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On The Role of Surface States in

Semiconductor Electrode

Photoelectrochemical Cells

by

Allen J. Bard, Fu-Ren F. Fan, Alberto S. Gioda,

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On the Role of Surface States in Semiconductor Electrode Photoelectrochemical Cells

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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-WSe₂ 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.

ROLE OF SURFACE STATES

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 photelectro-
chemical (PEC) cells.   A high density of these levels may lead to " Fermi level pin-
ning " in which the observed photopotential becomes independent of the redox poten-
tial 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 photodecomposi-
tion 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 pre-
viously 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

PRINCIPLES

The qualitative and quantitative aspects of Fermi level pinning at the semicon-
ductor–solution interface have been discussed in some detail,[7-9] so that only ...e 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}^o), 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
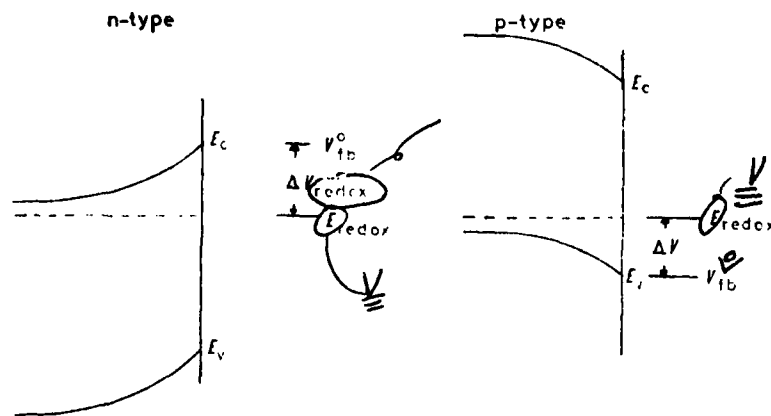
SCHEME 1

space charge region of the semiconductor, $\Delta\varphi_{sc}$, is zero. (In all cases we assume a 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 of 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 by either interaction with solution redox couples, 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):

$$\Delta V \approx e(E_c - E_{ss}) \qquad \text{(n-type)} \tag{3a}$$
$$\Delta V \approx e(E_{ss} - E_v) \qquad \text{(p-type).} \tag{3b}$$
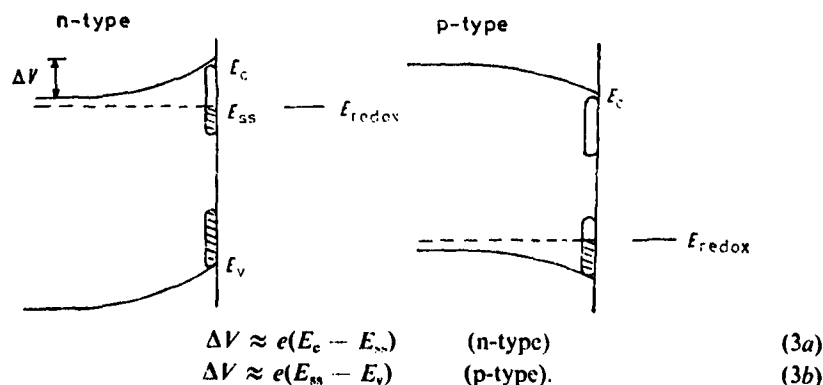
Scheme 2

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 flatband 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
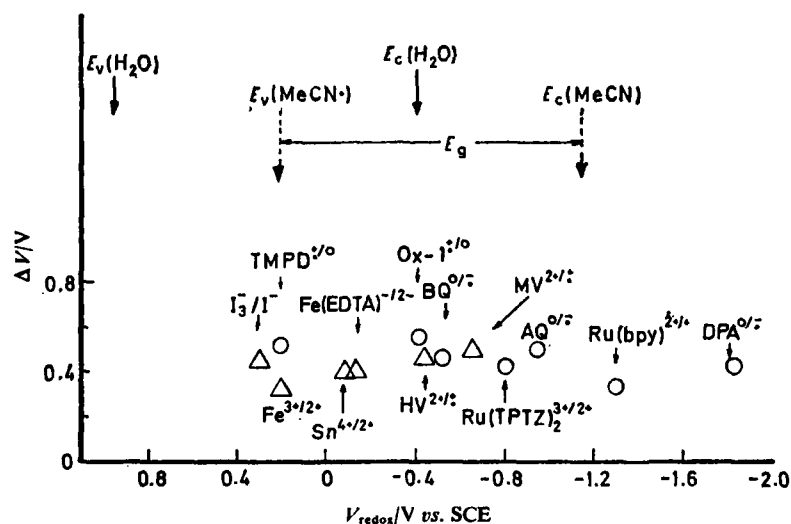
FIG. 1.—Photovoltage as a function of the standard potentials of redox couples. Photovoltage is taken to be the difference in the standard potential of the redox couple and the peak of the photocathodic wave in a cyclic voltammetry scan of the illuminated semiconductor under conditions where photocurrent is limited by diffusion of the redox reagent in the quiet solution (o for n-GaAs/MeCN, 0.1 mol dm^{-3} TBAP); ΔV in p-GaAs/H$_2$O (symbolized by Δ) 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 ₙn plots of ΔV vs. V_{redox} in Fig. 1. The deviation of the results from eq. (1) and the near independence of ΔV 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 $NH_3/0.1$ M 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
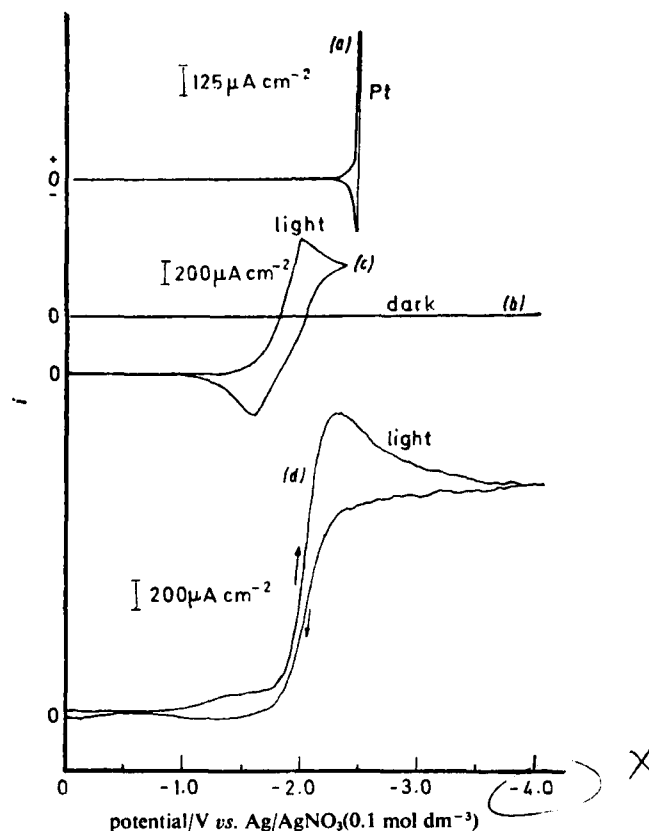
FIG. 2.—(a) Cyclic voltammetric background current for a Pt disc electrode in liquid ammonia. Scan rate 200 mV s^{-1}. (b) A similar scan for p-GaAs and p-Si in the dark. (c) p-GaAs under constant (sun-lamp) illumination. Scan rate 100 mV s^{-1}. (d) p-Si under constant (sunlamp) illumination. Scan rate 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}^0 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$_A$. 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 volt-ammetric behaviour of nitrobenzene (PhNO$_2$) shown in fig. 4. The photoelectro-
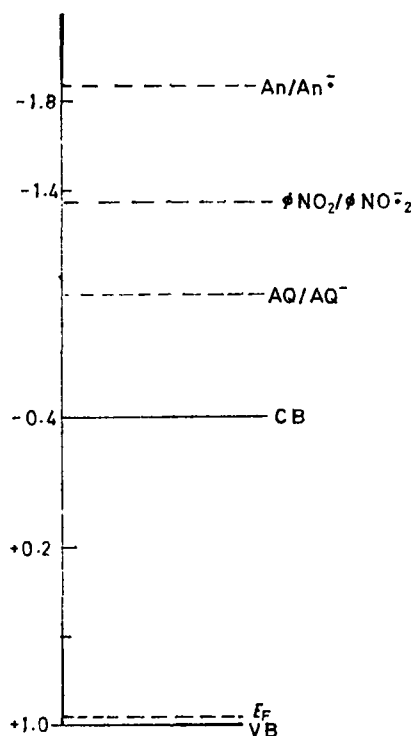
FIG. 3.—Schematic representation of the energetic situation at p-WSe$_2$/electrolyte interface.

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$_A$mol 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 anth-racene 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$_2$ is obtained.   At this point the conduction band is located at an energy
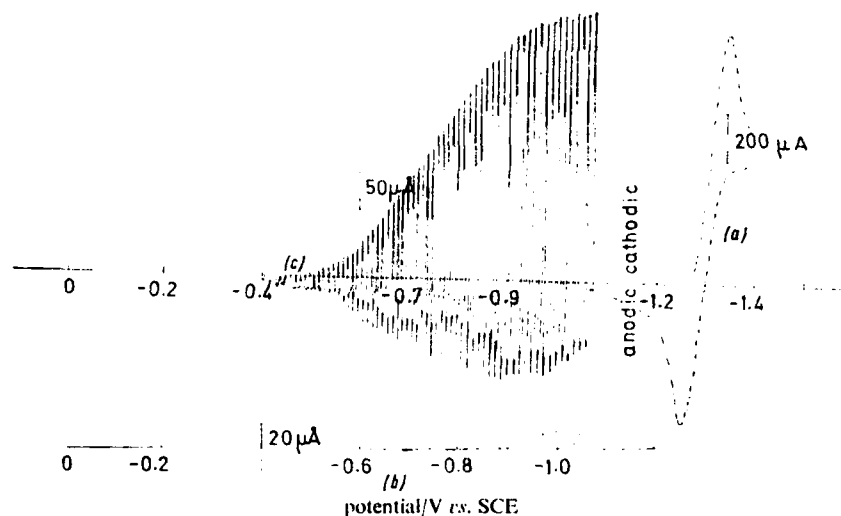where photogenerated electrons can be injected to produce more PhNO$_2^-$.

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 charac-
teristic 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 ex-
ample 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 de-
pendent 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 ") pro-
duce 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 elec-
trodes (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
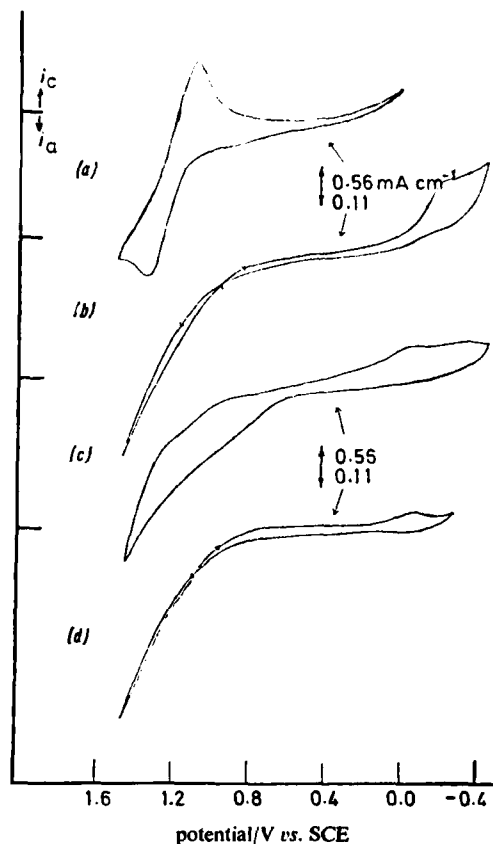

FIG. 5.—Effect of bulk halide on dark currents at Type E n-WSe$_2$ electrode. (a) 5 mmol dm^{-3} thianthrene (TH); (b) 5 mmol dm^{-3} TH and 15 mmol dm^{-3} TBAI; (c) 5 mmol dm^{-3} TH and 10. mmol dm^{-3} TBABr; (d) 5 mmol dm^{-3} TH and 10 mmol dm^{-3} TMACl.   Scan rate 100 mV s^{-1} 0.2 mol dm^{-3} 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 of 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
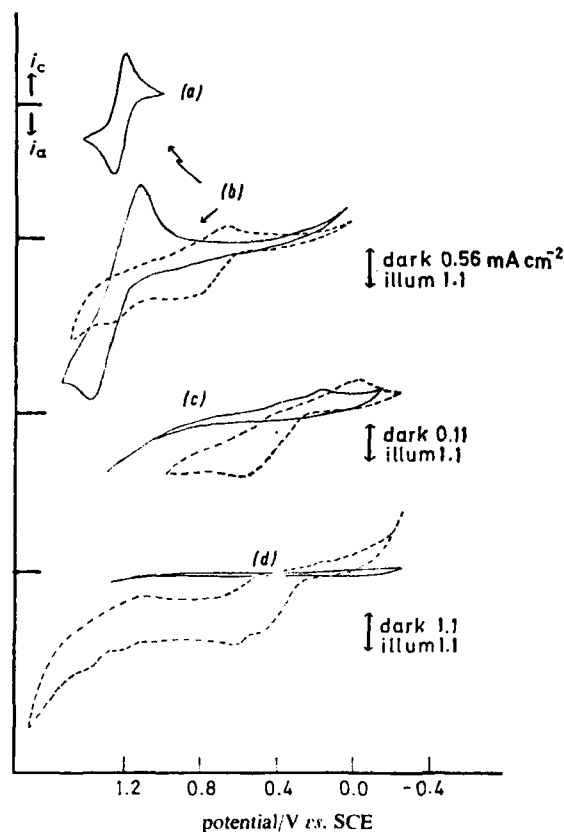
Fig. 6.—Effect of chloride on photo-oxidation of thianthrene; 5 mmol dm^{-3} TH, 10 mmol dm^{-3} TBACl and 0.2 mol dm^{-3} TBAP in acetonitrile solution. Solid lines indicate dark current; broken lines indicate photocurrent; ~~same conditions of TH and Cl⁻ in mixed solution.~~

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

(a) TH at platinum; (b) TH only; (c) 10 mM TEACl;
(d) 5 mM TH and 10 mM TEACl.

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.
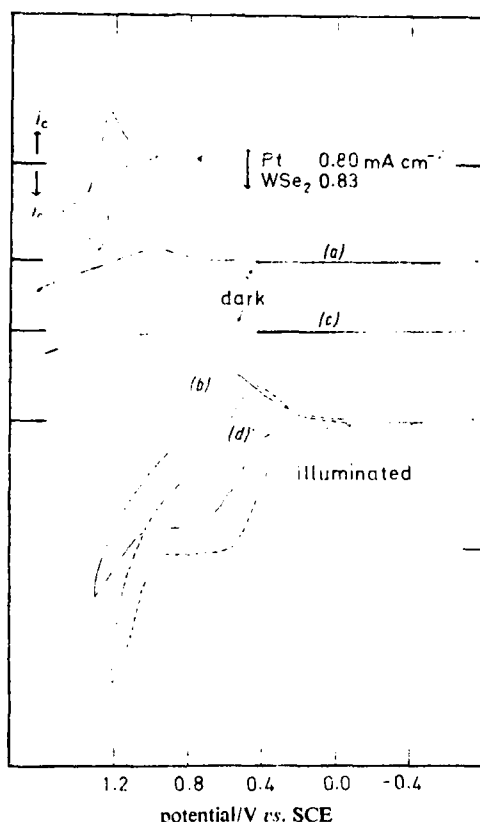

Fig. 7.—Effect of dipping Type E n-WSe$_2$ electrode into 7 mmol dm^{-3} TEACl solution.   (a) Dark oxidation of 5 mmol dm^{-3} TH on untreated electrode.   (b) Photo-oxidation of 5 mmol dm^{-3} TH on untreated electrode.   (c) Dark oxidation of TH after Cl^- treatment.   (d) Photocurrent after Cl^- 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 N,N'-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 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
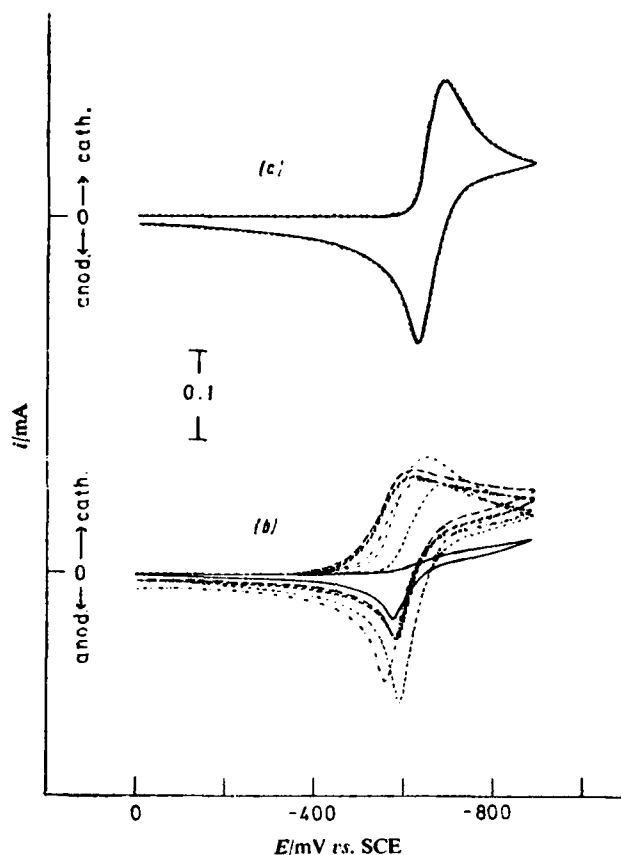
Fig. 8.—Cyclic voltammograms o methyl viologen (MV^{2+}) in 0.5 mol dm^{-3} Na$_2$SO$_4$ aqueous solution on p-GaAs electrode.   Scan rate 50 mV s^{-1}.   (a) On alumina polished electrode: (——) in the dark; (– – –) under illumination.   (b) On electrodes etched with 3.7 mol dm^{-3} HNO$_3$ acid: (——) 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 3.7 mol dm^{-3} HNO$_3$ for various lengths of time is illustrated in fig. 8 and 9.   Even a very brief immersion (~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]

[1] W. Schottky, Naturwiss., 1938, 26, 843.
[2] N. F. Mott, Proc. Cambridge Phil. Soc., 1938, 34, 568.
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100 μm

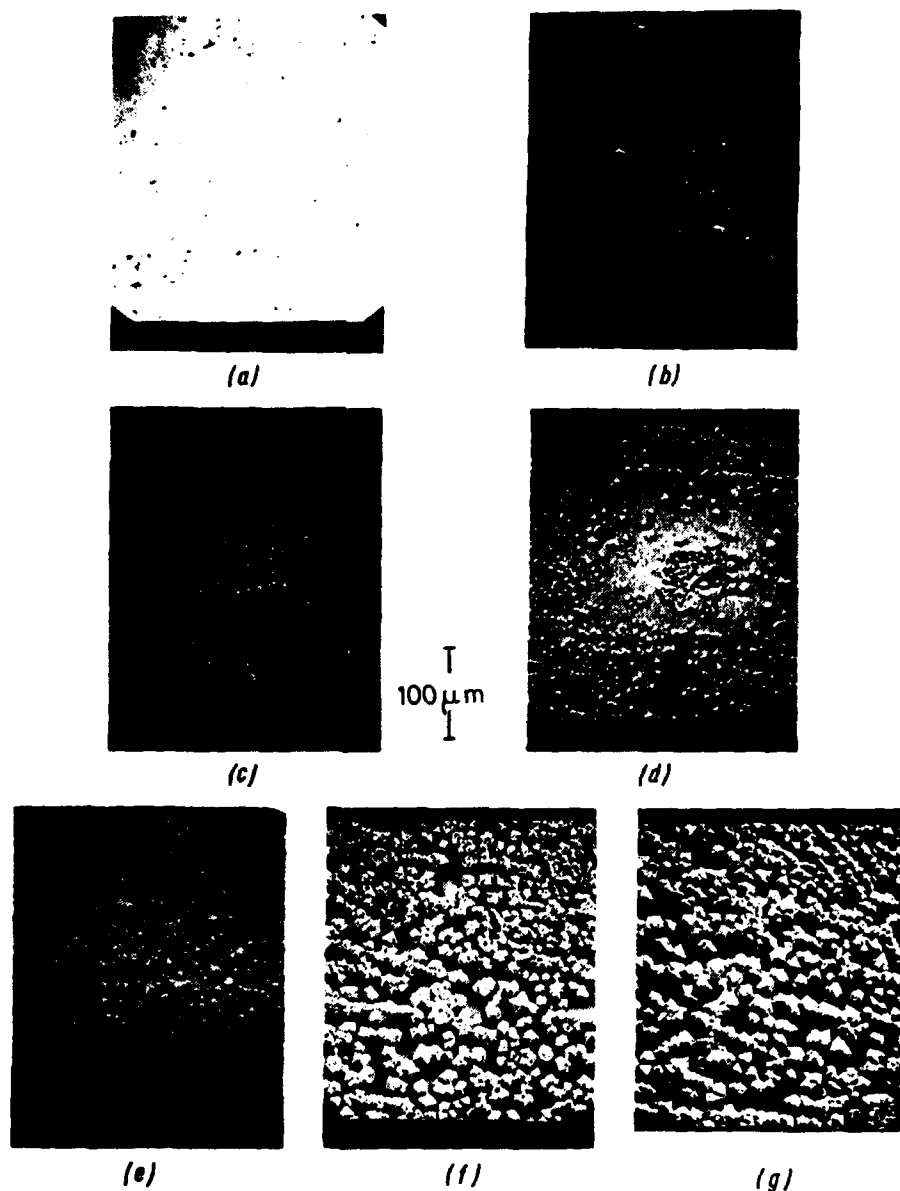FIG. 9.—Scanning electron micrographs for the electrode surface with different treatments: (a) polished with alumina; (b) etched in 3.7 mol dm⁻³ HNO₃ for 15 s; (c) etched in 3.7 mol dm⁻³ for 30 s; (d) 1 min etching; (e) 2 min etching; (f) 5 min etching; (g) 10 min etching.

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