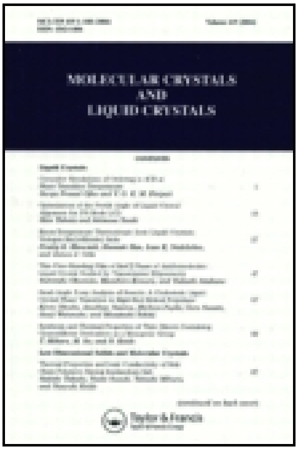

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POLYPYRROLE - SEMICONDUCTOR PHOTOVOLTAIC DEVICES

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Thin transparent and conductive films of polypyrrole have been grown by photoassisted electrochemical oxidation on n-type single crystal Si and hydrogenated amorphous Si electrodes. The junction formation between polypyrrole and Si has been studied and indicates an electronegativity of polypyrrole about the same as Au. Highly stable photoanodes based on n-Si protected with a thin coating of Pt and electrochemically grown polypyrrole films have been studied as electrochemical photovoltaic cells in aqueous I^-/I_3^-, $Fe^{2+/3+}$, and $Fe(CN)_6^{4-/3-}$ electrolytes. In the I^-/I_3^- electrolyte the cells are stable over a time period of weeks. Solid state Schottky cells using polypyrrole as the front contact yield efficiencies inferior to those of the electrochemcial cells due to high sheet resistivity in the polypyrrole layer.

INTRODUCTION

Solar cells based on semiconductor-electrolyte Schottky junctions have drawn considerable attention in recent years due to the possibility of manufacturing efficient and inexpensive junctions.[1]

The principles of operation of an electrochemical photovoltaic cell (EPC) based on an n-type semiconductor

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photoanode are illustrated in Figure 1. A sufficiently oxidative redox couple (A/A^+) spontaneously forms a rectifying (Schottky) junction with an n-type semiconductor upon immersion of the semiconductor in the electrolyte by equilibration of the bulk fermi level of the semiconductor with the redox potential of the electrolyte. Upon illumination with light of above band gap energy the photogenerated holes, migrating to the interface under the influence of the built-in potential will perform electrochemical oxidation by oxidating A to A^+ which is subsequently reduced at the counter electrode (e.g., Pt) to A for a zero net free energy change of the solutions. The key problem to widespread utilization remains the oxidative decomposition/passivation of small band gap semiconductors under illumination.

Lately, one of the innovative concepts proposed to protect the semiconductor surface against photocorrosion has been to coat the semiconductor with thin transparent films of highly conductive polypyrrole (PPy) doped with BF_4^-.[2-7] Electrochemically grown thin films of BF_4^- doped PPy have metallic conductivity, are insoluble and have long term stability.[8,9]

When PPy films are generated on the bare semiconductor surface only partial stabilization against photocorrosion results.[2,3,6] Long term stability can be achieved

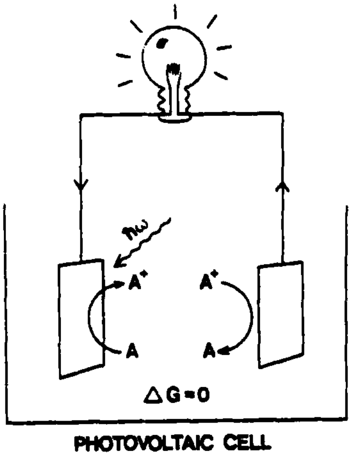

FIGURE 1 The principles of operation of a regenerative electrochemical photovoltaic cell (EPC).

with single crystal n-Si electrodes in aqueous iodide/triiodide electrolytes by modifying the semiconductor surface with a thin (5-20 Å) Pt layer before electro-deposition of the PPy.[4,5] Stable photoanodes of n-Si have also been reported with thin Au films and concentrated electrolyte solutions.[7]

In this paper we report on some recent studies with n-Si/Pt/PPy photoanodes in aqueous electrolytes containing the redox couples $Fe(CN)_6^{3-/4-}$, I^-/I_3^-, and $Fe^{2+/3+}$. We also report results with solid state Schottky barrier devices formed between PPy and single crystal n-Si and hydrogenated amorphous Si(a-Si:H). The solid state devices have been used to study the electronegativity of PPy by analyzing the barrier height formed with n-Si and a-Si:H substrates as well as from the point of view of solid state Schottky barrier solar cells. The results indicate a high electronegativity of PPy.

RESULTS AND DISCUSSION

The electrodes were fabricated using 2.0 ohm-cm single crystal n-Si wafers and were prepared and coated as described elsewhere.[5] Samples of glow discharge produced a-Si:H were provided by A. E. Delahoy, F. J. Kampas, and P. E. Vanier of Brookhaven National Laboratory. Electrolytes were prepared with reagent grade chemicals and doubly distilled water. The electrolytes used were the following:

A. 0.2M $K_4Fe(CN)_6$, 0.1M $K_3Fe(CN)_6$, 0.2M KCl pH=7.2
B. 1.0M KI, 0.1M I_2, 0.2M KCl pH=6.9
C. 0.5M $FeSO_4$, 0.15M $Fe_2(SO_4)_3$, 0.2M Na_2SO_4 pH=1.0

Figure 2 shows an energy level model of the PPy protective function on n-Si photoanodes. A bare n-Si electrode will be passivated by the growth of an insulating oxide film. A redox couple in the solution is not able to prevent the oxide formation which is thermodynamically and kinetically favored over hole scavenging by the reduced species of the redox ions. The polypyrrole film is able to change the charge transfer kinetics such that the thermodynamically less favored reaction with the redox species predominates over the thermodynamically more favored reaction of oxide growth. The polypyrrole in this case acts as a hole mediator between the semiconductor and the redox species. Since PPy is a metallic conductor the

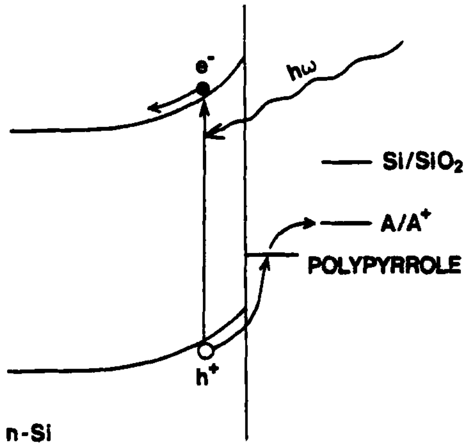

FIGURE 2 Energy level model of the PPy protective function on an n-Si photoanode.

holes would emerge at the fermi level of PPy. The scheme would only work if polypyrrole has a high electronegativity and forms a rectifying barrier with n-Si. A low electronegativity contact metal would lead to a reduced barrier height or even ohmic contact and consequently negligible photovoltage. The barrier height formed between PPy and n-Si therefore becomes an important parameter of the system.

Polypyrrole Electronegativity

We have used three techniques to measure the height of the Schottky barrier: current-voltage (I-V), capacitance-voltage (C-V), and internal photoemission (IPE). The contact to the front surface of the PPy was made with a gold plated wire on a microprobe. Au makes an ohmic contact with PPy. The I-V, C-V, and IPE measurements are described elsewhere.[10] The results of barrier height measurements on diodes formed with PPy on n-Si, n-Si/Pt, and a-Si:H substrates are given in Table I and compared with an n-Si/Au reference diode. The n-Si/PPy diodes yield an average barrier height value of 0.8 with a scatter between 0.7 and 0.9. The C-V measurements cannot be easily interpreted because the shape of the C-V curve as well as the capacitance level changed with time. The

Table I.

Sample	I(V)		C(V)		IPE
	ϕ_B (eV)	n	V_{bi} (V)	ϕ_B (eV)	ϕ_B (eV)
n-Si/PP	0.8	2.2	—	—	0.74
n-Si/20Å Pt/PP	0.74	1.4	0.8	1.06	—
a-Si/PP	0.8	2.25	—	—	0.9
n-Si/Au	0.75	1.11	0.49	0.75	0.75

Table I Barrier height measurements of PPy on n-Si, n-Si/20 Å Pt, a-Si:H as measured with three independent techniques: current-voltage, capacitance-voltage, and internal photoemission. A reference n-Si/Au diode is also included.

IPE yields the more consistent results and a barrier height about the same as that of Au.

The measurements on a-Si/PPy yield a barrier height of 0.9 eV which is about 0.2 eV lower than published values for a-Si/Pt diodes.

The results, when compared with the reference diodes, indicate an electronegativity (or work function) of PPy about the same as that of Au and slightly less than Pt.

Electrochemical Photovoltaic Cells

The illuminated current-voltage characteristics of n-Si/-Pt/PPy electrolyte Pt cells with 20 Å Pt coatings and about 1000 Å PPy films are shown in Figure 3. Power conversion efficiencies were 4.1%, 3.6%, and 3.0% with I^-/I_3^-, $Fe^{2+/3+}$, and $Fe(CN)_6{}^{4-/3-}$ redox couples respectively under illumination of 55 mW/cm^2 unfiltered tungsten-halogen light. No correction was made for reflection or electrolyte absorption. The efficiencies with the $Fe^{2+/3+}$ and $Fe(CN)_6{}^{3-/4-}$ redox couples were consistently lower suggesting less efficient charge transfer kinetics perhaps due to a preferred interdiffusion of I^- in the PPy film relative to that of the Fe^{2+} and $Fe(CN)_6{}^{4-}$ ions. Efficiencies as high as 5.5% under similar conditions have been achieved with the I^-/I_3^- redox couple.[5] Most cells fall in the 3-5% range. The fill factors and consequently the efficiencies decrease somewhat at higher light intensities. PPy coated p-Si

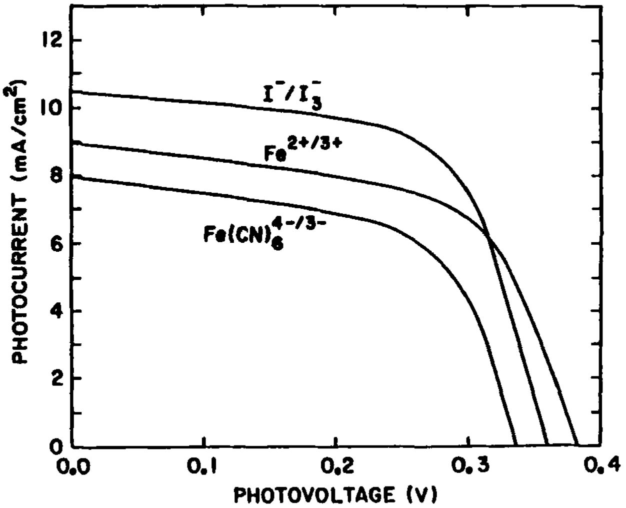

FIGURE 3 Illuminated current-voltage characteristics of n-Si/Pt/PPy||electrolyte||Pt cells with 20 Å Pt and about 1000 Å PPy films in electrolytes A, B, and C. The power conversion efficiencies were 4.1%, 3.6%, and 3.0% and the fill factors 0.62, 0.58, and 0.58 with the I^-/I_3^-, $Fe^{2+/3+}$, and $Fe(CN)_6^{4-/3-}$ respectively. The illumination was 55 mW/cm^2 tungsten-halogen light.

electrodes (with or without Pt), on the other hand, gave photopotentials in the mV range and μA photocurrents consistent with the data assigning a high electronegativity to PPy which would produce only a small barrier with p-Si.

The stability of the cells was determined by monitoring the photocurrent as a function of time with constant illumination. Absence of stability indicates growth of a passivating oxide layer at the semiconductor-polymer interface. Figure 4 shows the photocurrent vs time behavior for three representative cells. In the I^-/I_3^- electrolyte the cell showed no decay after more than 450 hours of illumination. With the $Fe^{2+/3+}$ and $Fe(CN)_6^{4/3-}$ electrolytes the cells did not show long term stability suggesting a kinetically inferior charge-transfer process. At lower light intensities (10-20 mA/cm^2) the degree of stability improved substantially. Electrodes with PPy films but without the Pt surface modification decayed in a few hours with no initial stabilization and bare Si

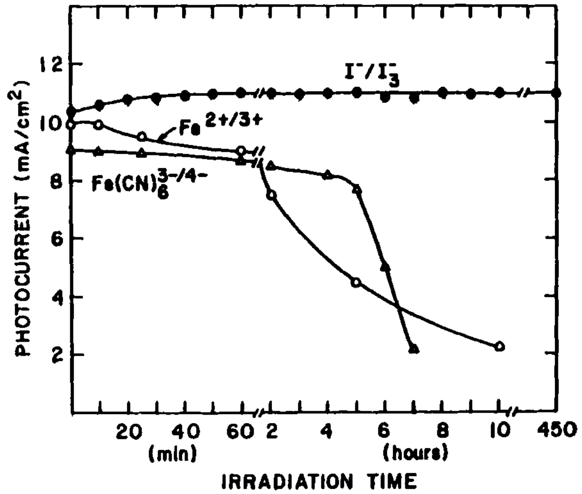

FIGURE 4 Photocurrent as a function of time with constant illumination for three n-Si/20 Å Pt/~1000 Å PPy electrodes in I^-/I_3^- (solid circles), $Fe^{2+/3+}$ (open circles), and $Fe(CN)_6^{4-/3-}$ (triangles) electrolytes under 55 mW/cm² tungsten-halogen illumination.

electrodes in less than one minute. Electrodes with only Pt coating (no PPy) also decayed more rapidly than those with Pt/PPy coating. Increased stability has also been achieved with a-Si:H electrodes and is reported elsewhere.[4] For the unstable cells the stability improves with lower light intensities and deteriorates further at higher light intensities.

The more rapid decay with electrodes without the Pt layer could be due to several factors. Scanning electron micrographs of PPy films grown on bare Si and Pt modified Si surfaces show a difference in morphology suggesting a more porous structure for the films grown on bare Si.[5] Films grown on Si/Pt are smooth and almost featureless. This may result in a better surface coverage facilitating the transport of holes to the electrolyte via the polymer. The smooth and featureless morphology is generated despite the fact that the Pt layer of the thickness in question forms isolated islands rather than continuous films.[11] In addition to forming islands on the surface the Pt layer also extends to considerable depths into the

Si crystal itself.[5] Auger electron spectroscopy shows that the surface layer is composed mostly of Pt and oxygen from the native oxide layer of about 10 Å thickness. Significant amounts of Pt is detected to depths of more than 100 Å below the surface probably due to interstitial diffusion of Pt.

A separate measure of the improved semiconductor-polymer interface contact (with the Pt coating) is provided by the lower value of the junction quality factor (n) (Table 1). A value of 1 indicates a perfect junction and values higher than 2 have been attributed to non-uniformities in the distribution of recombination centers at the interface.[12]

Thin PPy films have also been observed to adhere more strongly to Pt electrodes than to bare Si electrodes where they easily peel off. This stronger bonding may also aid in the charge transfer kinetics.

Schottky Barrier Cells

Solid state Schottky barrier cells made by growing thin transparent PPy films on n-Si substrates were tested for their solar energy conversion efficiency. Figure 5 is a schematic diagram of the structure of the cell. The front contact to the PPy could be made with a Hg drop or by a Au coated wire mounted on a microprobe. Evaporating front metal contacts proved difficult as the metal (Au or Al) diffuse through the PPy layer and form a direct contact with the semiconductor.

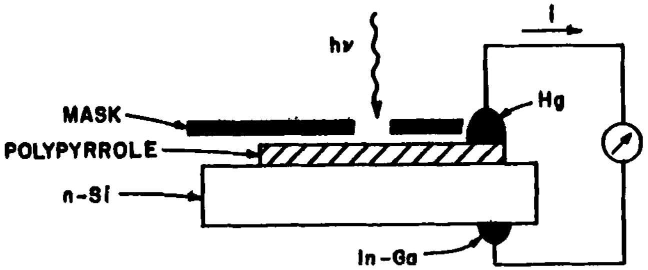

Figure 5 Schematic cell configuration of n-Si/PPy/Hg solid state cell. the mask left an exposed area of 3 mm^2.

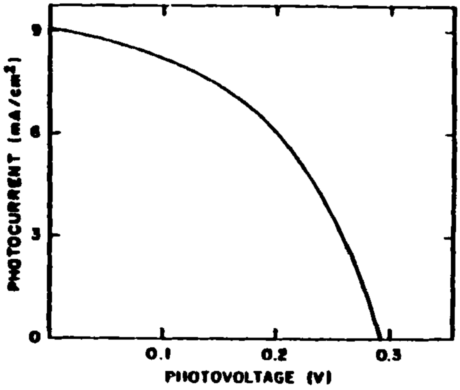

Figure 6 Illuminated current-voltage characteristics of an n-Si/PPy/Hg cell with #1000 Å PPy under illumination of 100 mW/cm^2 tungsten-halogen light.

Figure 6 shows the illuminated current-voltage characteristics of a n-Si/PPy/Hg cell with about 1000 Å PPy. The illumination was 100 mW/cm^2 tungsten-halogen light. The energy conversion efficiency was 1.24% with a fill factor of 0.46. The low fill factor can be attributed to a relatively high series resistance due to the sheet resistivity of the porous PPy film being considerably higher than that of common metals. Constructing conductive polymer-semiconductor Schottky barrier cells may be advantageous in the case where the polymer work function is larger than that of common metals (e.g. $(SN)_x$). This may yield barrier heights and consequently photovoltages which are higher than those available using high work function common metals.[13] There is no such advantage with PPy which has a work function about the same as Au. Using Pt modified electrodes did not lead to any substantial improvement in the conversion efficiency for the solid state cells.

CONCLUSION

The n-Si/Pt/PPy||electrolyte||Pt cells represent substantial progress in the development of stable and efficient Si based EPC devices. PPy is a high work function polymeric metal which forms a Schottky barrier with n-Si. The work function of PPy is about the same as that of Au giving a barrier height of 0.75V with n-Si. The work function of PPy is not as high as that of some other conductive polymers (e.g., $(SN)_x$), and this limits the output voltage of EPC and Schottky barrier devices and accounts for the high degree of surface pinning which has been observed.[5] Other polymers are under investigation which may possess the stability, conductivity, and ease of fabrication of PPy and with the requisite electronegativity for making efficient energy conversion devices.

ACKNOWLEDGEMENT

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