are observed. Thus, the derivatized photoelectrode shows the same sort of behavior as the n-type Si exposed to a solution of ferricenium/ferrocene: good anodic currents with illumination but good cathodic currents in the dark;¹ cyclic voltammetry shows photoanodic and cathodic peaks within 100 mV of those found for the derivatized electrodes.

That the electroactive material associated with the cyclic waves is attached to the electrode is substantiated by some additional points: (1) stirring the electrolyte solution does not influence the cyclic voltammetry; (2) the peak current is nearly directly proportional to scan rate¹⁹ (Figure 2); and (3) such waves do not appear unless the derivatization procedure has been carried out; re-etching a derivatized electrode removes the cyclic waves.

The photoanodic current peak occurs at a potential which is light intensity dependent and can be significantly more negative than the expected reversible potential. Further, note that the increased scan rates (Figure 2) move the photoanodic peak somewhat more positive, but the effect of scan rate on the cathodic peak is much larger. This is consistent with an oxidation rate which is limited by irradiation intensity, while the reduction is controlled by inherently sluggish electron transfer. The reversible potential for a Pt electrode derivatized with I is $+0.55 \pm 0.05$ V vs. SCE (10–200 mV/s).²⁰ Thus, there are several hundred millivolts of underpotential at the irradiated n-type Si derivatized with I. Though this output potential is not as great as at n-type Si exposed to ferricenium/ferrocene,¹ the output is respectable.

The stability of the derivatized Si electrodes is quite good; electrodes have been stored in the electrolyte solution for several days and still exhibit cyclic waves reflecting >50% of active derivative remaining. The surface attached electroactive material has been cycled between oxidized and reduced form hundreds of times for a number of electrodes. The experimental data in the figures are truly representative and have been repeated a number of times with different electrodes, preparations of I, etc. It is certain that the derivatized surface does protect the Si to a substantial extent from further SiO_2 formation, and the surface attached species are photoelectrochemically active with light and dark effects not exceptional for an n-type semiconductor photoelectrode. We are now investigating the possibilities for photoinduced mediated electron transfer using the derivatized photoelectrode.

Derivatization of p-type Si has been accomplished using procedures similar to those reported here. The photoeffects are opposite to those found for n-type Si, as expected. The results for p-type Si will be published in a full paper.

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