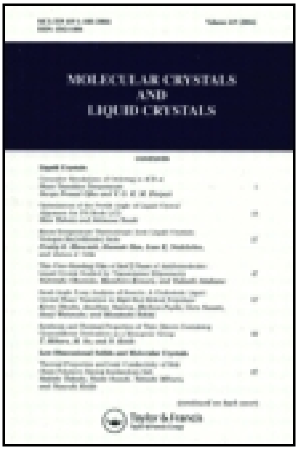

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PHOTOELECTROCHEMICAL SOLAR CELLS: STABILIZATION OF SMALL BAND GAP SEMICONDUCTOR IN AQUEOUS SOLUTION BY SURFACE-ATTACHED ORGANIC CONDUCTING POLYMER[a]

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Surface-attached polypyrrole films have been shown to produce a marked improvement in the stability of n-type single-crystal and polycrystalline Si against oxidation in an aqueous electrolyte. The current production of n-type polycrystalline Si coated with polypyrrole deteriorates less than 30% during 122 hr of irradiation whereas the unprotected bare electrode stops producing photocurrent within 30 s. The polymer protection of the n-type single-crystal Si is significantly less than that of the polycrystalline material because of differences in the adhesion of the polymer film to the electrode surfaces. The adhesion strength is shown to depend on various surface properties of Si and other electrode materials. Moreover, the surface morphology of the electrode affects the topography of the growing surface of the polypyrrole film. Requirements are discussed for the applications of organic conducting polymers to photoelectrochemical devices utilized for solar energy conversion.

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INTRODUCTION

Conversion of sunlight to electricity and fuels is an important but long-term option in providing for man's future energy needs. The possible application of photoactive semiconductor electrodes to solar energy conversion has contributed considerable impetus in recent years to the rapid advancement seen in the field of photoelectrochemistry (PEC). There are two principal forms of PEC cells[1]. In the first form, optical energy induces a current flow that produces a net chemical change in the electrolyte ($\Delta G \neq 0$). The electrolyte product may be stored as a fuel or represent a useful chemical. In the second form of PEC cell, the electrochemical photovoltaic cell, light quantum is converted into electrical energy with no net chemical change in the electrolyte ($\Delta G = 0$).

The focus of this paper is directed to the electrochemical photovoltaic cell, with only brief referral to our work in fuel production. The investigations discussed center on the most serious problem in the application of semiconductors to photoelectrochemical solar cells; namely, the susceptibility of narrow-band-gap n-type semiconductor photoanodes to oxidative degradation.

Figure 1 shows a typical configuration of an electrochemical photovoltaic cell. The cell consists of a reversible redox couple C^+/C a counter electrode and an n-type photoanode. Immersion of the n-type semiconductor and counter electrode into the redox electrolyte results in the interfacial energetics illustrated in the figure. The diagram shows the chemical potential of electrons in the semiconductor (the Fermi level) E_f in equilibirum with the chemical potential of electrons in the solution (the redox potential), E_{redox}. At equilibrium the conduction band CB and valence band VB are bent by up to $E_f - E_{redox}$. E_{BG} is the optical band gap of the semiconductor. Upon illumination of the semiconductor with band-gap radiation, electrons are promoted from the valence band to the conduction band, creating an electron-hole pair at or near the interface. Under the influence of the electric field in the space-charge region, the holes migrate to the semiconductor-liquid interface. The holes will oxidize the semiconductor unless prohibited thermodynamically, or unless scavenged by the reduced half of the redox couple C at the interface. Simultaneously, the electrons are driven into the bulk of the semiconductor, exit at the rear ohmic contact, flow through an external load, and then are injected at the counter electrode-liquid interface to the adsorbed oxidized half of the

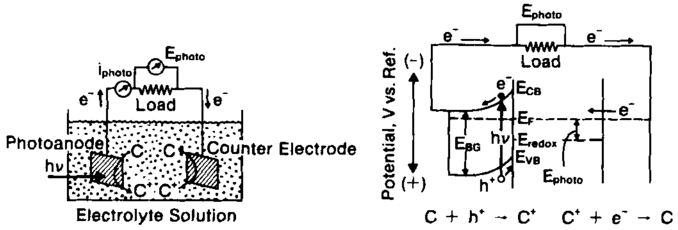

FIGURE 1 An electrochemical photovoltaic cell (left) in operation to convert light to electricity and the associated interface energetics (right).

redox couple C^+. The complementary reactions at the photoanode and the counter electrode produce no net chemical change in the liquid electrolyte; i.e., $\Delta G = 0$, and electrical power is produced in an external load through the photocurrent and photovoltage as a result of the optical excitation of the semiconductor.

The open-circuit photovoltage produced between the illuminated semiconductor and the metal electrode is equal to the difference between the Fermi level of the semiconductor and the redox potential of C^+/C. The photocurrent depends on the optical band gap, the quantum efficiency, and the radiation intensity. Under short-circuit conditions, the Fermi level of the semiconductor and the redox potential of the redox couple of the solution are equalized and a net charge flows during illumination.

Efficient conversion of light energy to electrical power requires the optimization of the product of the external photovoltage and photocurrent, a criterion which is satisfied by materials with band gaps between 1.0 and 1.6 eV, i.e., light absorption beginning between 1250 and 750 nm.

Unfortunately, all known n-type semiconductors with band gaps in this energy range are unstable to current flow in an aqueous electrolyte when exposed to band gap radiation. Instability of the semiconductor entails ionic dissolution, gas evolution, or the formation of a new phase of the electrode when photogenerated holes reach the surface. As a consequence, the simultaneous achievement of electrode stability to oxidation and solar energy conversion to electricity requires the kinetics of the oxidation of the reduced form of the redox couple to strongly predominate over the oxidation of the semiconductor.

Our approach to the corrosion problem has involved coating the surface of the semiconductor with a thin film of an organic conducting polymer to provide a conducting pathway for the removal of photogenerated holes from the electrode surface before they have an opportunity to oxidize the semiconductor. As the organic conducting polymer, polypyrrole was selected. The electrochemical synthesis of the polymer has been developed and characterized by Diaz and coworkers[2]; the resulting polymer exhibits conductivities between 10 and 100 S cm^{-1} and is relatively stable to chemical oxidation. Polypyrrole is conducting in the oxidized state and nonconducting in the neutral state. We have modified the electrochemical synthesis of polypyrrole on semiconductor surfaces to a photoelectrochemical technique as described earlier[3].

N-type Si was selected as the semiconductor electrode, partly because it would be a valuable material for an electrochemical photovoltaic cell if corrosion could be prevented, and partly because the corrosion product SiO_x is generally water insoluble and is an excellent insulator. These particular properties of SiO_x are important for the investigation since any corrosion of Si will be passivated and thus dissolution of the semiconductor surface beneath the polymer film cannot occur.

To monitor the oxide growth, photocurrent-time data were collected. The absence of stability means that the photogenerated holes reaching the surface contribute to the oxidation of Si. The growth of the insulating oxide layer is observable as a decline in the photocurrent with time. A reduced photocurrent is associated with a lower tunneling probability through the oxide. If, on the other hand, the polymer is effective in stabilizing the n-type Si electrode, the photocurrent would be maintained at a constant level with time.

RESULTS AND DISCUSSIONS

Polycrystalline n-type Si

The polycrystalline n-type Si (20 to 30-Ω-cm resistivity) consisted of grains of about 1.5 mm x 4 mm and was fabricated into electrodes as described elsewhere[3]. In Figure 2 the photocurrent-time behavior of the naked and the polypyrrole-coated polycrystalline n-type Si in aqueous iron sulfate solution at pH 1 is presented[3]. The unprotected electrode stops producing photocurrent within one minute, whereas polycrystalline n-type Si coated with polypyrrole

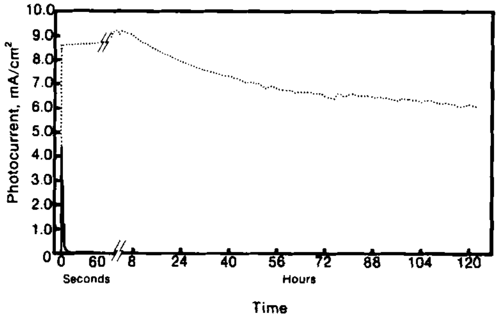

FIGURE 2 Short-circuit photocurrent of naked (-) and polypyrrole covered (•••) polycrystalline n-type Si electrodes in aqueous 0.15 M $FeSO_4$, 0.15 M $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ and 0.1 M Na_2SO_4 at pH 1 under tungsten-halogen illumination at 143 mW/cm^2. No precaution was taken to exclude air.[3]

increases current production about 6% for the first 5 hours and shows a 30% decline in current output over the entire 122 hours of irradiation. The film appeared to adhere well to the electrode surface and exhibited no evidence of dissolution after the transmission of ca. 3100 C/cm^2 at a current density between 6 and 9.2 mA/cm^2. The amount of charge passed after five days was more than 10^5 times that involved in the photoelectrochemical polymerization of the film.

Photocurrent-voltage measurements[3] of the naked and polymer-protected n-type polycrystalline Si were consistent with photocurrent-time data. The photoanodic current of the bare electrode dropped to zero after 1-2 cycles for voltage excursions between 0 and 0.6 V, whereas there was little difference between the photocurrents of the first and the fiftieth scan for the polymer-protected electrode.

The nature of the polymer protection is illustrated schematically in Figure 3. The protection is attributed to the polypyrrole coverage of potential oxide-forming sites on the electrode surface. During illumination, the polymer efficiently transmits holes generated in the semiconductor away from the electrode-polymer interface to ferrous ions before oxidation of the electrode takes place. The choice of the redox couple, the electrolyte, and the pH of the solution can influence the charge-transfer kinetics. The reduced half of the redox couple must compete effectively with the polymer film for the photogenerated holes if irreversible chemical oxidation of the film itself is to be precluded.

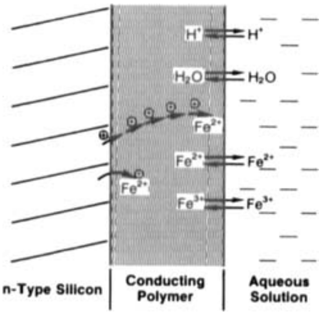

FIGURE 3 Solution-permeable, conducting polypyrrole film containing Fe^{3+}/Fe^{2+}. Charge transfer can take place between the semiconductor and the oxidizable Fe^{2+} ions within the matrix of the film and at the polymer-electrode and polymer-solution interfaces.

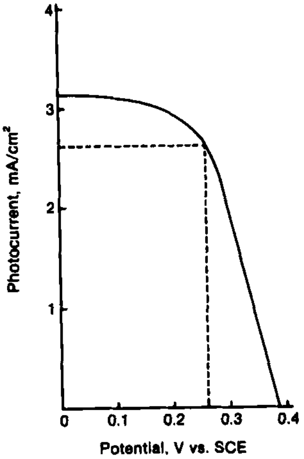

FIGURE 4 Power characteristics of polypyrrole-covered polycrystalline n-type Si electrode in aqueous 0.15 M $FeSO_4$, 0.15 M $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ and 0.1 M Na_2SO_4 at pH 1 under tungsten-halogen illumination at 24.5 mW/cm^2. The radiant power was corrected for absorption due to the electrolyte solution and infrared absorption (mainly, $\lambda < 1200$ nm) of a 4-cm-length water filter.

Figure 4 records the power characteristics of a 1200-Å-thick polypyrrole film coated polycrystalline n-type Si electrode[3]. No attempt was made to optimize the cell; nevertheless, the power conversion efficiency was 3% corresponding to a short-circuit current of 3.2 mA/cm^2, an open-circuit voltage of 0.39 V and a fill factor of 0.6 under tungsten-halogen illumination at 24.5 mW/cm^2. Presumably thinner films and redox couples of more positive potential than that of Fe^{3+}/Fe^{2+} would produce higher photocurrents and photovoltages, respectively. Unfortunately, the photocurrent-voltage curve under intense illumination shows a loss of fill factor and thus efficiency.

Single-crystal n-type Si

Single-crystal wafers of n-type Si (100) of 1 to 2-Ω-cm resistivity were mounted as electrodes and etched according to the procedure described for the polycrystalline n-type Si[3]. It can be seen in Figure 5 that polypyrrole stabilizes single-crystal n-type Si with respect to the bare electrode; the extent of photocurrent stability is, however, much lower for the single-crystal Si than for the polycrystalline materials (cf. Figure 2). The photocurrent of the polymer-protected single-crystal Si declines continuously whereas no signs of photocurrent deterioration are exhibited in the case of the polycrystalline Si over the same period. The difference in photocurrent stability is attributed, at least in part, to the adhesion strength of the polymer to the substrate surface. Adhesion depends on several factors, one of which is the roughness of the substrate surface.

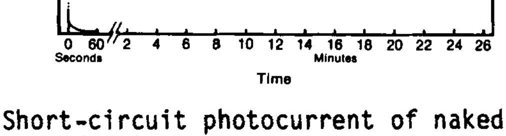

FIGURE 5 Short-circuit photocurrent of naked (-) and polypyrrole covered (•••) single-crystal n-type Si electrodes in aqueous 0.15 M $FeSO_4$, 0.15 M $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ and 0.1 M Na_2SO_4 at pH 1 under tungsten-halogen illumination at 100 mW/cm^2. No precaution was taken to exclude air.

Under similar experimental conditions, polypyrrole films were grown on as-cut single-crystal and as-grown polycrystalline Si. In each case, the polymer protected the substrates against oxide formation in manners similar to those indicated in Figures 2 and 5; however,the film could be removed easily from the single-crystal surfaces but not the polycrystalline surface. Complete disruption of the polymerization of pyrrole on the single-crystal Si surface resulted after the substrate was given a rough polish with 20-µm silicon carbide. The polymerizability of the Si surface was restored, however, after it was polished with 0.3-µm alumina. The effect of the 0.3-µm polish is believed to be associated with more intimate contact between the chemical species involved in the polymerization and the surface atoms of the Si substrate. Further polishing of the same single-crystal Si with still finer particles, 0.05-µm alumina, never produced the relatively strong adhesion observed using the as-grown polycrystalline material.

Another factor affecting adhesion may have been the difference between the surface morphologies of the single-crystal and polycrystalline Si. The polycrystalline Si electrodes employed were composed of millimeter-size grains. Such grains consist of various silicon planes with different spacings between the Si atoms along with dangling bonds present at the grain periphery. In contrast, the single-crystal material has only a single plane. The surface of both forms of Si are expected to be overlaid with a thin (ca. 15 Å) oxide layer to which polypyrrole binds. Differences in the orientation of the planes and lattice spacings may affect the nature of the oxide layer which, in turn, influences the interfacial chemistry taking place during polymerization and the intimate contact area between the polymer film and the substrate.

Doped Tin Oxide and Platinum Electrodes

In addition to Si, polypyrrole has been grown on antimony-doped tin oxide and effects on adhesion due to surface polarity have been observed. To remove hydrophobic contaminants, the surface of Sb/SnO_2 was cleaned with methanol, acetone, 100°C-concentrated H_2SO_4, and distilled water. This treatment produces a surface that water wets and one to which polypyrrole adheres well. In contrast, on the untreated hydrophobic Sb/SnO_2 surface, water beads and the polymer film adheres poorly.

The substrate surface affects, in addition to adhesion,

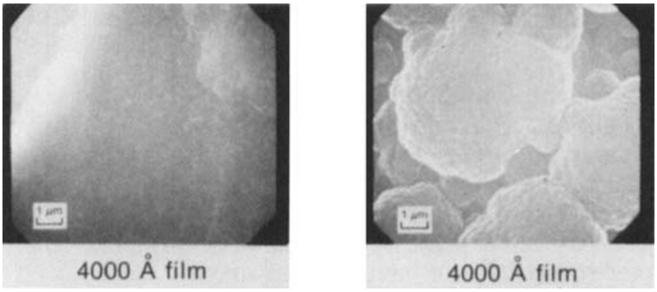

FIGURE 6 SEM of polypyrrole films grown on (a) platinum and (b) indium tin oxide.

the growth pattern of the polymer. The polymer morphology is important in determining the extent of protection imparted to the semiconductor substrate. In Figure 6a, a scanning electron micrograph reveals that the topography of the growing surface of a 4000-Å-thick film on platinum is more compact and featureless than it is on In/SnO_2. On In/SnO_2 (Figure 6b), the film has an uneven surface of hillocks resulting from the preferred growth. The difference in morphology of the polymer grown on the two substrates may be associated with variations in the uniformity of the charge density across the electrode surfaces. The surface of $InSnO_2$ is irregular; these irregularities produce local regions of different resistivities that exist even under constant-current conditions. Regions of high-current densitites produce higher rates of polymerization than those of low-current densitites. The thickness of the polymer film thus varies nonuniformly over the electrode surface. Such morphological change as a function of local variations in the charge density is consistent with the proposal[2] that the polymerization of pyrrole involves the oxidation of individual monomers and does not entail ion or free-radical chain processes.

Criteria for Selection of an Organic Conducting Polymer Material for Stabilization

Criteria can be formulated for the selection of a polymer coating for application in the stabilization of photoactive semiconductor electrodes employed in the photoelectrochemical conversion of solar energy. The specific physical and chemical properties required of a polymer depend on the nature of and the kinetic mechanism for the corrosion of the semiconductor and on the complexity of the kinetics of the redox electrolyte. In general, the corrosion mechanism of semiconductors is complex, involving chemical interaction with the solvent and bond disruption. When the photodecomposition begins, and how rapidly it proceeds, depends on the competition of other redox reactions. Thus the polymer film must conduct the photogenerated minorities in the semiconductor away from the semiconductor-polymer interface to the redox species at a rate that greatly exceeds the rate of photodegradation of the semiconductor.

Rapid charge transmission from the semiconductor can be achieved through several mechanisms. The large surface area of the conducting polymer can provide an entropic driving force for charge removal from the semiconductor due to the high capacitance of the polymer film. In the case of polypyrrole, this is an important effect[4]. Alternatively, electronic rectification at the semiconductor-polymer interface can facilitate charge transport away from the semiconductor. The specific interface energetics depends on whether or not the redox electrolyte can penetrate the polymer film to the semiconductor. If the polymer film is permeable to the solvent, as is the case for polypyrrole films in water, the semiconductor itself can rectify; i.e., form a Schottky barrier with the redox electrolyte. When the redox electrolyte is, to a large measure, excluded from contact with the semiconductor, rectification at the semiconductor-polymer interface depends on the work functions of the two materials. Thus, in this case, a prime consideration for selecting a potential organic conducting polymer material for stabilization is the relationship between the work function ϕ of the polymer P and that of semiconductor sc. Rectifying (Schottky) barriers are formed when $\phi_{sc}^{n\text{-type}} < \phi_{P}^{p\text{-type}}$ or when $\phi_{sc}^{p\text{-type}} < \phi_{P}^{n\text{-type}}$.

To protect the semiconductor against photocorrosion, the polymer must be kinetically inert and/or more thermodynamically stable than both the semiconductor and the redox electrolyte. Inertness depends on the composition of the redox electrolyte (solvent, redox species, counter-ions, etc.). The redox electrolyte must efficiently scavenge the transmitted minority carrier from the polymer if chemical corrosion of the polymer itself is to be avoided. Disruption of the electronic unsaturation of the polymer through chemical reactions with the solvent can produce deterioration of the electrical conductivity and a diminished effectiveness in the stabilization of the semiconductor. Fast removal of charge from the polymer is most likely in the case of single-charge transfer to redox species involving no kinetic complications. Such charge-transfer reactions have high rate constants and may proceed faster than possible chemical transformations of the polymer. This is the case for polypyrrole-coated n-type Si and aqueous Fe^{3+}/Fe^{2+}. Unfortunately, most redox reactions involving the solvent itself are complex (e.g., the electrolysis of water) and take place through a series of steps that can be as kinetically slow as may be the case for the corrosion of the polymer or of the semiconductor itself.

The polymer film must conduct either holes for n-type semiconductors or electrons for p-type materials; i.e., the polymer must possess p-type or n-type character, respectively. Since polypyrrole conducts holes and not electrons, it is most suitable for the protection of n-type materials. Other polymers [2,5] are able to conduct both holes and electrons depending on the chemical environment. The polymer must be able to conduct high densities of minority carriers induced by intense solar light without reducing the fill factor of the semiconductor. The saturation photocurrent will depend on the efficiency of the redox species to remove minority carriers from the polymer.

The extinction coefficient of the polymer should be small over the spectral region where the semiconductor absorbs so as not to attenuate the excitation energy of the semiconductor. Since the oxidized state of polypyrrole has strong, broad absorption bands in the near IR (ε_{max} = 8 x 10^4 cm^{-1}, λ_{max} = 1000 nm) and in the visible (ε_{max} = 5 x 10^4 cm^{-1}, λ_{max} = 400 nm) where Si absorbs (λ_{BG} < 1120 nm), the photocurrent is affected adversely. Finally, as has been discussed, the polymer must have strong adhesion in order to stabilize the semiconductor.

In summary, the required physical and chemical properties of a potentially efficient conducting polymer for stabilizing photoelectrochemical solar energy devices include:

(1) high conductivity;
(2) high rectification at polymer-semiconductor interface;
(3) good electronic transport at high solar light intensities (80-140 mW/cm^2);
(4) high transparency to solar light where semiconductor absorbs;
(5) strong adhesion to semiconductor; and
(6) long-term chemical and electrical stability at operating temperatures.

In addition to these properties, there are economic constraints for the application of a potentially efficient organic conducting polymer to a PEC cell. The economic considerations are that the material be inexpensive, readily available and easily fabricated into the device.

CONCLUSION

In conclusion, polypyrrole films produce a marked improvement in the stability of n-type Si against photoanodic corrosion in an aqueous electrolyte. The polymer exhibits good adhesion to polycrystalline n-type Si. The adhesion of the polymer to single-crystal n-type Si is not as good, although this situation may be remedied by surface treatment techniques[6,7]. Other electrode materials are being examined with polypyrrole films that are suitable for energy storage. The results of these studies[8,9] appear very promising for the potential application of organic conducting polymers to photoelectrochemical devices for solar energy conversion.

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