10, which again supports the second conclusion. At concentrations above 8M,  $k_2$  is independent of potential, probably because of the need for a preferential orientation of oxygen leading to the formation of  $H_2O_2$ .

5. The decrease in reaction rates at higher concentrations can be attributed to four causes: lower oxygen solubility, lower proton activity, increased specific adsorption of anions, and a thicker double layer. Complementary experiments that yielded the concentration dependence of the potential of zero charge on mercury support the view that specific adsorption of anions is quite strong.

6. Minima in the plots of  $i/c_{02}$  and of  $k_1$  vs. concentration at a fixed potential illustrate the effects of differential solvation between electrode and reaction species on oxygen reduction kinetics. Similar phenomena have been observed for other reactions in mixed solvents.

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## Semiconductor Electrodes

### LIV. Effect of Redox Couple, Doping Level, and Metal Type on the Electrochemical and Photoelectrochemical Behavior of Silicide-Coated n-Type Silicon Photoelectrodes

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#### ABSTRACT

The surface potentials of silicide-coated n-type silicon photoelectrodes as functions of the potential of solution redox couples and the bias potential show that the Fermi level of these photoelectrodes is strongly pinned at the silicide/Si interface. The built-in potential barrier is consistent with the constancy in the photovoltage observed in solutions containing various reversible couples with redox potentials spanning a range larger than the bandgap of silicon. The performance of these photoelectrodes depends strongly on the metal, the charge transfer kinetics at the silicide/solution interface, and the doping density of silicon substrate.

One approach to stabilizing small bandgap semiconductors against photocorrosion in photoelectrochemical (PEC) cells involves the utilization of a thin noble metal overlayer (1). We have recently demonstrated that noble metal silicide-coated n-Si electrodes and suitably modified forms (e.g., with RuO<sub>2</sub>) can photogenerate highly oxidizing species, such as chlorine and oxygen, with durable photoelectrochemical performance in aqueous solutions (2). In the previous work, we proposed that the photovoltage arises at the Si/ silicide junction, based on preliminary studies with a few redox species in solution, and suggested several factors which contribute to the high stability and good performance of these photoelectrodes. However, fundamental investigations of the interfacial energetics and the effect of the charge transfer kinetics at the silicide/ solution interface on the PEC performance were not reported. In this paper, we examine the surface potential of these photoelectrodes as functions of the potential of solution redox couples and the bias potential. We also demonstrate that the performance of these silicide-coated n-Si electrodes depends strongly upon the metal, the charge transfer kinetics at the (silicide/solution) interface, and the doping level of silicon substrate. Additionally, we confirm that constant photopotentials are observed on these electrodes for solution couples with redox potentials spanning a range from -0.67 to +1.1V vs. SCE, which is larger than the bandgap of silicon.

#### Experimental

Silicon substrates for silicide growth were n-Si(100) (0.02-2.5  $\Omega$ -cm) single crystals donated by Texas Instruments and n-Si ( $\sim 1 \Omega$ -cm) polycrystals donated by Dr. R. Noufi. Silicides were prepared by procedures reported previously (2). The detailed procedures for

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<sup>\*</sup> Electrochemical Society Active Member. Key words: semiconductor, photoelectrochemistry, silicides.

preparing the ohmic contacts and mounting and sealing the electrodes were also similar to those previously reported (3). The exposed area of the photoelectrodes ranged from 0.1-0.3 cm<sup>2</sup>. The light source, if not otherwise mentioned, was a tungsten-halogen lamp fitted with a 13 cm-thick water filter with an intensity of 65 mW/cm<sup>2</sup>. The voltammetric experiments were performed with the same apparatus and by procedures previously described. Reagent grade chemicals were used without further purification. All solutions were prepared from triply distilled water. All experiments were carried out with the solution under a nitrogen atmosphere. The electrode arrangement used in the measurement of surface potential is illustrated in Fig. 1. For electrodes used in surface potential measurements, a thicker Pt overlayer was deposited on the silicide layer to lower the sheet resistance to  $<100\Omega$ . A silver contact was made to a portion of silicide overlayer. This Ag layer was sealed, as was the back ohmic contact, with insulating silicone rubber. Strong rectifying behavior in the current-voltage curve was observed between these two contacts indicating the absence of shorts between the two metal layers.

#### **Results and Discussion**

Surface potential of Pt-silicide-coated n-Si electrode. —The surface potential (between PtSi and SCE),  $V_s$ , of n-Si(Pt) electrode at open circuit was the same as the redox potential of the solution, V°, as measured by an independent Pt electrode (see Fig. 2); this demonstrates that the silicide layer was in equilibrium with the solution redox couples.

In a solution containing supporting electrolyte  $(0.5M \text{ Na}_2\text{SO}_4, \text{ pH 5})$  only, no appreciable background current was observed at a Pt electrode over the potential range -0.6 to 0.6V vs. SCE and  $V_s$ , as shown in curve a of Fig. 3, was essentially equal to the applied potential



Fig. 1. The setup and the electrode configuration used in the measurement of surface potential of n-Si(Pt) electrode. V is the high impedance voltmeter consisting of a FET operational amplifier (Type NE 536T) in a voltage follower made with an input impedance  $> 10^8 \Omega$ .



Fig. 2. Surface potential ( $V_s$ ) and rest potential ( $V_{InGa}$ ) of n-Si(Pt) electrode vs. potential of redox couples ( $V^{\circ}$ ) in 1M KCl. a: Fe-EDTA<sup>-/2-</sup>. b: Fe(CN)<sub>6</sub><sup>3-/4-</sup>. c:  $I^-/I_3^-$ . d: Fe<sup>2+/3+</sup>. e: Fe(o-phenanthroline)<sub>3</sub><sup>2+/3+</sup>.



Fig. 3. Surface potential of n-Si(Pt) vs. applied potential in 0.5M Na<sub>2</sub>SO<sub>4</sub> (curve a) and in 0.5M Na<sub>2</sub>SO<sub>4</sub>, 0.5M K<sub>4</sub>Fe(CN)<sub>6</sub>, and 0.5M K<sub>8</sub>Fe(CN)<sub>6</sub> (curve b).

 $V_a$  (where  $V_a$  is the potential between the ohmic contact to Si and SCE). Since  $V_s$  represents the change of the potential drop between PtSi and solution, the results imply that the applied voltage is almost completely absorbed by changes of potential across the Helmholtz double layer (if the potential drop across the diffuse double layer and at the ohmic contact is neglected). (see Scheme I).

When equimolar (0.5M) amounts of  $Fe(CN)_6^{3-}$  and  $Fe(CN)_6^{4-}$  were added to the solution, the rest potential of the n-Si(Pt) electrodes was 0.25V vs. SCE, which is equal to formal potential,  $V^{o'}$ , of the  $Fe(CN)_6^{3-/4-}$  couple. In the dark, a small anodic current was observed when an anodic potential scan (Fig. 4, curve c) was applied to the n-Si(Pt) electrode



Helmholtz double layer

Scheme I. A, top: in terms of interfacial energetics, neglecting the potential drop across the diffuse double layer and at the ohmic contact.  $\Delta V_1 = \Delta V_H = V_a - \frac{F_{redox}}{e}$ ; band-bending unchanged. B, bottom: in terms of distribution of  $V_a$  (vs. reference electrode) in the system. Dotted line: no external bias. Solid line: with external bias.

through the InGa ohmic contact. The potential scan generates a peak current at about -0.38V vs. SCE at a scan rate of 100 mV/s due to mass transport limitations (Fig. 4c). The voltammetric curve of PtSi was obtained by applying a potential scan through the front Ag contact to the PtSi. As shown in curve a of Fig. 4, both anodic and cathodic currents were mass-transfer limited.

The current-voltage curve of the n-Si/PtSi diode (current flow and voltage,  $V_D$ , between InGa to Si and Ag contact to PtSi) is shown in curve b of Fig. 4. In the reverse bias (anodic bias) direction, the current was essentially the same as that in curve c and was much smaller than the anodic current (shown on curve a of Fig. 4) taking place on PtSi. In the forward bias direction, before mass-transfer limitation took over, the diode current was smaller than the cathodic current (shown on curve a of Fig. 4) on PtSi and was nearly equal to the real current flow through the n-Si(Pt) electrode (shown on curve c of Fig. 4).

The system can thus be modeled as the Si-PtSi diode in series with the PtSi/solution interface. At a given current,  $V_a$  is given by the sum of  $V_D$  and  $V_s$  plus any internal iR drops. As shown in curve b of Fig. 3, in the presence of equimolar  $Fe(CN)_{6}^{3-}$  and  $Fe(CN)_{6}^{4-}$ ,  $V_s$  was essentially fixed at  $V_{0}'$  of the  $Fe(CN)_{6}^{3-/4-}$  couple when  $V_a$  was positive of  $V_{0}'$ . When  $V_a$  was negative of the potential at which mass-transfer limitation or the electron-transfer kinetics on PtSi becomes important, the change of  $V_s$  was equal to the change of  $V_a$ . If we assume that the potential drop across the diffuse double layer and at the ohmic contact is negligible, we can calculate the distribution of the applied voltage into the change of band bending,  $\Delta V_b$ , (which is equivalent to the drop across the diode,  $V_D$ ), and the change of potential drop across Helmholtz double layer,  $\Delta V_{\rm H}$ ; this is plotted in Fig. 5. As shown in this figure,  $\Delta V_{\rm H} \simeq 0.0V$ when  $V_a$  is positive of  $V_o'$ , indicating that the applied voltage is mainly absorbed inside the semiconductor.



Fig. 4. a: voltammetric curve on PtSi (through Ag contact). b: current-voltage curve of the n-Si/PtSi diode. c: voltammetric curve on n-Si/PtSi (through InGa contact). Scan rate: 100 mV/s and in 0.5M Na<sub>2</sub>SO<sub>4</sub>, 0.5M K<sub>3</sub>Fe(CN)<sub>6</sub>, and 0.5M K<sub>4</sub>Fe(CN)<sub>6</sub>. pH 5. Exposed PtSi electrode area < 0.1 cm<sup>2</sup>.

When  $V_a$  is negative of  $V_o'$ , the applied voltage distributes both in  $\Delta V_{\rm H}$  and  $\Delta V_{\rm b}$  (Scheme II);  $\Delta V_{\rm b}$  approaches a maximum at a potential near the potential at which the peak current through the system was observed. Then  $\Delta V_{\rm H}$  increases and  $\Delta V_{\rm b}$  decreases steadily because of mass-transfer limitations to the current.

Interfacial energetics.—We have carried out cyclic voltammetry for a variety of redox couples with  $V_{redox}$ 



Fig. 5. The change of band-bending,  $\Delta V_b$ , and the change of potential drop across Helmholtz double layer,  $\Delta V_H$ , as functions of the applied potential,  $V_a$ . Scan rate: 100 mV/s and in 0.5M Na<sub>2</sub>SO<sub>4</sub>, 0.5M K<sub>3</sub>Fe(CN)<sub>6</sub>, and 0.5M K<sub>4</sub>Fe(CN)<sub>6</sub>. pH 5.



Scheme II. A, top: in terms of interfacial energetics.  $\Delta V_1 = \Delta V_H + (V_b' - V_b) V_a = V_s + (V_b' - V_b)$ ; band-bending unchanged. 8, bottom: in terms of distribution of  $V_a$  (vs. reference electrode) in the system.

values spanning a range that is wider than the bandgap of silicon in aqueous solution (see Scheme III). Those redox couples all show one-electron reversible cyclic voltammograms on a Pt electrode (Fig. 6), so that possible complications caused by different interfacial charge transfer kinetics at the silicide/solution interface are not important. As shown in Fig. 6, in the dark,  $MV^{2+}$  is reduced on an n-Si(Ir) electrode with a cathodic peak potential ( $V_{pc}$ ) of -0.9V vs. SCE. No anodic peak corresponding to the reoxidation of MV<sup>+</sup> was observed in the dark, because of the lack of holes in n-Si and the unfavorable energetics for electron injection from solution species. Under illumination with



#### Scheme III

65 mW/cm<sup>2</sup>, MV<sup>2+</sup> is reduced at more negative potential with  $V_{pc}$  at -1.07V and reoxidized with  $V_{pa}$  at -1.01V vs. SCE due to the photogeneration of holes. With  $V_{oc} = |V_{pa}[n-Si(Ir)] - V_{pa}(Pt)|$  (4, 5), this represents  $V_{oc} = 0.4V$  for  $MV^{2+/+}$ . Similar results were obtained for  $Fe(CN)_{6^{3-/4}}$  and  $Fe(o-phenan-throline)^{2+/3+}$ . This constancy of  $V_{oc}$  for various oneelectron reversible redox couples with potentials beyond the bandedges of silicon is consistent with our previous results over a more restricted range (2) and suggests that the electrolyte solution species do not interact with silicon substrate. Rather, the interaction is with the silicide overlayer and the interfacial energetics is dominated by this interaction. Apparently, the interfacial energetics depend strongly upon the coverage of silicide on silicon substrate. Electron spectroscopic (AES and XPS) analyses (2, 8) show that most of the silicide layer we prepared were richer in silicon than in metal. Even under those conditions, n-Si(M) electrodes behave as if the surface of Si electrode were wholly covered by a uniform metal layer. The effect of variation of the thickness of the metal overlayer, the annealing conditions, and coverage of silicides or metals on the interfacial energetics is currently under investigation.

Effect of charge transfer kinetics.—The charge transfer kinetics at the electrode/solution interface might



Fig. 6. Cyclic voltammograms of three reversible couples at scan rate of 100 mV/s on Pt (A) and on n-Si(Ir) (B) in the dark (broken lines) and under illumination with 65 mW/cm<sup>2</sup> (solid curves). Curve a:  $MV^{2+/+}$ . Curve b: Fe(CN)<sub>6</sub><sup>3-/4-</sup>. Curve C: Fe(o-phenanthroline)<sub>3</sub><sup>2+/3+</sup>.

affect the potential at which processes occur, as well as the voltammetric behavior of the photoelectrode and the observed photopotentials (6, 7). This was investigated in the following several experiments. The charge transfer kinetics of the Fe(II)/Fe(III) couple was changed by variation of the concentration of chloride ion,  $[Cl^-]$ . As shown in Fig. 7a, an increase in the concentration of Cl- increased the rate of Fe(II)/ Fe(III) redox reaction at Pt electrode.  $\Delta V_p (\Delta V_p = V_{pa} - V_{pc})$  decreased from 330 mV at [Cl<sup>-</sup>] = 0.0M to 60 mV when  $[Cl^-] = 6M$ , where the reaction approached reversible behavior, without a significant shift in the midpoint potential. The ratio of the anodic peak current  $(i_{pa})$  vs. the cathodic peak current  $(i_{pc})$  approaches unity when  $[Cl^-]$  is increased (9). A similar trend was observed with an n-Si(Ir) electrode under illumination with 80 mW/cm<sup>2</sup> (see Fig. 7b), although the peak potentials were shifted towards more negative values by about 0.4V, as compared with those on Pt (corresponding to the photovoltage observed on those electrodes). This similarity of behavior suggests that the rate-limiting process under illumination is the kinetics of charge transfer at the Si(M)/solution interface.

Effect of dopant concentration in the silicon substrate and type metal (M) overlayer on the voltammetric behavior of n-Si(M) electrode.—The deposition of a metal onto a semiconductor will usually result in the formation of an ohmic contact or a Schottky barrier, depending on the relative work functions of semiconductor and metal, the surface treatment of semiconductor before deposition, and the interfacial chemistry that occurs upon deposition or during annealing (10). By keeping the conditions for etching, metal deposition, and postannealing constant and varying the doping density of silicon substrate, we found very different voltammetric behavior in the dark and under illumination (see Fig. 8). The dark oxidation current increased and the reduction current decreased systematically with decreased resistivity of the silicon wafers, suggesting that samples with a higher resistivity form better rectifying junctions with silicide. Corresponding to this behavior, a better photoeffect was observed on samples with higher resistivity. The photoelectron spectroscopic results (8) suggested that metal diffuses a few hundred angstroms into the silicon substrate. The incorporated transition metal could facilitate electron transfer and recombination in the spacecharge layer. This effect will be more prominent when the width of the space-charge layer becomes narrower due to higher doping density. The incorporated transition metal in the space-charge layer might also form effective recombination centers that scavenge photogenerated holes and thus degrade the photoeffect. This is consistent with the results shown in Fig. 8.

The effect of the nature of the metal on the voltammetric behavior is summarized in Fig. 9. Several interesting conclusions result from these studies. First, the work function of metals listed in Fig. 9 covers a range of at least 0.8V (11); however,  $V_{oc}$  of these silicide-coated n-Si electrodes only covers about 0.25V. This insensitivity of  $V_{oc}$  with respect to the work function of metal is basically consistent with the results observed in solid-state devices (12). Secondly, the higher the rectifying ratio  $(R_r)$  is (the absolute ratio of the dark reduction current vs. the dark oxidation current at equal potential difference with respect to the rest potential), the better the photoeffect is. Both Pt and Ir show very high  $R_r$  values and have high  $V_{oc}$ and short-circuit photocurrents  $(i_{sc})$ , whereas Ru shows poor  $R_r$ ,  $V_{oc}$ , and  $i_{sc}$ . The factors contributing to the poor photoeffect on n-Si(Ru) electrodes are not clear and require further investigation.



Fig. 7. Cl<sup>-</sup> concentration dependence of cyclic voltammograms of Fe<sup>2+</sup> at scan rate of 100 mV/s on Pt (A) and on n-Si(1r) (B) under illumination with 80 mW/cm<sup>2</sup>. Curve a: 5 mM FeSO<sub>4</sub> in 0.5M H<sub>2</sub>SO<sub>4</sub>. Curve b: 5 mM FeSO<sub>4</sub> in 0.5M H<sub>2</sub>SO<sub>4</sub> and 3M NaCl. Curve c: 5 mM FeSO<sub>4</sub> in 1M HCl and 5M LiCl. (Note that potential axis for n-Si(1r) is shifted by 0.4V w.r.t. that for Pt.)



Fig. 8. Effect of doping density on voltammetric behavior of n-Si(1r) in 0.5M K<sub>4</sub>Fe(CN)<sub>6</sub>, 0.1M K<sub>3</sub>Fe(CN)<sub>6</sub>, and 0.5M Na<sub>2</sub>SO<sub>4</sub>. Light intensity at 65 mW/cm<sup>2</sup>. Annealing at 500°C and 10<sup>-6</sup> torr for 10 min. Curves 1 (in the dark) and 2 (under illumination): 2.5  $\Omega$ -cm. Curves 3 (in the dark) and 4 (in the light): 0.2  $\Omega$ -cm. Curves 5 (in the dark) and 6 (under illumination): 0.02  $\Omega$ -cm.

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Fig. 9. Voltammetric behavior of n-Si coated with various kinds of metals in 0.5M K<sub>4</sub>Fe(CN)<sub>6</sub>, 0.1M K<sub>3</sub>Fe(CN)<sub>6</sub>, and 0.5M Na<sub>2</sub>SO<sub>4</sub>. Light intensity 65 mW/cm<sup>2</sup>. Postannealed at 200°-500°C for 5-10 min. Ir: 1 (dark), 2 (light). Pt: 3 (dark), 4 (light). Rh: 5 (dark), 6 (light). Pd: 7 (dark), 8 (light). Ru: 9 (dark), 10 (light).

In conclusion, the measurement of the surface potential of n-Si electrodes coated with a thin layer of noble metal silicide reveals that changes in the applied potential on these electrodes are mainly absorbed across Helmholtz double layer either in the dark or under illumination. A constancy of open-circuit photovoltage was observed on these electrodes for reversible redox couples which span a potential range larger than the bandgap. These EC and PEC characteristics simulate those found when Fermi-level pinning occurs (13). The interfacial charge transfer kinetics at the silicide/ solution interface also plays an important role in the EC and PEC performance, as does the doping density of silicon substrate and the type of metal overlayer.

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# Redox Conduction: Its Use in Electronic Devices

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#### ABSTRACT

A sandwich electrode composed of a film of the electroactive polymer  $[Os(bpy)_2(vpy)_2]^{s+}$ , sandwiched between a Pt disk electrode and a porous Au film, becomes conductive when the Pt and Au potentials are properly poised in relation to the potential at which the Os(III/II) mixed valent state becomes generated. The potential control is normally judged in relation to a reference electrode. The reference electrode can be shorted to, or made common with, the Au electrode, so that twoterminal potential control circuitry can be employed to cause or not cause redox conduction through the sandwich. Such arrangements are used to illustrate principles for using the sandwich electrode as a two-terminal device that acts in a manner similar to a Zener diode, and as a triode-like three-terminal device in which the current between two terminals is controlled by the potential applied at the third.

That electrochemical charge can be transported through films of redox polymer saturated with electrolyte solution and coated on electrodes has been recognized since 1978 (1). Such films can contain the equiv-

Key words: osmium, polymer modified electrode, electron dif-fusion, diode, triode.

alent of thousands of monomolecular layers of electroactive sites yet be rapidly oxidized and reduced by the electrode (2). For a pyrazoline polymer, where the electroactive sites were affixed to the polymer lattice, Kaufman et al. (3) proposed that charge transport can occur by electron self-exchange reactions between oxi-