On the Role of Surface States in Semiconductor Electrode Photoelectrochemical Cells

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FARADAY DISCUSSIONS
OF
THE ROYAL SOCIETY OF CHEMISTRY

No. 70
PHOTOELECTROCHEMISTRY

1980

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Received 6th May, 1980

Surface states that occur at the semiconductor–liquid interface play an important role in the behaviour of that interface and affect the efficiency of photoelectrochemical solar devices. The nature of such states and evidence for their existence will be briefly reviewed. Their role in dark electron transfer reactions for redox couples with energies within the band-gap region and in mediating surface recombinations will be discussed. The importance of Fermi-level pinning by surface states at moderate densities in GaAs and Si in controlling the open-circuit photovoltage and the observed electrochemical behaviour will be described. The effect of the surface pretreatment on the photoelectrochemical behaviour of p-GaAs and n-WSe_2 will be demonstrated.

In many ways the development of models for the semiconductor–liquid interface has paralleled that for the metal–semiconductor (M/SC) junction. The earliest models of M/SC junctions (Schottky barriers) by Schottky[1] and Mott[2] proposed a barrier equal to the difference in work functions between the metal and the semiconductor forming the contact. Subsequent experimental studies, however, showed considerable deviations from the predicted behaviour and the suggestion was put forth[3] that surface states at the interface play an important role in determining the barrier height. Many theoretical and experimental studies have subsequently demonstrated the existence of such states and their effects on the junction characteristics. [See, for example ref. (4), (5) and references therein.] In a similar way the barrier at the semiconductor–solution interface has often been taken to be the difference between the flat-band potential of the semiconductor, V_{fb}, and the redox potential of a solution couple, V_{redox}, although as early as 1959 the importance of surface states in determining the potential distribution at this interface was indicated.[6] It now appears clear that the behaviour of semiconductor electrodes is critically dependent upon the nature of the electrode surface and that the ideal model involving a state-free band gap is rarely applicable.

For the purposes of this paper surface states will be taken to mean surface electronic energy levels with energies different from the allowed levels in the bulk semiconductor. They may be states which arise because the lattice is terminated (" dangling bonds " or " intrinsic surface states "), because of lattice defects, vacancies or differences between the surface composition and that of the bulk, or because of adsorption of electron acceptor or donor species (" impurity states ") which may act as surface states themselves or induce defect states in the semiconductor material. The number, distribution and energies of the surface states may depend not only upon the type of material employed and the crystal face exposed, but also upon the composition of the solution phase and the nature of the surface pretreatment before the junction is formed.

Surface states can play an important role in the behaviour of semiconductor elec-

trodes. Dark redox processes of couples with energies located in the gap region may be promoted by such states. Under these circumstances the states may also behave as recombination centres and lead to decreased quantum efficiencies in photelectrochemical (PEC) cells. A high density of these levels may lead to " Fermi-level pinning " in which the observed photopotential becomes independent of the redox potential of the solution couple and photoprocesses are observed for couples whose energy levels apparently lie well outside the band-gap region (as determined by measurements made in the absence of the redox couple).[7–9] Surface states may also play a role in the catalysis of electron-transfer reactions at the semiconductor electrode surface, in the quenching of spectral sensitization processes by dye layers, and in the photodecomposition reactions of the semiconductors. In this paper we discuss and give several examples of surface-state effects in PEC cells and demonstrate that surface treatments of the semiconductor can be significant factors in the behaviour of these electrodes.

EXPERIMENTAL

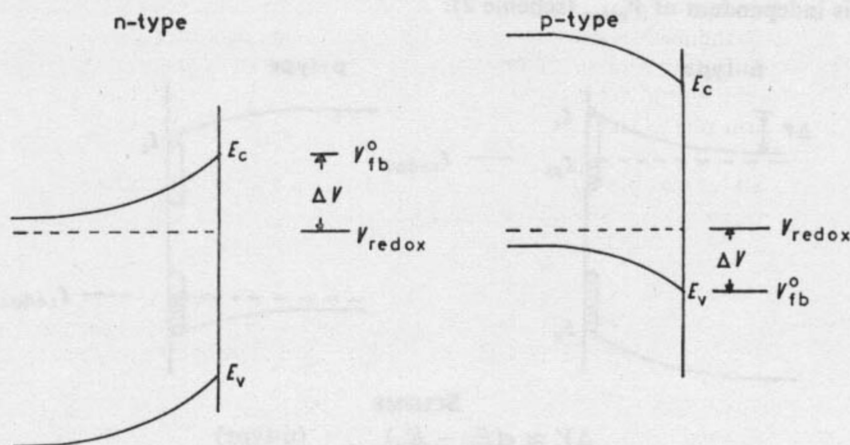
The sources of the semiconductor materials (all single crystals), the method of mounting and producing ohmic contacts, and the apparatus used in the measurements have been previously described.[9–11] The electrodes were illuminated with either a 450 W Xe lamp with suitable filters or a 1.6 mW He–Ne laser.

RESULTS AND DISCUSSION

FERMI-LEVEL PINNING BY SURFACE STATES

PRINCIPLE

The qualitative and quantitative aspects of Fermi-level pinning at the semiconductor–solution interface have been discussed in some detail,[7–9] so that only the basic principles will be reviewed here. The model for the surface-state–free-semiconductor function can be represented as shown in scheme 1.[12,13] The flat-band potential, V_{fb}, measured in a solution in the absence of a redox couple (V°_{fb}), corresponds fairly closely to the energy of the conduction band edge (E_c) in an n-type semiconductor or to the valence band edge (E_v) in a p-type material. At V_{fb} in the absence of specific adsorption, the potential drop across the Helmholtz layer, $\Delta\varphi_H$, corresponds to that attributable to oriented dipoles at the interface, V_d, while the potential drop across the space-charge region of the semiconductor, $\Delta\varphi_{SC}$, is zero. (In all cases we assume a



SCHEME 1

reasonably concentrated electrolyte so that the potential drop across the diffuse double layer can be neglected.) When the potential difference between the bulk semiconductor and the solution is varied either by application of an external potential or by introduction of an appropriate redox couple (located at $E_{redox} = -eV_{redox}$) in solution, $\Delta\varphi_H$ remains largely unchanged while $\Delta\varphi_{SC}$ essentially equals that of the applied potential (assuming no specific adsorption of the redox couple and no change in V_d). This is the basis for the usual model in which the band edges are said to remain fixed [*i.e.*, $\Delta(\Delta\varphi_H) \approx 0$] and in which the open-circuit photopotential (ΔV) under high illumination intensities is

$$\Delta V = | V^{\circ}_{fb} - V_{redox} |. \tag{1}$$

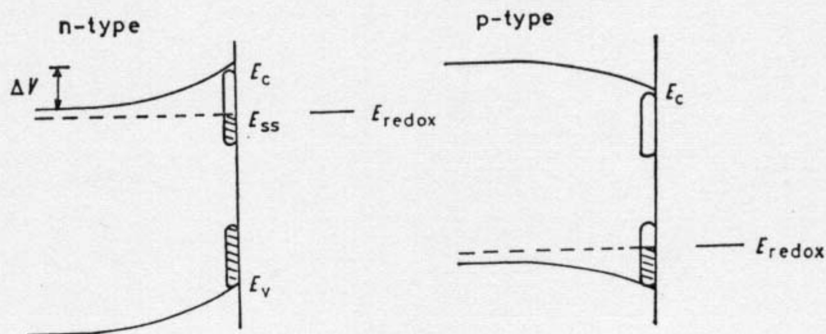
For couples with energies outside the band gap, no photoresponse is expected. Eqn (1) is the basis for the selection of redox couples with potentials corresponding to energies near the valence band edge (for n-type) or near the conduction band edge (for p-type) to maximize the output photovoltage of a PEC cell.

The flat-band potential will be shifted by specific adsorption of ions, since the potential drop across the Helmholtz layer in the presence of surface charge, q_s, is given by

$$\Delta\varphi_H = \frac{q_s}{C_H} + V_d = \frac{q_s}{\varepsilon\varepsilon_0/d} + V_d \tag{2}$$

where C_H is the Helmholtz layer capacitance, ε is the dielectric constant, ε_0 the permittivity of free space, and d the thickness of the Helmholtz layer. Thus adsorption of anions ($q_s < 0$) will cause a negative shift in V_{fb}, while cation adsorption ($q_s > 0$) causes a positive shift.

If surface states are present, they may be filled or emptied either by interaction with solution redox couples, or by photoprocesses or by charge redistribution within the semiconductor. The overall effect of such filling or emptying of the surface states is to produce surface charge which is a function of the number of surface states and their occupancy. As suggested by eqn (2) the flat-band potential will shift, producing a shift in the relative location of the conduction and valence band edges with respect to a solution redox-couple energy level. If the surface state density is sufficiently large, a potential change between semiconductor and solution will result in an almost equal change in $\Delta\varphi_H$ (with $\Delta\varphi_{SC}$ remaining almost constant). Under these conditions the Fermi level is pinned to the energy level of the surface states (E_{ss}) and the photopotential is independent of V_{redox} (scheme 2):



SCHEME

$$\Delta V \approx e(E_c - E_{ss}) \quad \text{(n-type)} \tag{3a}$$

$$\Delta V \approx e(E - E) \quad \text{(p-type).} \tag{3b}$$

When Fermi-level pinning exists, photoeffects may be observed for couples whose redox potentials are such that they are apparently located outside of the gap region (based on the V°_{fb} value). We have previously suggested[7] that the high density of surface states can be viewed as a metal overlayer on the semiconductor. This overlayer forms a Schottky barrier with the semiconductor with a height which is independent of the solution redox couple. The overlayer will come into electronic equilibrium with the solution redox couple.

The main point of the argument is that surface charge can cause shifts in the flat-band potential and under some conditions lead to pinning. While we have described these effects in terms of surface states (rather broadly defined), electron injection into the conduction band or hole injection into the valence band (inversion layer formation,[14] or the modification of the electrode surface by the attachment of donor or acceptor molecules[15] can also produce such effects.

We and Wrighton and co-workers[7–9] previously gave examples of the Fermi-level

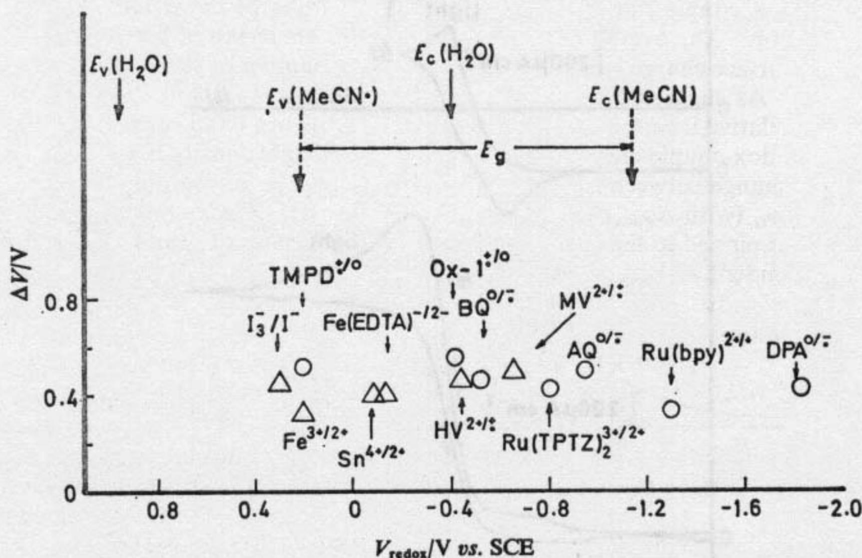


FIG. 1.—Photovoltage as a function of the standard potentials of redox couples. Photovoltage is taken to be the difference in the standard potential of the redox couple and the peak of the photocathodic wave in a cyclic voltammetry scan of the illuminated semiconductor under conditions where photocurrent is limited by diffusion of the redox reagent in the quiet solution (○ for n-GaAs/MeCN, 0.1 mol dm^{-3} TBAP); ΔV in p-GaAs/H_2O (symbolized by △) is the difference between the standard potential of the redox couple and the onset photopotential of the photocathodic wave. Abbreviations: TMPD = *NNN'N'*-tetramethyl-*p*-phenylene-diamine; Ox-1 = oxazine-1; BQ = benzoquinone; HV = *NN'*-diheptyl-4,4'-bipyridium; MV = *NN'*-dimethyl-4,4'-bipyridium; AQ = anthraquinone; bpy = 2,2'-bipyridine; TPTZ = 2,4,6-tripyridyl-*s*-triazine; DPA = diphenylanthracene: EDTA = ethylenediamine-tetra-acetic acid.

pinning effects at n- and p-GaAs and p-Si in acetonitrile (MeCN) and aqueous solutions. Typical results for n-GaAs in MeCN[16] and p-GaAs in water[9] are shown in plots of ΔV *vs.* V_{redox} in fig. 1. The deviation of the results from eqn (1) and the near independence of $V\Delta$ for couples spanning a potential range wider than E_g for GaAs is consistent with the pinning model.

Liquid ammonia cells.—A particularly striking result of Fermi-level pinning is observed in electrochemical studies of p-GaAs and p-Si in liquid ammonia.[17,18]

Typical results are shown in fig. 2. The cyclic voltammetric scan in NH_3/0.1 mol dm^{-3} KI at a Pt electrode [curve (*a*)] shows that the cathodic current attributable to solvated electron injection starts at -2.4 V [*vs.* $Ag/Ag^+(NH_3)$], with the collection of electrons occurring on scan reversal.[19] At p-GaAs in the same solution negligible currents are observed in the dark in this potential range. However, under steady or chopped illumination with light of energy greater than E_g, a cathodic photocurrent commencing

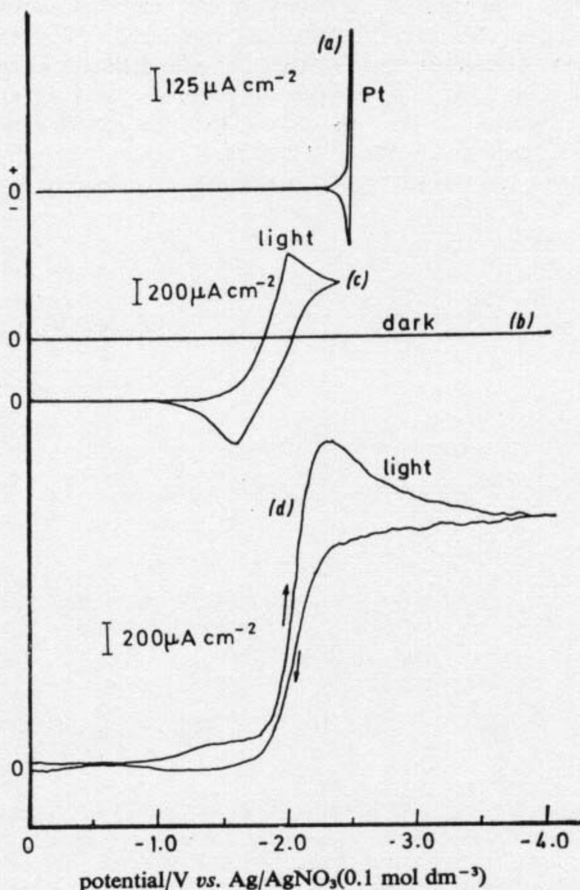


FIG. 2.—(*a*) Cyclic voltammetric background current for a Pt disc electrode in liquid ammonia. Scan rate 200 mV s^{-1}. (*b*) A similar scan for p-GaAs and p-Si in the dark. (*c*) p-GaAs under constant (sun-lamp) illumination. Scan rate 100 mV s^{-1}. (*d*) p-Si under constant (sunlamp) illumination. Scan rate 100 mV s^{-1}.

at *ca* -1.5 V is observed [curve (*c*)]. The blue coloration near the electrode surface during the cathodic pulses clearly indicates that the process is the photoinjection of electrons which occurs at potentials considerably less negative than the reversible value for this process. The V°_{fb}-value for n-GaAs determined by capacitance measurements in this solvent (Schottky–Mott plot) is *ca* -1.2 V. Very similar effects are found for p-Si in liquid ammonia [curve (*d*)] where V°_{fb} for n-Si in the absence of excess electrons is *ca* -0.8 V.[18] For both semiconductors, PEC cells can be constructed. The cell p-GaAs/e_s^-, KI, NH_3/Pt shows an open-circuit photovoltage (V_{oc}) of 0.7 V, while the

cell p-Si/e_s^-, KI, NH_3/Pt yields $V_{oc} = 0.57$ V. Details of the behaviour of these and several other semiconductors with several redox couples in liquid NH_3 will be published elsewhere.[18]

p-WSe_2-NITROBENZENE SYSTEMS

With p-WSe_2 in MeCN photocurrents are also observed for couples located at redox potentials more negative than the conduction band edge [as determined from V_{fb}° of p- and n-WSe_2 in 0.1 mol dm^{-3} tetra-n-butyl ammonium perchlorate (TBAP)/MeCN]. The band structure and relevant energy levels are shown in fig. 3. Consider the voltammetric behaviour of nitrobenzene ($PhNO_2$) shown in fig. 4. The photoelectro-

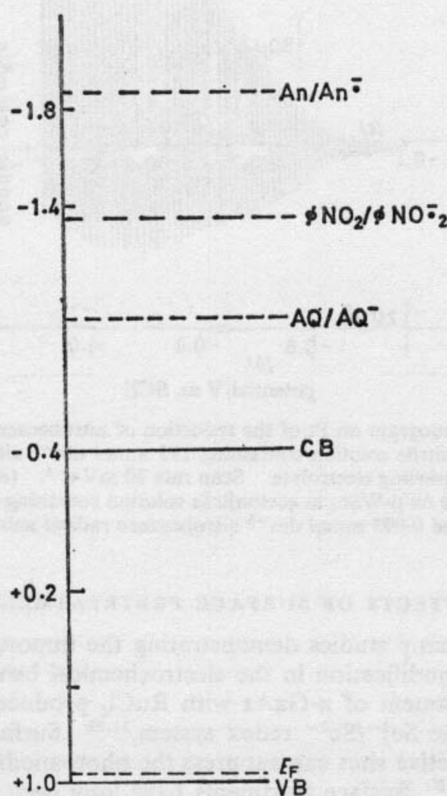


FIG. 3.—Schematic representation of the energetic situation at p-WSe_2/electrolyte interface.

chemical behaviour of $PhNO_2$ is of interest because highly concentrated solutions of it and its radical anion can be prepared in MeCN, thus minimizing the mass transfer limitations often observed in non-aqueous PEC cells.[20] The reduction of $PhNO_2$ at Pt occurs at -1.33 V *vs.* SCE [curve (*a*)]. Under illumination with the chopped beam of a He–Ne laser (1.6 mW) no photocurrent is observed at p-WSe_2 even when the potential is swept to -1.0 V [curve (*b*)] for a solution of 0.2 mol dm^{-3} $PhNO_2$ + 0.1 mol dm^{-3} TBAP/MeCN. However, if a small amount (*ca.* 0.095 mmol dm^{-3}) of $PhNO_2^-$ is electrogenerated in the solution at a Pt electrode, a photocurrent is observed at p-WSe_2 beginning at *ca.* -0.4 V [curve (*c*)]. Similar effects are observed with anthracene and anthraquinone at p-WSe_2 in MeCN. No cathodic photocurrents are

observed unless radical anion is first generated in the solution. We propose that the electrogenerated radical anions inject charge into the p-WSe_2 surface. This negative charge causes a shift in V_{fb} to more negative values until pinning at the potential of the $PhNO_2/PhNO_2^{\cdot-}$ is obtained. At this point the conduction band is located at an energy where photogenerated electrons can be injected to produce more $PhNO_2^{\cdot-}$.

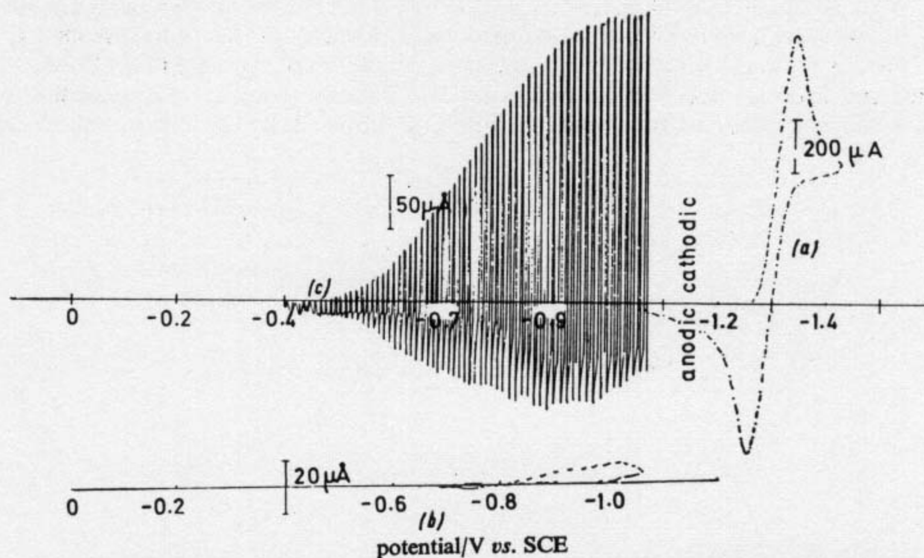


FIG. 4.—(*a*) Cyclic voltammogram on Pt of the reduction of nitrobenzene. (*b*) Dark voltammetric curve on p-WSe_2 in acetonitrile solution containing 195 mmol dm^{-3} nitrobenzene. 0.1 mol dm^{-3} TBAP was used as the supporting electrolyte. Scan rate 20 mV s^{-1}. (*c*) Current–potential characteristic under chopped light on p-WSe_2 in acetonitrile solution contaning 0.2 mol dm^{-3} nitrobenzene and 0.095 mmol dm^{-3} nitrobenzene radical anion.

EFFECTS OF SURFACE PRETREATMENTS

There have been many studies demonstrating the importance of semiconductor surface treatment or modification in the electrochemical behaviour.[15,21–25] For example the surface treatment of n-GaAs with $RuCl_3$ produced higher efficiencies in PEC cells based on the Se_2^{2-}/Se^{2-} redox system.[21,22] Surface modification by the attachment of electroactive sites can suppress the photoanodic decomposition of the semiconductor lattice.[15] Surface treatments have long been used in the fabrication of solid-state devices. We discuss here two examples of the application of surface treatments to suppress recombination and improve photoresponse.

EFFECT OF Cl^- ON n-WSe_2/MeCN SYSTEM

Layered-type transition metal chalcogenides such as $MoSe_2$ and WSe_2 have been investigated rather extensively.[26–34] The behaviour of such materials is critically dependent upon the character of the surface. Thus single crystals which show smooth and defect-free van der Waals surfaces ($\perp$ *c* axis) (referred to here as " Type S ") produce low dark currents and high efficiencies in PEC cells. However, the presence of defects, discontinuities or exposed edges on the van der Waals surface produce electrodes (referred to here as " Type E ") which show appreciable dark currents and

poorer photoresponse presumably because these edges provide sites for dark oxidation (at the n-type material) and recombination.[33,34] We report here experiments on n-WSe_2 in MeCN and the effect of surface treatment on the behaviour of Type E electrodes. Typical behaviour of a Type E n-WSe_2 electrode in MeCN/0.2 mol dm^{-3} TBAP containing thianthrene (TH) is shown in fig. 5. A quasireversible oxidation

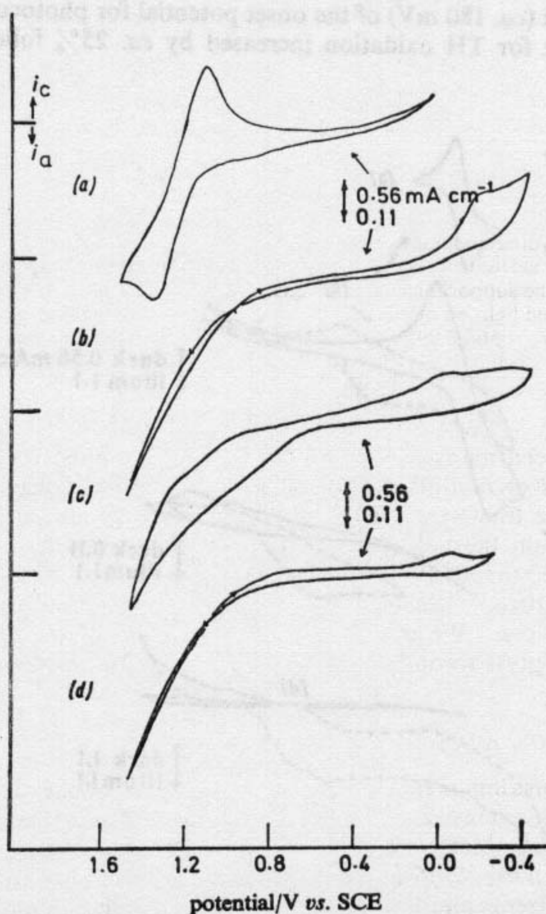


FIG. 5.—Effect of bulk halide on dark currents at Type E n-WSe_2 electrode. (*a*) 5 mmol dm^{-3} thianthrene (TH); (*b*) 5 mmol dm^{-3} TH and 15 mmol dm^{-3} TBAI; (*c*) 5 mmol dm^{-3} TH and 10. mmol dm^{-3} TBABr; (*d*) 5 mmol dm^{-3} TH and 10 mmol dm^{-3} TEACl. Scan rate 100 mV s^{-1} 0.2 mol dm^{-3} TBAP as the supporting electrolyte.

wave is shown in the dark [curve (*a*)]; the charge transfer leading to the oxidation has been attributed to conduction along the edges of the van der Waals planes to surface discontinuities.[34] Addition of 5-10 mmol dm^{-3} of I^-, Br^- or Cl^- to the solution causes significant decreases in the dark current [curves (*b*), (*c*) and (*d*)]. Addition of Cl^- also affects the photo-oxidation of TH at n-WSe_2 (fig. 6); the anodic photocurrent for TH oxidation starts at potentials *ca.* 0.23 V less positive in solutions containing Cl^-. Neither Br^- nor I^- show this effect on the TH photocurrent in MeCN. To demonstrate that this effect results from the interaction of Cl^- with the surface discontinuities, the experiment illustrated by fig. 7 was undertaken.

A fresh Type E electrode was prepared and the dark- and photo-oxidation of TH was observed [curves (*a*) and (*b*)]. The electrode was then removed and dipped into a MeCN solution of 7.0 mmol dm^{-3} TBACl in the dark without any external electrical connection. After 30 s, the electrode was removed, rinsed thoroughly with MeCN and placed back into the original TH-containing solution. The resulting cyclic voltammograms [curves (*c*) and (*d*)] showed an immediate decrease in the dark current and a negative shift (*ca.* 180 mV) of the onset potential for photocurrent. The maximum photocurrent for TH oxidation increased by *ca.* 25% following this surface

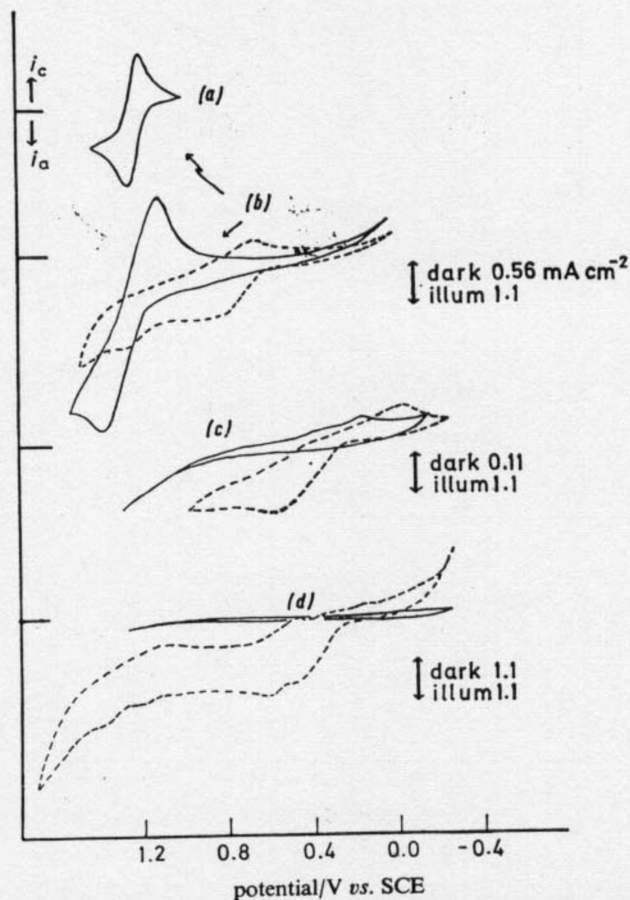


FIG. 6.—Effect of chloride on photo-oxidation of thianthrene; 5 mmol dm^{-3} TH, 10 mmol dm^{-3} TBACl and 0.2 mol dm^{-3} TBAP in acetonitrile solution. Solid lines indicate dark current; broken lines indicate photocurrent; (*a*) TH at platinum, (*b*) TH only, (*c*) 10 mmol dm^{-3} TEACl, (*d*) 5 mmol dm^{-3} TH and 10 mmol dm^{-3} TEACl.

treatment. This improved photocurrent–potential curve remained unchanged for at least 30 min of continuous cycling. When a similar experiment was carried out with a Type S electrode, no changes in the dark oxidation current (which was negligible) or the photocurrent was found by a Cl$^-$ pretreatment. Note that the decrease in dark current for the Type E electrode upon treatment with Cl$^-$ takes place without any possibility of photo-oxidation occurring during the exposure of the electrode to Cl$^-$ so that the formation of a light-induced complex between the electrode and Cl$^-$ is

unlikely. The observed effect can be ascribed to interactions of the Cl^- with surface discontinuities leading to modification or passivation of these sites. Similar shifts in photopotential of redox couples in aqueous media have been found by Tributsch and co-workers[26,30] by the addition of the I^-/I_2 couple.

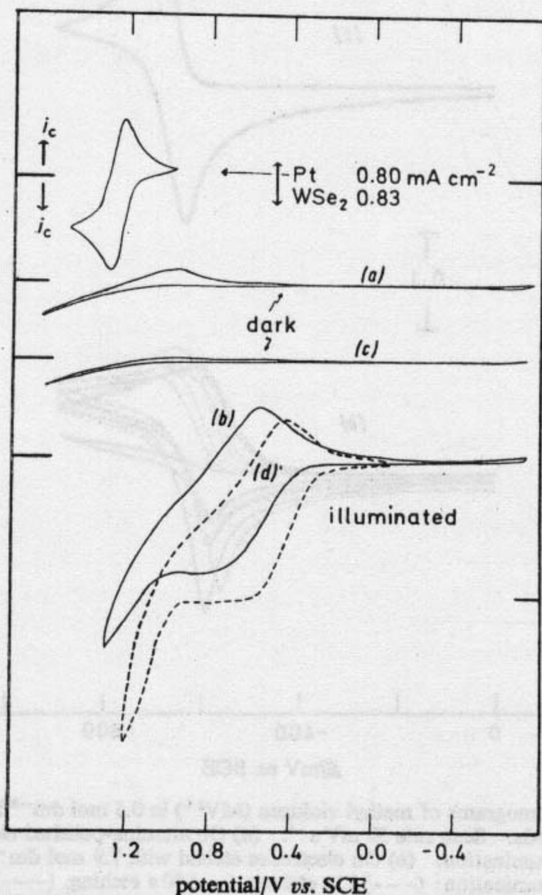


Fig. 7.—Effect of dipping Type E n-WSe_2 electrode into 7 mmol dm^{-3} TEACl solution. (*a*) Dark oxidation of 5 mmol dm^{-3} TH on untreated electrode. (*b*) Photo-oxidation of 5 mmol dm^{-3} TH on untreated electrode. (*c*) Dark oxidation of TH after Cl^- treatment. (*d*) Photocurrent after Cl^- treatment.

HNO_3 ETCHING OF p-GaAs

Surface pretreatment also affected the dark and photoresponses of a p-GaAs electrode. The behaviour of an HCl-etched p-GaAs single-crystal electrode in aqueous solution of *NN'*-dimethyl-4,4'-bipyridinium (or methyl viologen, MV^{2+}) has been reported.[10] When a p-GaAs crystal (100 face) was polished first with SiC paper and then with 0.5 μm alumina powder on felt until a mirror-like surface is obtained and then used as an electrode in the MV^{2+} medium, the dark *i–V* curves were practically the same as those observed at a metal electrode and no photoresponse was obtained (fig. 8) [curve (*a*)]. A scanning electron micrograph of this surface is shown in fig. 9 (*a*). X-ray fluorescence measurements of this electrode surface show *K*-series peaks for

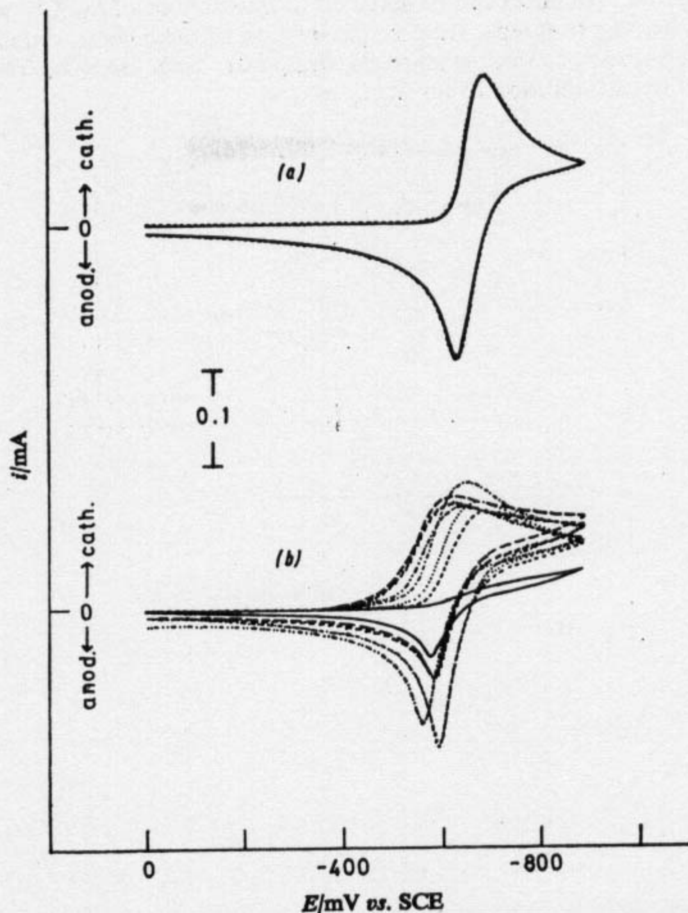


FIG. 8.—Cyclic voltammograms of methyl viologen (MV^{2+}) in 0.5 mol dm^{-3} Na_2SO_4 aqueous solution on p-GaAs electrode. Scan rate 50 mV s^{-1}. (*a*) On alumina-polished electrode: (——) in the dark; (– – –) under illumination. (*b*) On electrodes etched with 7.9 mol dm^{-3} HNO_3 acid: (——) in the dark; under illumination: (– – –) 15 s etching, (· · ·) 30 s etching, (–·–·–) 1 min etching, (–··–) 2 min etching, (⁓⁓⁓) 5 min etching, and (— — —) 10 min etching.

Ga (9.25 keV) and As (10.54 keV) with the Ga peaks larger than the ones for As. The effect of etching the electrode with 7.9 mol dm^{-3} HNO_3 for various lengths of time is illustrated in fig. 8 and 9. Even a very brief immersion (*ca.* 15 s) causes a significant decrease in the dark current and improved photoresponse [curve (*b*)]. Continued etching for times up to 10 min showed constant improvement in the photoresponse and changes in the electrode surface. X-ray fluorescence measurements show a continual increase in the ratio of As/Ga peak heights with the electrode which has been etched for 10 min yielding almost no Ga peak. The high As levels appear to be associated with the crystallites which are formed on the surface during etching, since X-ray fluorescence measurements on the exposed flat surfaces of the electrodes in fig. 9 (*b*), (*c*) and (*d*) continue to show a As/Ga peak height ratio close to that for the polished electrode. Etching with 0.9 mol dm^{-3} HNO_3 for periods of up to 80 min was ineffective in improving the dark current or photoresponse of the p-GaAs electrode and an electrode so treated showed behaviour similar to that in fig. 8(*a*).

These results can be interpreted in terms of the existence of a very disturbed surface with a high population of states formed by the polishing. Grinding or polishing of semiconductors is known to induce states in the gap.[35] The material then shows a metallic behaviour. Etching of the surface removes the damaged layer and may also cause passivation of surface states. Recent experiments have suggested that deposition of small amounts of metal on the electrode surface can produce similar effects.

CONCLUSIONS

The results here, as well as numerous past studies of junctions to semiconductors, demonstrate the importance of surface states in the interpretation of photoelectrochemical behaviour. For semiconductors where pinning is observed these effects allow photoprocesses to occur which would not be predicted from V°_{fb} measurements. This has been demonstrated here for p-type materials where the photoreduction of couples with very negative redox potentials is found. In principle a similar effect should be possible at n-type semiconductors and couples with very positive redox levels. However, in this case hole injection into the valence band with decomposition of the semiconductor may occur.

Surface states may also play an important role in the catalysis of surface chemical reactions in a manner similar to that seen in electrochemical reactions at metal electrodes. For example the photoproduction of hydrogen probably involves as a first step the formation of a hydrogen atom (H·). Since the potential for this reaction in bulk aqueous solution is very negative (*ca.* -2.1 V *vs.* NHE), production of H_2 will probably require the presence of surface sites which will adsorb H· quite strongly and also promote their combination. Similarly adsorption of hydroxyl radicals is required for O_2 production.

An understanding of the chemical and physical nature of the surface states on a molecular level is clearly needed. Such an understanding is only now beginning to emerge in studies of semiconductor surfaces in a high vacuum environment. For example the pinning of GaSb, GaAs and InP surface at the same level by submonolayer coverage of metals and oxygen has recently been reported and ascribed to the induced formation of defect levels by the adatoms.[4] Induced defect levels and impurity levels may similarly be formed at the semiconductor–liquid interfaces (*i.e.*, the surfaces may change in the act of forming the junction), but *in situ* molecular or microscopic characterization of these will be difficult. A general observation from all of these results is that the character of the semiconductor–liquid junction is very specific for the particular conditions existing at that junction and the method of pretreatment of the surface. It will be very difficult therefore to provide a general theoretical model which will allow prediction of the interface properties simply from the characteristics of semiconductor and solution phases. Similar opinions have been expressed concerning the metal–semiconductor Schottky barrier.[36]

The support of this research by the National Science Foundation, the Solar Energy Research Institute and the Office of Naval Research is gratefully acknowledged. We are indebted to Dr. Richard Malpas for the liquid ammonia measurements. We also acknowledge a fellowship to A. S. G. by the Consejo Nacional de Investigaciones Científicas y Técnicas de la Republica Argentina.

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