CHAPTER 16

Photo-Excitation of Semiconductor Electrodes

16.1 INTRODUCTION

Molecular photo-excitation (Chapter 15) is of course a very important branch of photoelectrochemistry. However, the quantum yield and efficiency, the long-term stability, the cell fabrication aspects and many other practical difficulties still remain to be solved in this area. Comparatively, the photo-excitation of electrode surfaces has developed much faster. Even here one can photo-excite any electrode, material, a metal [1], a semiconductor, a comparatively passive film [2] or even an organic insulator material [3]. Basically all these electrode materials have a band structure for the conducting electrons. The main difference between these materials from the electrochemical viewpoint is the energy difference or energy gap between the occupied electronic levels and empty levels. In metals there is practically no gap between these two levels. In all other materials, these two levels are called valency and conduction band. As would be seen shortly (Section 16.2.1) the presence of an optimum band gap is an important factor for achieving charge separation and efficient charge transfer. For this reason, semiconductors are much more useful electrode materials for electrochemical energy conversion by photo-excitation when compared with metals (which have no band gap) as well as organic and inorganic insulators (which have very wide band gaps). The area of semiconductor photo-excitation is much more prevalent and popular in photo-electrochemistry when compared with molecular photo-excitation (Chapter 15) and photo-excitation of metallic and insulator electrode materials. Hence, the very name photoelectrochemistry is commonly associated solely with semiconductor photo-excitation. The general photoelectrochemical literature cited for example in Chapter 15 (Ref. 1–3 and 2–20 in Chapter 15) mostly deals with semiconductor photo-excitation. Hence in the present chapter, one is primarily dealing with the new field of semiconductor photo-excitation although other aspects of electrode photo-excitations [1–3] on passing are also considered.

The basic foundations of dark as well as photoprocesses at semiconductor-electrolyte interfaces were laid as early as 1955 [4, 5]. But this field remained one of academic interest for almost two decades. In 1972 it was shown that one can produce H_2 from water by photo-excited electron transfer of *n*-type TiO_2 semiconductor material [6]. This observation gave a new thrust and orientation to the field. Obtaining H_2 fuel from an inexhaustible resource, water, using another inexhaustible energy source, the solar energy, is certainly not a mean objective or ambition. A variety of new semiconductor materials were tested and evaluated. Practically, all the solvent-supporting electrolytes known in electrochemistry were investigated. Apart from H_2O electrolysis, photoelectrochemical oxidation and reduction of many organic, inorganic and organometallic systems were investigated. Many research and development organizations throughout the world are engaged in developing methods and materials in this promising new field. The ultimate goal of developing a successful and economically viable photoelectrochemical system is yet to be achieved. But the potentiality in this field is so great that it will continue to attract old and new talent until new goals are achieved.

Attempting to introduce such a new and fast-growing field in a brief chapter of the present type is indeed a tough task. Hence no attempt is made to treat the subject comprehensively and exhaustively. Our effort primarily will be towards introducing the basic concepts involved and methodologies adopted in the emerging field. Special efforts are made to familiarize the electrochemists with the terminologies that have been brought into this area from semiconductor physics. Once this is achieved, the new model concepts involved in photo-electrochemistry (Section 16.2) can very easily be understood by the electrochemists since one is essentially dealing with the same phenomenological models in a different context. After a brief discussion on voltammetric methods (Section 16.3) the recent developments in the photoelectrochemical processes as such are considered (Section 16.4). Several controversies and approaches that are being critically assessed are presented without attempting any immature assessment of the situation. One hopes that the readers will follow or even participate and contribute to these lively debates in this emerging field. Even if the present treatment is not exhaustive, one can refer to the vast literature [7–16] for further study. The original literature cited throughout this chapter would also be of considerable help in this regard.

16.2 THE MODEL

16.2.1 ENERGY LEVEL DIAGRAM: THE DIRECTION OF CHARGE TRANSFER

The major differences between electrodes made of metallic conductors discussed sofar (Chapters 13 to 15) and the semiconductor electrodes considered here arise because of the nature of bonding involved. The atoms of a metal are linked by metallic bonding where the cationic lattice is held together by loosely bound electronic cloud. The high concentration of electrons ensures good electronic conductivity. The energy difference between the filled and empty energy levels of electrons is practically zero. On the other hand, the semiconductors consist of covalently bonded lattices. The energy difference between the bonding and antibonding energy levels of such covalent bonding systems are quite high. This gives rise to distinct valency and conduction bands for semiconductors. The relative concentrations of charge carriers are low when compared with metals, which is responsible for the lower conductivity of these materials. These aspects are discussed in somewhat greater detail in Section 1.2.1 (see Fig. 1.1). The lower electronic conductivity and the band structure of the semiconductors make them totally useless for applications as normal electrode materials in the absence of photo-excitation (the so-called dark current application), but as will be seen it is the very same band gap and lower charge carrier density which makes them the electrodes of choice in photoelectrochemistry.

The most important consequence of lower charge carrier concentration on a semiconductor electrode is the presence of a space charge region on the semiconductor side of the semiconductor-eletrolyte interface. In the metal-electrolyte interface, the space charge region lies in the electrolyte side (it is called diffused double layer region by electrochemists; the semiconductor physics people call it space charge) since the charge carrier concentration in the electrolyte is lower when compared with the metal. The reverse is true in the case of semiconductor electrolyte interface. The charge carrier concentration is lower on the electrode side and so the space charge is located there. This aspect has also briefly been touched upon earlier (Section 1.3.1).

The relative energy levels, energy gaps and voltage drop in the space charge are measured in terms of electron volts in semiconductor physics. Measurement of absolute potential differences is a simple and straightforward job in semiconductor physics, but as seen throughout, a relative scale for voltage measurement is being used in electrochemistry. Hence a reference point for each semiconductor electrode to construct its energy level diagram and predict its electrochemical behaviour with respect to different redox couples is always needed. Such a reference point is the so-called flat band potential. The flat band (E_{FB}) is again analogous to the well-known potential of zero charge (E_{pzc}) used by electrochemists in diffuse double layer theory. It is the potential (measured with respect to *NHE* or any other reference electrode) at which the excess charge on either side of the semiconductor-electrolyte interface is zero. At potentials more negative than E_{FB}, the space charge on the semiconductor will contain excess negative charge and *vice versa.*

The capacity-potential measurement at semiconductor electrolyte interface has been discussed (Section 1.3.1) which is the predominant method for evaluating the flat-band potentials. An intrinsic semiconductor gives a symmetric capacity-potential curve (Fig. 1.13) showing minimum capacity at the flat-band potential. Knowing that E_{FB} on the electrochemical potential scale and the band-gap between E_V and E_C from spectroscopic absorption spectra of the semiconductor, one can establish all the energy levels in the electrochemical scale. As noted E_{FB} lies exactly at the middle of E_V and E_C for an intrinsic semiconductor (Fig. 1.1).

The estimation of E_{FB} for a highly doped or compound semiconductors (Section 1.2.1) is slightly more involved. For *n*-type semiconductors, the bulk concentration of electrons (n_o) is very much higher than the bulk concentration of holes (p_o), that is, $n_o \gg p_o$. Similarly, for *p*-type semiconductors, $p_o \gg n_o$. This inequality in the charge carrier concentrations shows up in the capacity-potential curve as well as in the form of three sloped regions. Consider the capacitance behaviour of an *n*-type semiconductor as an example (Fig. 16.1). At extreme negative potentials, the space charge region itself will be negative and the surface concentration of electrons n_s will be greater than n_o. This region ($n_s > n_o$ and $n_s \gg p_o$) is called the accumulation region with high capacity values and high slopes. At potential close and positive to the flat-band potential, the space charge will be positive. The n_s will now be less than n_o but still be greater than the surface concentration of holes, p_s ($n_s < n_o$ but $n_s > p_s$). This region is called depletion region. At extreme positive potential the surface concentration of electrons will be extremely low

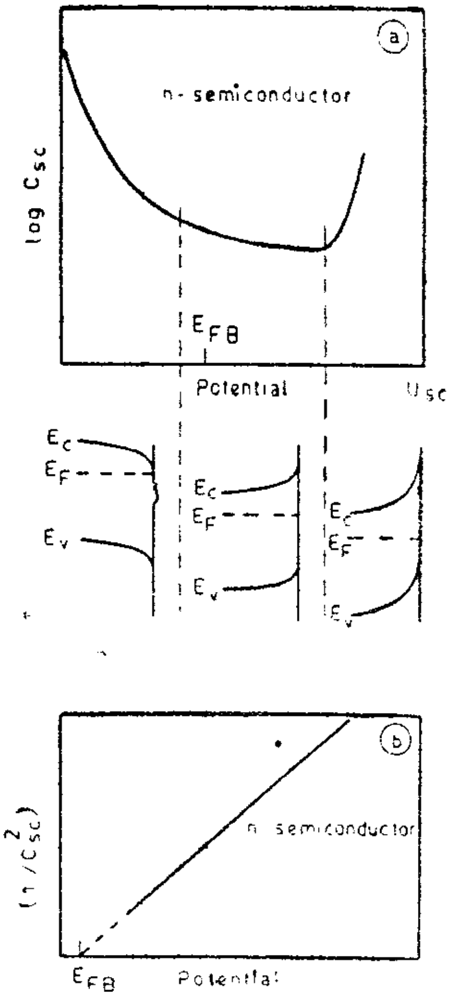

Fig. 16.1 (a) Space charge capacity of an *n*-type semiconductor and the corresponding energy level diagram.
(b) Typical linear MOH-Schotky plot showing $1/C^2$ versus E relation.

and it will be lower than the surface concentration of holes themselves. ($n_s < n_o$ and $n_s < p_s$). This region is called the inversion region. Figure 16.1 shows the change in the capacitance-potential slope in these regions.

Theoretical derivations of capacitance-potential relations (C versus V relation) for such n, p type semiconductors are much more involved. But they do show a simple relationship of $1/C^2$ versus V in the depletion region. The extrapolation of this linear plot to the potential axis gives E_{FB} (Fig. 16.1). For highly doped semiconductors E_{FB} lie very close to E_C and E_V for *n* and *p* type semiconductors respectively. Hence, knowing E_{FB} and band gap from absorption measurements, one can again construct the energy level diagrams of these electrodes.

The flat-type of energy level diagrams where the energy levels of E_V, E_C and E_F are parallel hold good only when the Fermi level of the electrode-electrolyte interface E_F is maintained at the flat-band potential. (The very name of E_{FB} arises because of the flat nature of all the energy bands at this potential), One can shift the E_F level by applying more negative or positive potential just as one can apply any potential away from E_{pzc}. Now the potential drop (under ideal conditions) occurs completely in the space charge layer. The E_F level can be raised or lowered in the energy diagram by applying more negative or positive potential respectively. The edge of E_V and E_C level at the interface always remains intact, but the bulk energy levels again are parallel. This gives rise to band bending as shown in Fig. 16.1 in the accumulation, depletion and inversion regions.

The energy level diagrams involving band bending essentially contain a lot of useful information. Hence a closer look is needed at the energy band structure of *n*-type and *p*-type semiconductors in the depletion region (Fig. 16.2). The top region of such a diagram shows higher energy level for the electron and the lower region corresponds to higher energy for holes or positive charges. The electrons have a tendency to come down the bend energy curve and the holes have a tendency to move up. With this basic idea in mind, one can always predict the charge flow direction and the charged state of the space charge layer. For the case of *n*-type semiconductor, for example, the electrons would move down the slope towards the semiconductor bulk (Fig. 16.2.a). The holes on the other hand would move upwards. Hence an electric field with positive charge near the interface is set up. The opposite situation prevails in the depletion region of the *p*-type semiconductor (Fig. 16.2.b). When photo-excitation takes place, it is exactly this space charge which assists the separation of newly generated electrons and holes by moving them in opposite directions (Sections 16.2.2 and 16.2.3).

The same type of electron movement also controls the electron transfer between the redox couples and the semiconductor surface. Electrons can move only downwards. The redox couples above conduction band edge can transfer electrons to the semiconductor conduction band and not *vice versa.* The redox couples in the band gap can accept conduction band electron or valence band hole and not *vice versa.* The redox couple below the valence band can only be reduced by valence band electrons and the oxidation cannot proceed. These rules apply at ideal conditions. Many other exceptions can arise. Some of them are referred to later (Section 6.2.4).

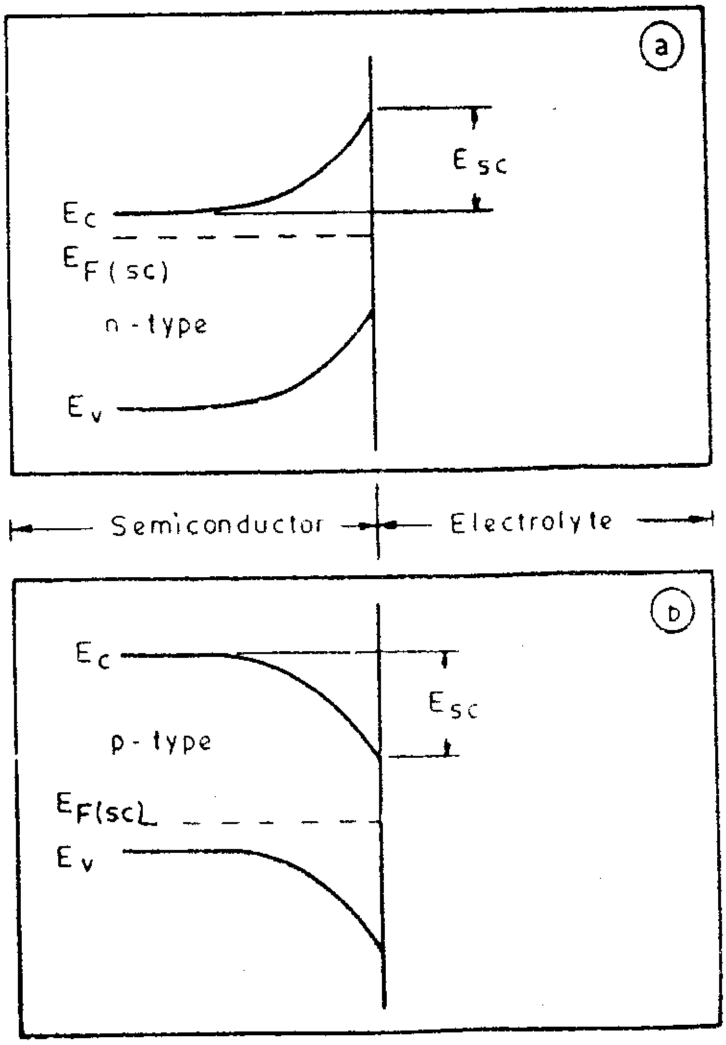

Fig. 16.2 Band bending at n-type (a) and p-type (b) semiconductors under open circuit conditions when the E_F level lies in the depletion region.

16.2.2 CONSEQUENCES OF SEMICONDUCTOR PHOTO-EXCITATION

It is quite easy to photo-excite an electron in metal. Even a very small amount of energy may be sufficient since vacant energy levels exist very close to the Fermi level (Fig. 1.1). However, unless there is a fast mechanism by which one can transfer the electron from the electrode into the electrolyte, the excited electron will transfer the excess energy as heat to the electrode itself and reach the ground state again. Hence this process generally is inefficient from photo-conversion viewpoint [1] although some efforts still continue in this direction (Section 16.4.2).

On the other hand, most of the passive oxide films [2, 9, 10] and organic semiconductors [3] require more than 3 *eV* energy for photo-exciting a lattice bond to generate an electron hole pair. Most part of the solar energy spectrum is inefficient to achieve this goal. Hence these systems are not quite useful in photoelectrochemical applications. However, these systems are investigated for undertanding the film growth mechanisms (Section 16.4.3) and electron injection processes (Section 16.4.2).

Hence narrow band gap semiconductors ($E_g \simeq 1.5\ eV$) are the best choice for the photoelectrochemical applications. They absorb light and generate an electron hole pair.

$$\text{Lattice} + h\nu_0 \rightarrow e^- + h^+ \qquad 16.1$$

The space charge that is present in the depletion layer ensures charge separation. Again consider the *n*-type semiconductor. The space charge is positive in the depletion region even before photo-excitation (Section 16.2.1). Now when the new electron-hole pair is generated (Fig. 16.3) the electron reaches the conduction band and moves downwards towards the bulk of the semiconductor. The hole generated in the semiconductor moves upwards towards the surface. Thus, on photo-excitation, the minority carriers move towards the interface and majority carriers move towards the bulk. Now if the minority carriers are transferred to the redox species in solution, photo-current is achieved.

One should also consider one more aspect. In an *n*-type semiconductor, the minority carrier concentration (p_o) is considerably less than the majority carrier concentration (n_o). Hence, although photo-excitation generates equal number of excited electrons (n^*)

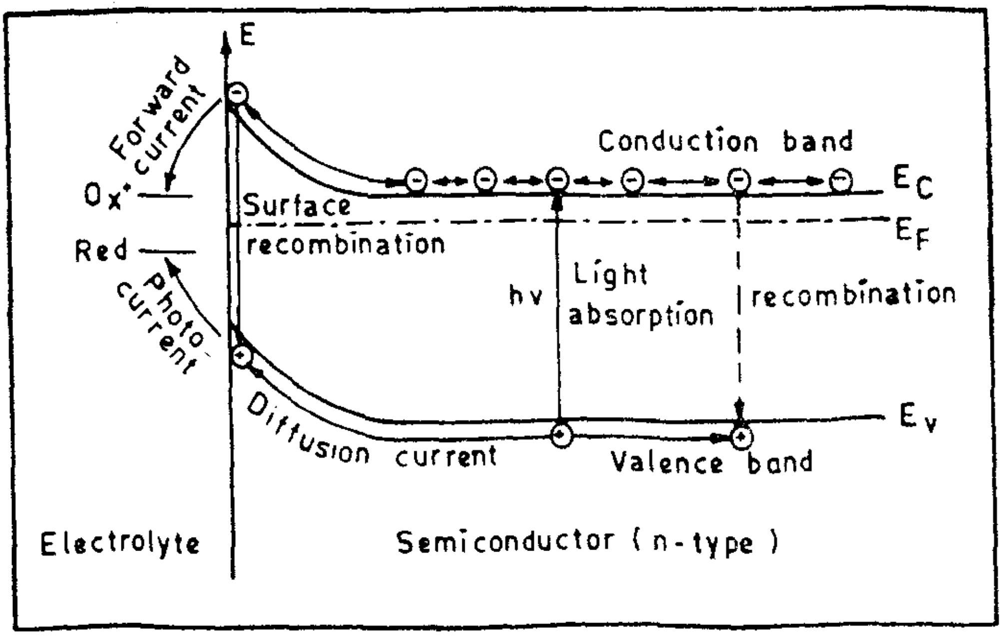

Fig. 16.3 Photoexcitation and the associated kinetic processes under steady state conditions on an *n*-type semiconductor.

and holes (p^*) according to equation 16.1 the relative change of minority carrier concentration ($p^* - p_o$) is considerably greater than the relative change of majority carrier concentration ($n^* - n_o$). This relatively larger change of minority concentrations as well as their favourable drift towards the interface (Fig. 16.3) ensures that the photocurrent is mainly contributed by the minority carriers. This is in contrast with the dark current which is mainly contributed by the majority carriers.

The qualitative description of photo-excitation processes so far might create an impression that everything is fine with semiconductors with regard to photoelectrochemical energy conversion. However, this impression is far from the truth. At least four types of processes are involved in the photo-excited electron transfer being considered here: (a) photon absorption and generation of charge carriers, (b) transport of the charge carriers under the influence of field and concentration gradients, (c) stability and life time of photo-excited charge carriers, and (d) the transfer of charge carrier to the redox couple across the semiconductor-electrolyte interface (semiconductor physics prefers the term junction or barrier for interface used in electrochemistry). All these four components can determine the success of the photoelectrochemical conversion or contribute to the poor overall quantum yield of the process. Quantitative treatment of all these problems is very well developed in semiconductor physics [17]. Recently, attempts are being made to adopt these theoretical approaches to semiconductor photoelectrochemistry as well. At least two recent reviews [13, 14] try to present an overview of the recent developments in this area. In the present context, one cannot treat these questions in detail. However, even a qualitative description of the phenomena involved would certainly help us grasp the difficulties in the successful development of photoelectrochemical cells. One may at least understand why the quantum efficiencies do not cross 12.0 per cent in spite of so much interest and enthusiasm in the field. In the rest of the present section, therefore, some of the problems associated with the first three types of processes (a-c) mentioned above are treated and the charge transfer aspects are considered in the next section.

a) *Generation of charge carriers*

Equation 16.1 assumes that the semiconductor absorbs the photon with frequency ν_0 that directly corresponds to the energy band gap. This is only a very small part of solar energy spectrum. In practice, however, the electron-hole pair can be formed by photons whose frequencies are greater than or equal to the critical frequency ν_o. However the excess photo-energy absorbed in this fashion does not contribute to electrical energy conversion and hence would lead to quantum efficiency loss.

The absorption coefficient of photons by the semiconductor also depends on whether a direct or indirect transition is taking place. The energy levels of valency and conduction bands are actually described by wave vectors. If the transition occurs between the minima or maxima of the wave vectors of the energy band, the transition is called direct transition. If the transition occurs between the maxima of valence band wave vector and the minima of the conduction band wave vector, the transition is termed indirect. The adsorption coefficient is defined by different expressions for these two types of transitions. Direct transitions are of course more efficient although they involve slightly higher band gap energies.

The optical absorption itself depends on the distance between the semiconductor surface where the incident photons are focussed and the site at which the photon absorption takes place. In general, the photoabsorption and hence the photogeneration rate falls off with increasing distance from the surface (see Fig. 16.3).

It is needless to say that the correct theoretical expression for photogeneration rate should take into account all these factors.

b) *Transport of the charge carrier*

In Section 16.2.1 the movement of electrons and holes was talked about when a new Fermi level from the external circuit was imposed. The charges migrate in the space charge region under transient conditions and reach an equilibrium charge distribution which do not change further. The energy level diagrams just correspond to this ultimate equilibrium distribution at any applied electrode potential.

Now, this equilibrium is disturbed by photo-excitation. New electrons and holes are generated at different rates at different depths from the electrode surface. This would initiate many transport processes. There are essentially two driving forces for charge transport, the field gradient and the concentration gradient.

In an *n*-type semiconductor, for example, there is a field which is favourable for movement of the holes towards the surface and electrons towards the bulk. The field, however, operates only within the space charge region. The width of the space charge region (w) is an important boundary condition over which the carrier migration operates. But an interesting aspect is that the width of the space charge also depends on carrier concentration and hence on photo-excitation.

The concentration of the minority carrier (p^*) near the semiconductor surface will be much higher than the bulk concentration p_o. This would set up a concentration gradient. The minority carriers would diffuse towards the bulk under this condition. The diffusion layer thickness (t) that develops under this concentration gradient has nothing to do with the space charge layer thickness (w) mentioned above.

The overall transport expression should contain both Concentration gradient and migration effects that operate at different thicknesses and with different boundary conditions.

c) *Stability and life time of charge carriers*

Both the electrons and holes generated by photo-excitation possess relatively high energies. These excited states are relatively unstable. They can approach ground state or be made inactive by different mechanisms. The excited states can be trapped at some defect regions of the semiconductor. The energy transfer between the lattice and the excited state can take place. A far more important reaction is the recombination of electrons and holes that are moving under high flux conditions.

$$e^- + h^+ \rightarrow \text{Lattice} + \text{heat} \qquad 16.2$$

The overall effect of reactions 16.1 and 16.2 is conversion of photon energy into heat. This is one of the major causes of quantum efficiency loss.

It should be noted that the recombination rate also depends on the distance x from the surface. Thus the construction of the correct rate expression for recombination becomes a tough task.

In discussions so far (Sections 6.2.1 and 6.2.2) we have assumed an ideal defect-free semiconductor. To be more specific, any specific role for the surface sites has not been assumed. This is an oversimplification. Surface effects are very important and crucial in deciding the behaviour of photo-excited states. This question is reverted to (Section 16.2.4) after considering the general concepts of electron transfer at semiconductor-electrolyte interfaces in the next section.

16.2.3 CHARGE TRANSFER KINETICS: THE DARK AND PHOTOCURRENTS

Semiconductor electrodes can give rise to charge transfer at the electrode-electrolyte interface just like metal electrodes in the absence of photo-excitation. However, there are a number of differences between the behaviour of metal and semiconductor electrodes. These subtle differences are briefly treated in the dark current behaviour before touching upon photocurrents.

a) One can also change the Fermi level of the semiconductor-electrolyte interface by changing the applied potential in the positive or negative direction just like the change effected in metal-electrolyte interfaces. But the charge transfer between the semiconductor and electrolyte takes place only with the conduction and valence band edges and not at the Fermi level. Hence the redox system in the electrolyte can exchange electrons only with E_c or E_v. If the redox potential of the solution redox couple is close to E_c the charge transfer will proceed *via* conduction band. If the redox potential is close to E_v the charge transfer will be with valence band. As the redox potential of the redox couple shifts away from both these band edges, the probability of charge transfer decreases substantially.

b) The charge carrier concentration in the semiconductor is very much lower than that of metal. Hence, on most occasions, the rate of electron transfer is determined by the properties of the semiconductor. This is in contrast with the electrode-electrolyte interface, where the emphasis is on the kinetic and transport properties of the electrolyte to understand voltammetric behaviour (Chapters 3 to 5). The charge transfer at thesemiconductor-electrolyte interface depends on the charge carrier concentration in bulk of the semiconductor, its transport by diffusion and migration towards the interface and so on. Because the objective is to study these semiconductor properties on most occasions, one also takes high concentrations of redox species in the electrolyte solution so that their mass transport does not interfere with the semiconductor response.

c) In metal-electrolyte interface, the applied potential drop occurs at the electrolyte side of the interface and changes charge transfer properties of the redox couple. Hence on either side of the E_{eq} of the redox couple, one obtains a symmetric current-potential relation. In semiconductor-electrolyte interface, the potential drop occurs predominantly in the space charge. This gives rise to a very distinct feature of this type of process—the unsymmetric current potential behaviour.

Consider the behaviour with a typical conduction band process. The cathodic current ($\bar{i_c}$) depend on the surface concentration of electrons (n_s) which can be increased by increasing the negative overpotential when compared with the flat band potential (η). The surface concentration of electrons at any overvoltage η is given by equation 16.3.

$$n_s(\eta) = n_s(o) \exp\left(\frac{-e\eta}{kT}\right) \qquad 16.3$$

Hence the cathodic current of the conduction band process (i_c^-) which depends on n_s, increases exponentially with overpotential. However, the anodic reaction at the conduction band (i_c^+) depends on the vacant sites for electron acceptance at the conduction band. These acceptor states do not depend on η. Hence the i_c^+ is potential-independent and it is always equal to the exchange current density of the conduction band process. This gives rise to unsymmetric $i_c - \eta$ relation as shown in Fig. 16.4.

The same type of unsymmetry will be noticed in the valence band process. Here the anodic valence band current i_v^+ will be potential-dependent and the cathodic valence band current i_v^- will be potential-independent (Fig. 16.4). The potential dependence of i_v^+ of course arises due to the potential dependence of hole concentration with η which is given by equation 16.11.

$$p_s(\eta) = p_s(o)\cdot \exp\left(\frac{e\eta}{kT}\right) \qquad 16.4$$

This important property can be made use of for determining whether a particular electron transfer process is a conduction band process or a valence band process. The axchange current density can also be obtained directly from the potential-independent branch of the voltammetric curve.

d) Another interesting property which is also related to the above concept is observed when two different redox systems with widely different redox potentials are investigated on *n*-or *p*-type semiconductors. Because of the large difference in redox potentials, one reaction would proceed *via* conduction band and the other one would proceed *via* valence band. Suppose H_2SO_4 medium is taken and H_2 and O_2 evolutions are the cathodic and anodic reactions. H_2 evolution would proceed *via* conduction band and O_2 evolution would proceed *via* valence band. Now, an *n*-type semiconductor can donate electrons from its conduction band and hence H_2 evolution would proceed smoothly. But the hole concentration is very low and hence O_2 evolution will not proceed. Similary, the dark H_2 evolution current will almost be zero on a *p*-type semiconductor.

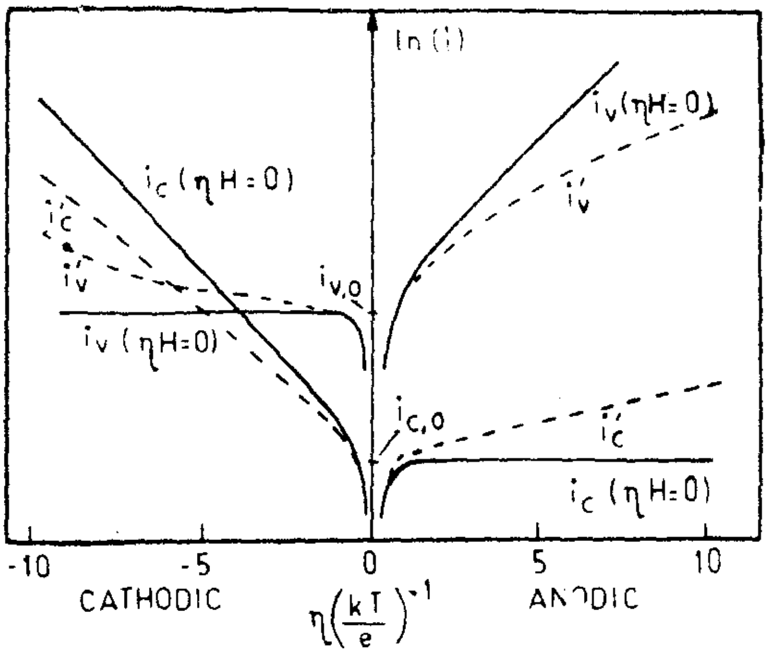

Fig. 16.4. Current voltage curves for semiconductors with redox reactions *via* the conduction band (i_c) or the valence band (i_v). Ideal behaviour when the whole voltage drop occurs in the semiconductor (full line) and derivations due to potential drops in the Helmholtz layer (broken lines) are shown separately.

[From H Gerischer in Photoelectrochemistry, Photocatalysis and Photoreactors (M Schiavello, Ed) NATO AST series. D Riedel, Dodrecht (1985) 39]

It is exactly this trend which is reversed during photo-excitation. During photo-excitation, one essentially brings out a large increase in minority carrier concentration. The minority carriers also move towards the interface (Section 16.2.2). Hence *the photocurrent is mainly contributed by minority charge carriers in contrast with the dark current which is mainly contributed by the majority carriers.* Thus *n*-type semiconductors are the electrodes of choice for photoelectrochemical O_2 evolution and *p*-type semiconductors are the electrodes of choice for photoelectrochemical H_2 evolution. This is the general rule for any other photo-oxidation and reduction (See 16.4).

Let us have a closer look at the energy level diagram during photo-excitation (Fig. 16.5) with an *n*-type semiconductor as an example. Under dark condition (Fig. 16.5.a) the Fermi level is decided by the E^o of the redox couple and the energy level diagram shows a

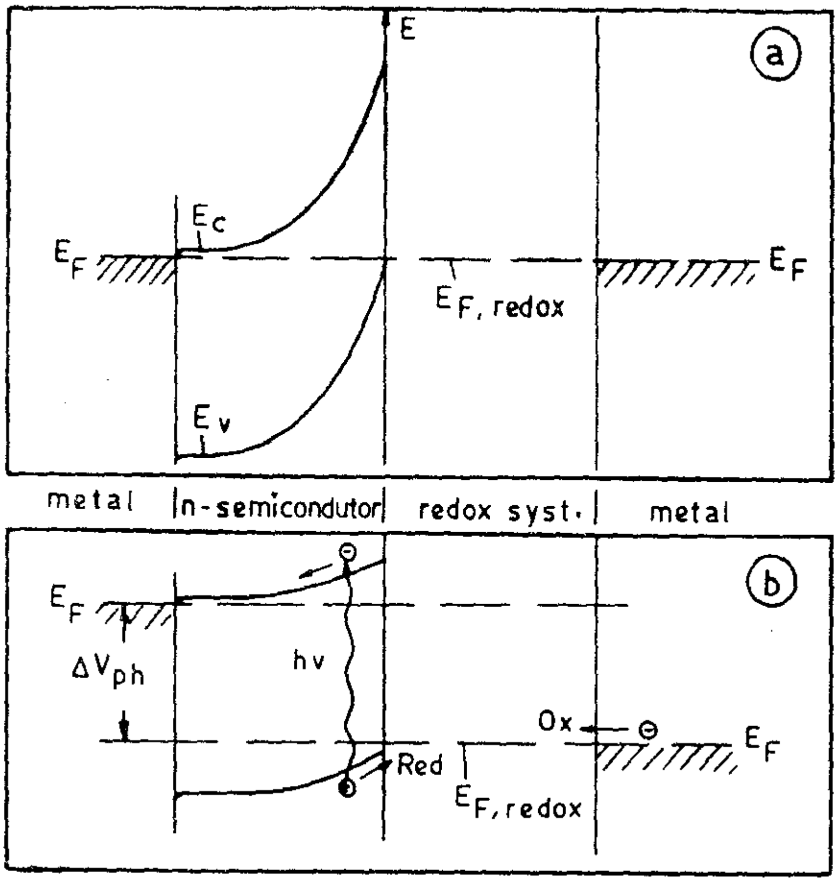

Fig. 16.5 Energy scheme of an ideal electrochemical photovoltaic cell with an *n*-type semiconductor at equilibrium (a) and during illumination. (b).

high level of band bending. Under illumination due to the generation of excess charge carriers, the band bending decreases substantially. The new quasi-Fermi level E_F^* is now very close to the valence band or minority charge carrier level. The difference between the quasi-Fermi level and the bulk Fermi level is obtained as the photovoltage of the photoelectrochemical process.

In Fig. 16.5 of the redox system whose E^o is close to the minority band level has been selected. This would ensure maximum overlap interaction between the energy levels and hence maximum charge transfer rate. In narrow band gap semiconductors, this approach can also lead to another interesting effect. Very high band bending can cause the formation of inversion layers where minority concentration at the surface will reach quite high values even without photo-excitation. Once such inversion layer is formed, any further change in the E^o of the redox couple further down the energy diagram will not cause enhancement of photovoltage. This type of charge transfer through inversion layer cannot be distinguished from' Fermi level pinning effect' to be introduced in the next section (Section 16.2.4).

More comprehensive and quantitative treatments of charge transfer kinetics at semiconductor-electrolyte interface are available [7–16]. Quantum mechanical transition probability models are employed for describing dark current potential characteristics. Excellent reviews covering the theory and classical experimental results with evaluation of kinetic parameters are available [7, 10]. In these treatments, it is generally assumed that the potential drop is primarily in the semiconductor bulk and the change in potential drop at the Helmholtz layer is assumed to be negligible. Even a small change in potential drop in the Helmholtz layer will have little effect on the voltammetric behaviour as shown by the dotted lines in Fig. 16.4.

The independence of charge transfer rates on the potential drop at the electrode-electrolyte interface is also assumed in photo-excited electron transfer [18, 19]. Since the photo-excited minority carriers are highly reactive, it is generally assumed that the charge transfer at the interface is very fast. The simple models assuming minority carrier generation and transport alone as the rate processes [20, 21] are found to be realistic in a number of situations. Different methods are adopted to assess the influence of slower charge transfer kinetics and recombination effects [22, 23]. However, the theoretical treatments of photocurrent-voltage relations are still at an elementary level. Many of the concepts still require experimental verification [13, 14].

16.2.4 SURFACE STATES AND THEIR EFFECTS ON CHARGE TRANSFER

In discussions so far, it is assumed that the semiconductor electrode is an ideal homogeneous material. However, any electrode has a surface and the surface structure, defects, treatments and modification can influence any electron-transfer process. In recent times, more and more attention is being drawn towards investigating the surface properties of the semiconductors to improve their overall performance.

The surface atomic species of a pure semiconductor itself would possess different surface free energies when compared with the bulk. In addition, the surface might contain lattice defects and many other kinds of imperfections and impurities. All these surface structures would show optoelectronic properties that are quite different from the semiconductor bulk. In semiconductor physics, these are termed as surface states. In recent photoelectrochemical literature, even other surface modifications such as ionic specific adsorption are included in this 'surface state' description. In this section, the type of modifications that can be brought out by any surface state on the bulk properties of the semiconductors are briefly listed.

a) The surface states can retain a large excess of positive or negative charges depending on the applied potential. These charges can modify the capacitance-voltage behaviour of the semiconductor-electrolyte interface. This can create problems in the determination of semiconductor properties such as flat band potential [24].

b) The surface states can absorb photon energy whose energy is lower or slightly higher than the band gap. The absorbance spectrum actually is one of the easiest means for the identification of the surface states. The absorption frequency would give the energy level of the surface state and the relative absorbance would give the concentration of surface states. The relative energy levels of the surface states of *n*-ZnO obtained by measurements of this type [25] for example are presented in Table 16.1.

c) The surface states can form electron-hole pairs at much lower photon energies when compared with the band gap. These charge carriers can contribute to the photocurrent substantially.

d) The surface atoms are much more loosely bound to the lattice when compared with the bulk atomic species. Photo-excitation of the surface states and formation of holes can further decrease this bond strength and activate lattice dissolution. This type of dissolution can be more aggressive in the case of compound semiconductors of the type AB ($GaAs$, CdS etc.).

$$(AB)_{lat} + h\nu \rightleftharpoons (AB^{+})_{lat} + e^{-} \qquad 16.5$$

$$(AB)^{+}_{lat} \rightarrow (B^{n-})_{lat} + A^{n+}_{sol} + (n-1)\,e \qquad 16.6$$

Table 16.1

Energy levels in ZnO-electrolyte phase boundary

Type of energy level	Energy (V vs SHE)	Conditions-remark
E_C	−0.25	Vacuum level based
E_V	2.95	Vacuum level based
E_F	−0.05	Vacuum level based
E_{FB}	−0.28	Vacuum level based
E_{CS}	−0.20	Vacuum level based
E_{CS}	−0.18	Electrolyte pH = 4.8
	−0.37	Electrolyte pH = 9.2
	−0.48	Electrolyte pH = 12
E_{SS}	+0.056	Vacuum level based
	+0.33	Vacuum level based
	+0 52	CH_3CN solvent

Adapted from Ref [25]

For *GaAs*, $n = 3$ and for *CdS*, $n = 2$ and so on. This type of lattice dissolution is one of the major problems that comes in the way of developing efficient photoelectrochemical cells.

e) Surface states can act as recombination centres for electrons and holes generated by bulk photo-excitation. This can be a very important cause for quantum efficiency loss, especially when the charge transfer across the interface is slow and large concentrations of excess charge carriers accumulate on the surface.

f) Surface states are directly in contact with the electrolyte medium containing the redox couple. Hence the excited surface state contribute to the charge transfer across the interface. A surface state (S)-mediated oxidation through hole capture for example can be represented as

$$S + h^{+}_{(\mathrm{bulk})} \rightleftharpoons S^{+} \qquad 16.7$$

$$S^{+} + R_{\mathrm{electrolyte}} \rightarrow S + Ox \qquad 16.8$$

This catalytic sequence can repeat as long as S^{+} does not lead to recombination by capturing another excited electron. Detailed theoretical treatments assuming that the entire charge transfer to the electrolyte proceeds by such surface states are available [26, 27]. A more general treatment covering direct charge fransfer as well as charge transfer through surface states is also available [28, 29]. One can view the charge transfer through active surface states (reaction sequence involving equations 16.7 and 16.8) and photodissolution of surface states (reaction sequence involving equations 16.5 and 16.6) as two competitive processes [30]. Theoretical treatments actually indicate that the dissolution of many semiconductors are inhibited by the redox couple oxidations, exactly because of this kinetic limitation (Section 16.4.3).

g) If the concentration of surface states is quite high, one can observe another interesting phenomenon. Suppose there are some surface states in the bond gap, that can donate electrons easily and acquire positive charge. When the Fermi level is moved in the positive direction close enough to the energy level of this surface state, they start acquiring positive charge near the interface. Any additional positive potential shift only increases the positive charge on the electrode surface near the interface and the space charge does not change further. Because of the increasing positive charge on the surface side of the semiconductor, the double layer structure near the electrolyte starts changing and acquires negative charge. In effect, because of the surface states, the potential drop across the semiconductor is halted and the potential drop across the electrode-electrolyte interface changes. This is exactly what happens at the metallic conductor-electrolyte interface. Since the Fermi level in the semiconductor is now fixed near the surface state level, this phenomenon is called Fermi level pinning. Many interesting consequences arise out of this phenomenon. The semiconductor-electrolyte interface starts behaving like a metal-electrolyte interface. Some highly controversial theories have been proposed in semiconductor photoelectrochemistry where the charge transfer is assumed to proceed just like the one at metal-electrolyte interface [31–33]. Some experimental evidences to support this view are also proposed. One cannot deny that this contribution should be taken into consideration to some extent. It is quite difficult to visualize the photo-excited hot carrier injection into the electrolyte solution being controlled by the typical Butler-Volmer type of relation. However, this is an interesting angle that requires some serious consideration.

There is also another interesting consequence when surface states cause Fermi level pinning. The maximum photovoltage that can be obtained is limited to the energy gap between flat-band potential and the energy of the surface state E_{ss}. A large volume of data showing this type of behaviour is available in the literature (Section 16.4.2). However, this type of behaviour can also be explained by assuming inversion layer formation. Some detailed discussion on the consequences of Fermi level pinning will be gone into when examples of photo-excited simple electron transfer processes are considered.

16.2.5 PHOTOREDOX CATALYSIS AT SEMICONDUCTORS

The concept of redox catalysis has been introduced in a number of contexts throughout the text (Chapters 5, 13, 14 and 15). The photoredox catalysis on semiconductor electrodes is quite similar to the redox catalysis involving molecular photo-excitation (Chapter 15). The only obvious difference is that the photo-excitation is on the semiconductor rather than the redox catalyst involved. One can write down the reaction sequence as follows where Ox/R is the redox couple and A/B is the substrate couple.

$$\text{Lattice} + h\nu \rightarrow h^+ + e \qquad 16.1$$

$$R + h^+ \rightleftharpoons Ox \qquad 16.9$$

$$Ox + A \rightarrow R + B \qquad 16.10$$

One can easily notice the similarity between the redox-catalytic mechanism suggested here and the electron transfer involving surface states proposed in reactions 16.7 and 16.8. As seen later the primary purpose of redox modification of semiconductor surfaces (Section 16.4.6) is to protect the surface from photodissolution, although some catalytic enhancement of the rate of the substrate couple may also be involved.

16.3 THE METHOD

16.3.1 CHOPPED LIGHT PHOTOCURRENT VOLTAMMETRY

As far as the methodology of photocurrent voltammetry is concerned, there is practically no difference between the measurement of molecular photo-excitation and semiconductor photo-excitation. Hence all the typical methods listed in Table 15.1 can for example be applied in semiconductor photoelectrochemistry as well. However, the practical considerations in semiconductor photo-electrochemistry are much more stringent. Proper care must be taken in every experimental step [34] since one is dealing with very high purity semiconductor materials that can be contaminated in many different ways leading to spurious results. On most occasions, one is dealing with the processes taking place at the semiconductor side of the interface. Although no theoretical methodology for analysing photocurrent voltammetric data is available, one can at least construct the typical response based on the phenomenological components involved. One can cite the methods developed for the measurement of absorption coefficients and diffusion length as an example [35]. Application of voltammetry in the photoelectrochemical context very much depends on the problems at band and the ingenuity of the experimental works. Some typical results are discussed (Section 16.4.)in the next section.

One important difference between molecular photo-excitation (Chapter 15) and the semiconductor photo-excitation is the energy of the photons involved. In general, quite high excitation energies are involved in the present context. One should hence ensure that the photons do not affect other properties of the cell system especially the molecular species involved in the redox reactions. Measurement of *dark background current* in the presence of the redox couple as also of the *background photocurrent* in the absence of the redox couple if possible is necessary for proper understanding and interpretation.

One method that is often employed when high intensity laser beams are used as the photo source is to switch on and switch off the light source at regular intervals [36]. These types of voltammograms would contain oscillating current transients in each photopulse region. Although the analysis of data and design of instruments are slightly more complicated, this type of measurement enables one to evaluate the desired properties of the system without many side effects. The current-time transient between pulses can also lead to additional information. Figure 16.6 for example contains the transient pulses distinctly recorded on an α-Fe_2O_3 oxide electrode [24]. One notices that the transient current spikes have minimum values around $-0.5V$ versus SCE. This type of behaviour should correspond to the flat-band potential of the electrode. Other measurements have of course confirmed this interpretation [24].

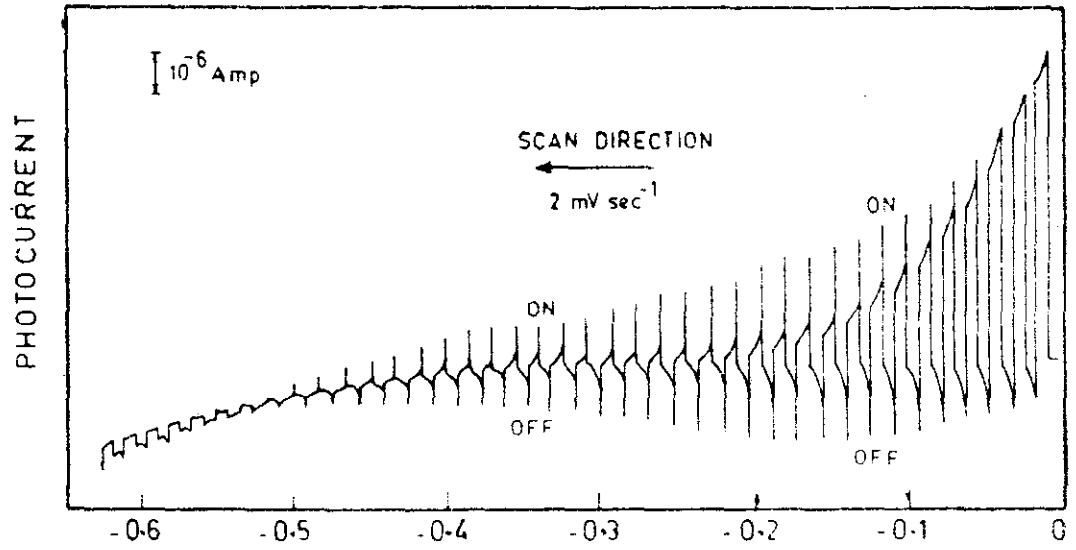

Fig. 16.6 Transient background photocurrents in α Fe_2O_3 electrode as a function of potential in 0.5 M NaOH.

[From A Hamnett, in Photogeneration of Hydrogen (A Harriman and MA West, Ed.) Academic Press, N York (1982) p. 147]

16.4 THE PROCESS

It is quite impossible to discuss in detail all the developments that are taking place in the field of semiconductor photoelectrochemistry in the present context. The references cited in the previous (Ref. 1-3 and 7-20 in Chapter 15) and the present chapters give more details on each specific systems that have received attention. The primary objectives in the present section are to introduce the types of developments that are taking place in the field and to cite some examples.

This section starts to with a brief discussion on various semiconductor electrodes employed in photoelectrochemistry (Section 16.4.1). The electrochemical solution phase processes without strong adsorption of intermediates (Section 16.4,2) and surface processes involving dissolution, passivation and film growth processes (Section 16.4.3) are then treated. The protection of semiconductor surfaces against dissolution and at the same time keeping them photoelectrochemically active is one of the crucial problems in this field. One treats the important methods employed in this area in a separate section (Section 16.4.4). The photoelectrochemical processes involving adsorbed intermediates that show great promise for the future are then considered (Section 16.4.5). Redox modification of semiconductor surfaces and redox catalysis through the redox films are growing areas of interest that are treated in a final section.

16.4.1 SEMICONDUCTOR ELECTRODES, BAND GAPS AND ENERGY LEVELS

As emphasized above (Section 16.2.1) one of the important aspects of semiconductors is the energy levels and band gaps. The energy levels of some typical semiconductor electrodes are presented in Fig. 16.7. The redox energy levels of some typical redox systems are also presented in the figure. The energy levels (in the left corner) are presented in NHE scale which is commonly employed in electrochemistry as well as vacuum based scale commonly employed in semiconductor physics. One may note that these two scales differ by approximately 4.5 *e*V.

Semiconductors of narrow band gaps would be better candidates for solar energy collection. But they should also be stable in the electrolyte medium. Classical electrodes with narrow band gaps generally lack this crucial property. Germanium undergoes extensive photodissolution (Section 16.4.3). Single crystal silicon, which is the most successful candidate in solid state photovoltaics also undergoes dissolution in most electrolytes. Some efforts are on to make these electrodes useful in electrochemistry (Section 16.4.4). *n*-GaAs and *p*-InP electrodes are probably the most sought after III-V compound semiconductors in electrochemistry.

Cadmium chalcogenides and other closely related compounds are another important class of semiconductors. These semiconductors especially find applications in electrochemical photovoltaic systems. In these cells, sulphide/polysulphide redox couple undergoes oxidation on photoanodes and reduction on metal electrode.

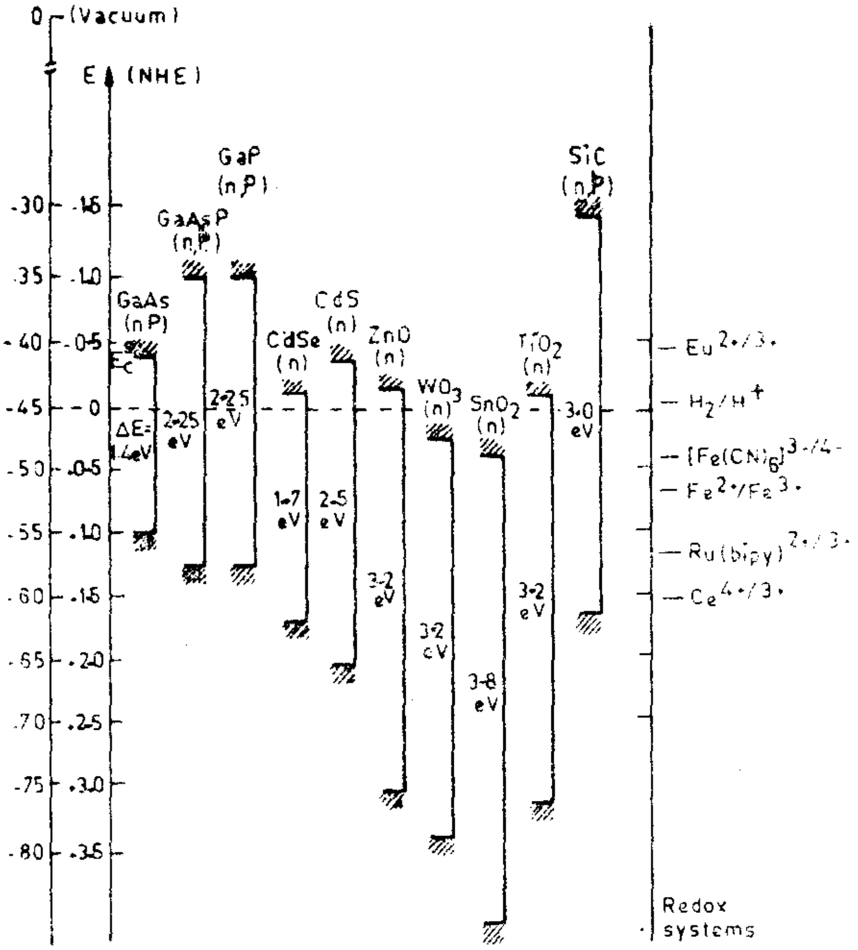

Fig. 16.7 Position of energy bands at the surface of various semiconductors pH = 1
[From R Memming in Electroanal Chem Vol. II (AJ Bard, Ed) Marcel Dekker, N York (1979) p. 1]

In recent times, another class of narrow band gap semiconductors including MoS_2, $MoSe_2$ and WSe_2 have received considerable attention. These transition metal dichalcogenides show both stability towards photodissolution and electrocatalytic activity towards other reactions. Photoelectrochemical splitting of water requires about 2.2 *e*V of energy. Since this reaction was originally investigated on TiO_2 [6], extensive investigations were made on this electrode. Although the oxide layers show good stability, their band gap is too high for efficient solar energy collection. Extensive work centres around modifying the oxide structure [37] to improve the electrocatalytic properties.

The names of extensively investigated semiconductors have just been traced here. A number of other rate systems such as *n*-silicon carbide [38], InSb [39] and even polyacetylene films [40] are being investigated for possible applications as semiconductors in photoelectrochemistry.

16.4.2 SIMPLE ELECTRON TRANSFER REACTIONS

Simple electron transfer reactions that show fast electron transfer kinetics on metal electrodes are quite ideal for characterizing new semiconductor electrode materials in electrochemistry. Since H_2O itself can be photooxidized or photoreduced on *n* and *p* type semiconductor respectively, non-aqueous solvents are usually employed in such investigations. Comparison of voltammograms at Pt and the new semiconductor electrodes directly give the relative photopotential and energetic information of semiconductor-electrolyte interfaces. One may cite the detailed cyclic voltammetric investigations on *n*-WS_2 [41], *p*-WS_2 [42] and *n*-CdS, *n*-CdTe [43] electrodes as typical examples of this type.

Cyclic voltammetry may be used for constructing the energy level diagrams of new semiconductor materials [44, 45]. A typical illustrative example is presented in Fig. 16.8. Of the two redox couples investigated, Ruthen bipyridyl complex gives some type of response on Pt and *n*-type CdSe electrodes. The dimethyl bipyridinium couple however does not give dark voltammetric response on the *n*-type material in the positive potentials involved. This is probably because the E^o of the redox couple is close to the energy level of the minority carrier (E_v in this case). On photo-excitation, one finds a photocurrent response supporting this view. This suggests the E_v level lies somewhere in this region.

An interesting redox couple is the solvated electron/solvent system. The photoelectrochemical emission of solvated electrons can be investigated in liquid ammonia where these highly reactive species show substantial stability [46, 47]. The photoelectric emission of electron from the semiconductor [46, 47] would be

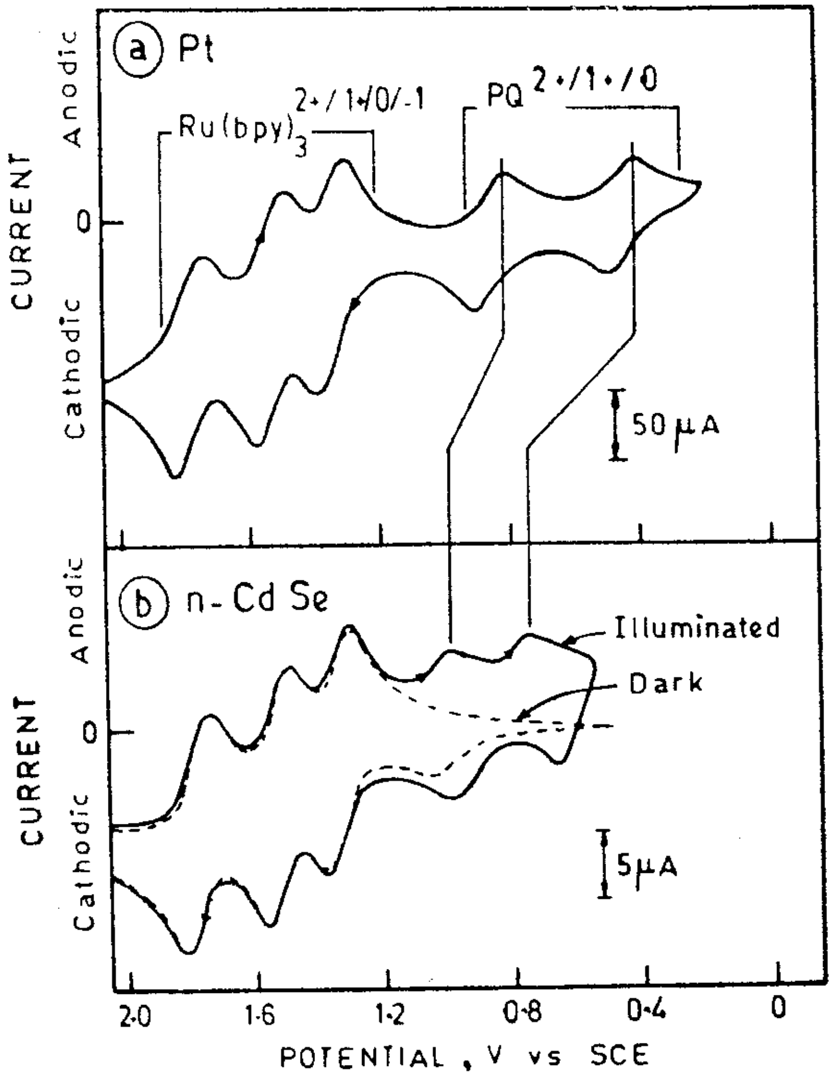

Fig. 16.8 Comparison of cyclic voltammetry at Pt (a) and illuminated (full line, 632.8 nm, ~ 50 mW cm^{-2}) and dark (broken line) *n* CdSe (b) in presence of 1 mM dimethyl viologen (PQ^{2+}) and 1 mM ($Ru(bpy)_3^{2+}$) in CH_3CN containing 0.1M *n*-butyl ammonium perchlorate. Sweep rate = 100 mV s^{-1}.

[From A Aruchamy, JA Bruce, S Tanaka and MS Wrighton, J Electrochem Soc 130 (1983) 359].

more efficient than from metal electrodes [48] which is well-known for a very long time [1].

The amount of photovoltage that can be generated at a semiconductor-electrolyte interface is an important parameter in solar collection efficiency. Theoretically, one should obtain a maximum photovoltage corresponding to the band gap. In a large number of investigations on narrow band gap semiconductor electrolyte interfaces, it was found that in systematic variation of redox systems with known linearly varying E^0 levels, the photovoltage (ΔV) obtained increases linearly and reaches a maximum limit which is invariably narrower than the band gap [34, 36, 49–54]. The maximum value for *p*-InP electrode, for example, is 0.8 V whereas the energy gap is as much as 1.35 *e*V [55]. This type of phenomenon is usually termed as 'Fermi-level pinning' and is generally assumed to be due to the presence of surface states (Section 16.2.4). It has been pointed out that this phenomenon on narrow band gap semiconductors may also be explained by assuming the formation of inversion layer [56] as discussed in Section 16.2.3. Some surface conductivity measurements have been presented in support of this view [57]. However, there are increasing evidences in favour of Fermi level pinning model. Detailed impedance analysis seems to support this model [58]. The very ΔV invarient limit can be modified by surface treatments indicating that a surface rather than the bulk property of the semiconductor is involved [59]. It is possible to compare quantitatively the Fermi level pinning effect in semiconductor-electrolyte interface with that of semiconductor-metal interface, where this effect has been well-established for a very long time [60].

So far the voltammetric investigations with special reference to energy level diagrams have been considered. In these treatments, one generally ignores the kinetic aspects of electron emission. There are however a few reports dealing with the carrier transport in the semiconductor [35], hot charge carrier injection into the electrolyte and its consequences [61], and charge transfer, kinetics at the interface proper [62]. It is hoped that these kinetic investigations would receive greater attention in the years to come.

16.4.3 SEMICONDUCTOR SURFACE PROCESSES

Most, if not all, of the compound semiconductors are formed from base metals whose metal/metal ion redox equilibrium potentials are very much in the negative direction. Hence the dissolution process is a highly favourable process from thermodynamic viewpoint. Hence the fact that many semiconductors show photochemical stability should be considered highly fortunate. This is particularly due to slow metal dissolution kinetics when compared with other charge transfer processes involved. The basic aspects [18, 63] and the details of classical dissolution studies on semiconductors [7, 9] have received comprehensive treatment in the literature. The dissolution kinetics of single crystal surfaces are also being investigated [64]. Figure 16.9 for example presents one of the classical photodissolution results obtained from *n*-Ge electrode [5]. The photocurrent increases with the intensity of the absorbed light under otherwise identical conditions, an important criterion that establishes a photoprocess [5].

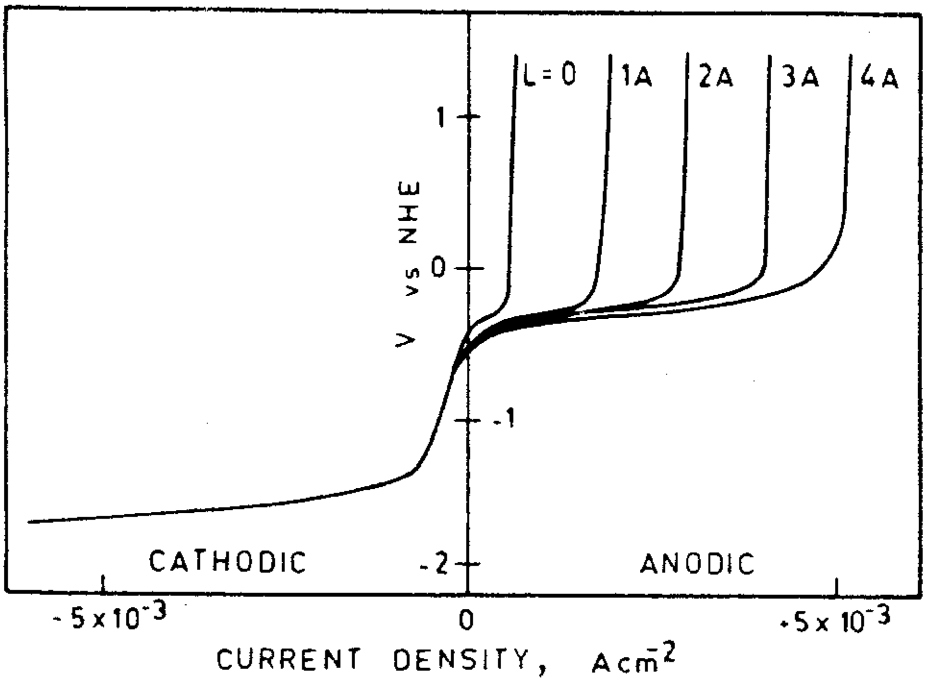

Fig. 16.9 Current voltage plots for *n*-Ge in 0.1N KOH at different light intensities where *A* is an arbitrary unit. Original data points have been deleted for clarity.

[From WH Bratton and GB Garralt, Bell Syst Tech J 34 (1955) 129]

Photodissolution of semiconductors forms the basis of electrochemical etching, a technologically important process in the field of semiconductors. Some detailed investigations on GaAs electrodes have, for example, shown that one can very accurately etch out this surface and also carry out surface profiling investigations at different depths from semiconductor surface planes [65].

Many semiconductor surfaces easily form oxide films on their electrode surfaces. The thickness of the passive oxide films and their stability in the electrolyte medium sometimes decide the electrochemical properties of the non-oxide semiconductors. This question shall again be taken up shortly (Section 16.4.4).

n-TiO_2 is the most familiar oxide semiconductor which is being investigated in electrochemistry. Most of the other metals also form oxide films that show semiconductor or insulator properties depending on the band gap of oxide films [2]. The oxide layers on Fe [66], Pb [67–69] and Cu [70[for example are quite relevant materials in semiconductor electrochemistry. Photo-excitation can also contribute to the oxide growth in addition to other redox processes on these oxide electrode materials when employed as photoelectrodes. This oxide growth process can have important consequences on the overall quantum efficiency [71].

16.4.4 SURFACE CHEMISTRY AND ITS EFFECTS ON REDOX REACTIONS

The main factor that stabilizes a semiconductor against photodissolution is the slow kinetics of this process as discussed above (Sections 16.2.4 and 16.4.3). If a redox reaction with much faster kinetics can consume the photogenerated holes in a semiconductor, one can achieve efficient solar conversion. This type of behaviour of sulphide/polysulphide, selenide/polyselenide, ferricyanide/ferrocyanide and a host of other redox reactions on cadmium chalcogenides is the main reason for the successful development of electrochemical photovoltaic cells. A number of detailed investigations [72–74] and a detailed review [75] may be consulted for further information on this interesting aspect.

The photodissolution is primarily caused by holes. The *n*-type semiconductors usually contain a small net positive charge near the interface under open circuit condition. The electric field also favours the movement of these holes towards the interface and hence creates enhanced opportunity for photodissolution. On the other hand, *p*-type materials under illumination acquires a negative charge and a sort of cathodic protection of the surface is achieved. This is the cause of comparatively stable performance of *p*-type semiconductors over *n*-type materials.

In most semiconductors, photo-excitation actually causes the breaking of chemical bonds and hence make the electrodes more prone to dissolution. The transition metal-based layer-type dichalcogenides (WS_2, $MoSe_2$ etc.) have another peculiar property. These electrodes have empty *d* levels. The photo-excitation is in the energy levels of the transition metal atom itself and no bond-breaking is involved. This extraordinary stability coupled with the well-known catalytic properties of the transition metal centres make them an important class of semiconductors for photoelectrochemical applications [66, 77].

Even single crystal electrodes can in fact contain surface defects which would be more prone to dissolution. Specific adsorption or adatom formation can stabilize such active sites. Halide adsorption, especially iodide adsorption, are found to be quite useful in the case of transition metal dichalcogenides. I^- ions seem to be chemisorbed on these electrodes and even serve as redox couple for oxidation of SO_2 [78]. Similarly Ag deposition is found to have substantial effect on the solar collection efficiency of *p*-InP [79].

Oxide films can protect the semiconductor electrodes from photodissolution. However, fairly thick oxide films can affect the adsorption of photons and hence photoefficiency. The oxide layer on *n*-Si is found to exhibit such negative effect [80]. The oxide layer on *p*-InP is found to be relatively thin and this has a positive effect of protection without loss of photocollection efficiency [81].

The formation of thick oxide layer on silicon may probably be avoided by producing a thin hydrogenated silicon layer [82, 83]. The amorphous Si electrodes that were hydrogenated in this fashion are found to give much better performance than the untreated counterparts.

The discussions in this section so far would already suggest the importance of semiconductor surface pretreatment on its photoelectrochemical behaviour Chemical etching, for example, can cause profound modification of semiconductor properties [84, 85]. Figure 16.10 for example shows the effects of oxidative ($Cr_2O_7^{2-}/HNO_3$) and reductive ($S_2O_4^{2-}/OH^-$) surface treatments on the voltammetric behaviour of *p*-CdTe. The extreme differences in the behaviour are obvious from the voltammograms [85]. The actual causes of most of the surface pretreatments are not quite clear as yet. But the wide variations in the response certainly open up the great potentialities of the surface modification of this type and offer extensive scope for further work.

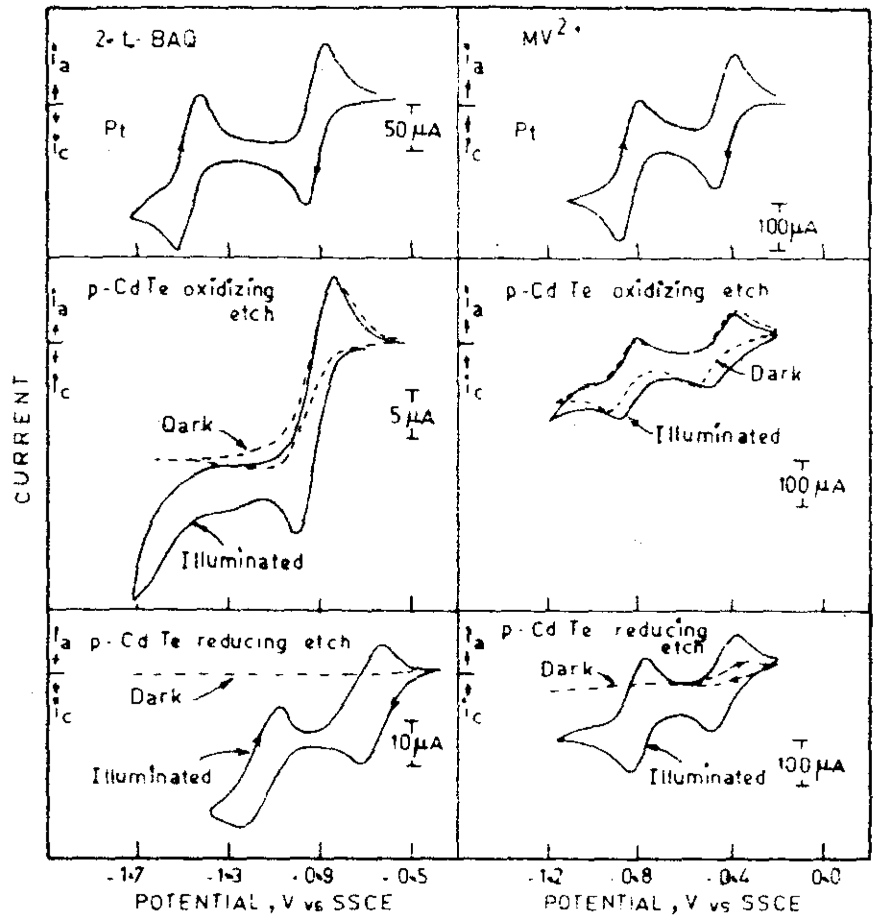

Fig. 16.10 Cyclic voltammograms of 2 t-butyl anthraquinone (2-t-BAQ) and methyl viologen (MV^{2+}) at Pt and 'oxidized' and 'reduced' *p*-type Cd-Te under dark (broken lines) and illuminated (full lines) conditions at 632.8 nm and ~ 40 mW cm^{-2}. The voltammograms were recorded in CH_3CN, 0.2 M tetra *n*-butyl ammonium fluoborate at a sweep rate of 100 mV s^{-1}.

[From HS White, AJ Ricco and MS Wrighton, J Phys Chem 87 (1983) 5140]

Surface modification can also be achieved by forming films of well-known chemical properties. The conducting polymer films physically prevent electrode dissolution [86]. But such films should be fairly thin. Thicker films would retard the charge transport through the film and hence the overall charge transfer rate. The redox modifications and their catalytic effects are treated in a separate section (Section 16.4.6) later.

16.4.5 REACTIONS INVOLVING ADSORBED INTERMEDIATES

As seen many earlier, technologically important reactions such as H_2, O_2 and Cl_2 evolution, or O_2 reduction *via* adsorbed intermediates require catalytic surfaces for enhanced rate, even on metal electrodes (Chapter 12). The photoelectrochemistry of these processes is also very important and the processes do need catalytic surfaces. Many attempts towards developing successful processes of this type has been made [87, 88]. This section just concentrates on a few sample references of each type of processes.

H_2O oxidation on *n*-type semiconductors, mostly *n*-TiO_2, still predominates the photoelectrochemical research [37]. A variety of modifications such as porous oxide formation [89], noble metal deposition [90], and surface polishing and pretreatment effects [91] are still being investigated. Since O_2 evolution can be catalyzed by RuO_2 layers, the incorporation of this layer on *n*-GaP electrodes has been investigated [92].

But in recent times, much faster pace of progress is noticed in the water reduction to H_2 on *p*-type materials, particularly on *p*-InP. A few comprehensive reviews covering recent developments are available [93, 94]. Each specific factor that can influence collection efficiency has been comprehensively analyzed for this system. The effect of alloying elements [95] and chemical passivation of recombination centres are cited [96] as examples. Although *p*-InP holds promise as a good photocathode for H_2 evolution, other electrodes such as *p*-Si are still being investigated for this purpose [97]. An interesting co-precipitated ZnS-CdS electrode has been developed, which enables photoassisted hydrogen generation by absorbing visible light [98]. However the photovoltage obtained on these *p*-type materials is usually less than 1.0 V and hence one has to apply a great deal of bias voltage to achieve photodecomposition. A probable answer lies in coupling a photocathode of this type with another photoanode for O_2 evolution and achieve an overall two-photon process. Although this concept is well-known, a successful development of a system for H_2O decomposition is yet to emerge.

In contrast, with the decomposition of water, HCl, HBr and HI require very little decomposition voltage and a single photon absorbing *p*-InP is enough for this purpose [94]. Figure 16.11 for example shows that the cathodic photocurrent wave in HI starts before the

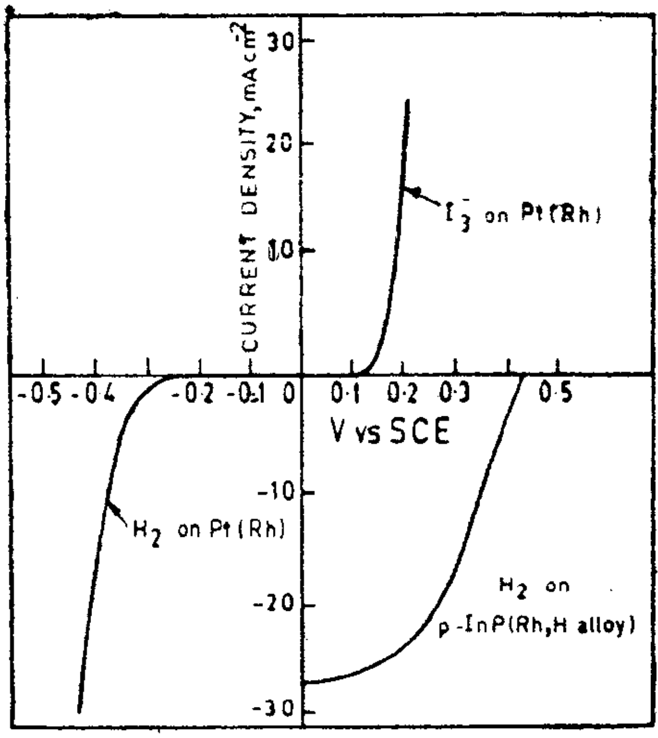

Fig. 16.11 Current voltage characteristics of *p*-InP (Rh, H alloy) photocathode in 2M HI + 2M $NaClO_4$ under tungsten-halogen irradiance. The current-voltage curves of Pt (Rh) anode and cathode are also shown for comparison.

[From A Heller in Proc. Int. Conf. Photochem. Storage Sol. Energy 4th A (1982) p 63].

anodic I^- oxidation wave. This cell can thus produce H_2 and I_2 with simultaneous production of electricity. More details on photoelectrolysis involving halide ions are available in the literature [94].

Apart from the above processes that have received considerably greater attention, the photo-oxidation of organic compounds [99], reduction of SO_2 [100] and O_2 [101] and many other small molecular systems are also being investigated. CO_2 reduction [102] and N_2 reduction [103] are two important photochemical processes of nature. Serious efforts are on to achieve what has been achieved by nature through photoelectrochemical route.

One would certainly agree that activation of molecular species at the interface is necessary for the electron transfer processes like H_2 and O_2 evolution and O_2 reduction. It is in this context that the potential drop at the Helmholtz layer is being proposed [31-33, 104]. Although the experimental results support the model proposed by these authors (Section 16.2.4) these results are yet to be confirmed by other research workers in this field.

16.4.6 REDOX MODIFICATIONS AND REDOX CATALYSIS

One of the earliest applications thought of for polymer modified electrodes (Chapter 10) was the protection of narrow band gap

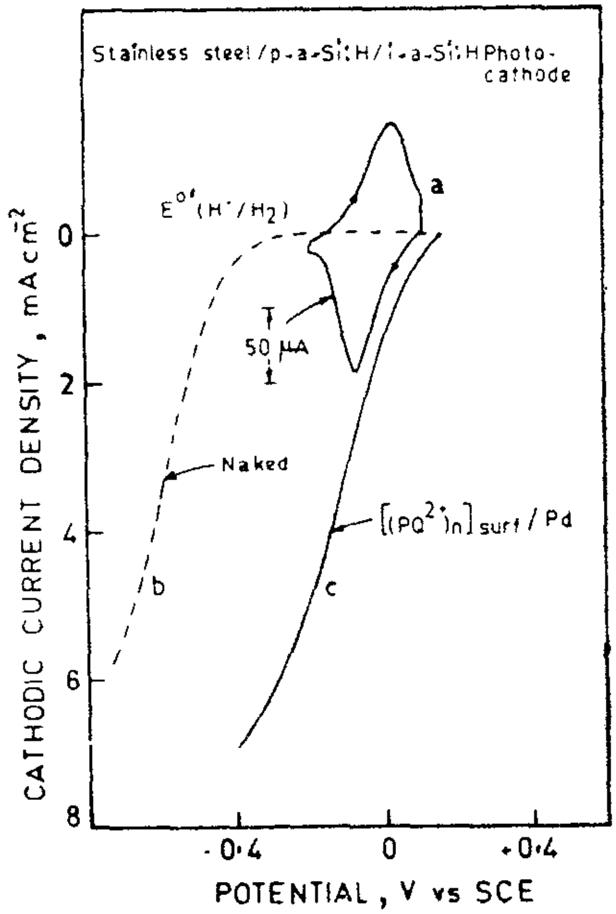

Fig. 16.12 Cyclic photocurrent voltammogram of surface bond dialkyl bipyridinium (PQ^{2+}) (a) and the photocurrent-voltage curve of H_2 evolution reaction at a naked pSi electrode (b) and redox modified electrode with Pd loading on the redox film (c) conditions 0.5M LiCl, pH = 4.0 in acetate buffer, tungsten lamp illumination ~ 250 mW cm^{-2}.

[From MS Wrighton, J Vac Sci Technol A.2 (1984) 795].

semiconductor surfaces. Polyvinyl ferrocene films were formed on *n*-Si [105, 106], *n*-Ge [107], *n*-GaAs [108] and even on fairly stable *n*-TiO_2 [109] electrodes. These modified electrodes were found to catalyze a number of simple electron transfer reactions under photoexcited conditions [110].

Among the photoredox catalytic reactions investigated, the H_2 evolution on alkyl-viologen systems is probably the most comprehensively investigated one [88, 111–114]. Figure 16·12, for example, shows the photocurrent due to a naked semiconductor, the redox property of the alkyl viologen film and the catalytic influence of this film on H_2 evolution. Comprehensive analysis of this redox catalytic process is available [111–114]. Redox catalytic pathways are also being developed for CO_2 reduction to HCHO, HCOOH and CH_3OH [115] and O_2 reduction to H_2O_2 [116].

As mentioned earlier (Section 16.4.4), protection and electron transfer characteristics of conducting polymer films such a polypyrrole [117] and polyacetylene [118] films are being reported. Quantitative methods for detailed surface characterization of these films are now available [119]. Attempts are also being made to investigate the band gaps and semiconductor properties of these conducting polymer films [120]. One may hope for some interesting developments in this area in the near future.

16.5 ANALYTICAL APPLICATIONS AND SCOPE

Although voltammetric methods are often employed in energy level studies and photocurrent responses, this method as such has not become quite popular like capacitance measurements, for example. However, these methods can be very useful in obtaining quick results on the surface chemistry and the influence of surface pretreatments. The information obtained from cyclic voltammetry, for example, is much more straightforward from the electrochemical viewpoint when compared with the Mott-Schottky plots. However, the field as such is still dominated by the methodologies that are in use in semiconductor physics probably because the people who enter into the field are still from the solid state physics rather than from chemistry and electrochemistry.

The emphasis on the chemistry of the surfaces and surface modification is very much necessary for further developments in the field.

There is unlimited scope for further studies. New electrodes are becoming commercially available. The importance of surface chemistry is being recognized. New cell assemblies are being constructed and evaluated. There is certainly a lot of scope for improving the collection efficiency beyond 12 per cent in single crystal electrodes and beyond 6 per cent in polycrystalline electrodes which have been the maximum levels attained for quite some time now. Looking at the recent developments, one certainly hopes that the whole field of photoelectrochemistry is quite close to a take-off stage in terms of technology development. Once this is achieved, the fundamental and applied sciences would grow hand in hand at a much faster pace.

REFERENCES

1 Yu Ya Gurevich, Yu V Pleskov and ZA Rotenberg, Photoelectrochemistry, Consultants Bureau, N York (1980).

2 U Stimming, Electrochim Acta 31 (1986) 415.

3 F Willig, Adv Electrochem Electrochem Eng 12 (1981) 1.

4 WH Brattan and GB Garret, Bell Syst Tech J 32 (1955) 1.

5 WH Brattan and GB Garret, Bell Syst Tech J 34 (1955) 129.

6 A Fujishima and K Honda, Nature 238 (1972) 37.

7 H Gerischer, Adv Electrochem Electrochem Eng 1 (1961) 139.

8 VA Myamlin and Yu V Pleskov, Electrochemistry of Semiconductors, Plenum, N York (1966).

9 AK Vijh, Electrochemistry of Metals and Semiconductors, Marcel Dekker, N York (1971).

10 R Memming in Electroanal Chem 11 (1979) 1.

11 SR Morrison, Electrochemistry at Semiconductor and Oxidized Metal Electrodes, Plenum N York (1980).

12 Photovoltaic and Photoelectrochemical Energy Conversion (F Cardon, WP Gomes and W Dekeyser, Ed) NATO ASI series, Plenum, N York (1981).

13 S Chandra, Photoelectrochemical Solar Cells, Gorden and Breach Science Publishers, N York (1985).

14 LM Peter in Electrochemistry 9 (1984) 66.

15 Photoelectrochemistry, Photocatalysis and Photoreactors (M Schiavello, Ed) NATO ASI series, D Riedel, Dodrecht (1985).

16 Yu V Pleskov and Yu Ya Gurevich, Semiconductor Photoelectrochemistry, Consultants Bureau, N York (1986).

17 Handbook on Semiconductors, Vol. 1-4 (TS Moss, Ed) North-Holland, Amsterdam (1980).
18 H Gerisher, Page 39 in ref 15.
19 R Memming, Page 107 in ref 15.
20 WW Gartner, Phys Rev 116 (1959) 84.
21 MA Butler, J Appl Phys 48 (1977) 1914.
22 J Reichman, Appl Phys Lett 36 (1980) 574.
23 J Albery PN Bartlett, A Hamnett and MP Dare-Edwards, J Electrochem Soc 128 (1981) 1492.
24 A Hamnett in Photogeneration of Hydrogen (A Harriman and MA West, Ed) Academic Press N York, (1982) p. 147.
25 W Hirschwald in Current Topics in Materials Science, Vol. 6 (E Kaldis, Ed) North-Holland Publishing Co, Amsterdam (1980) p. 109.
26 JN Chazalviel, J Electrochem Soc 129 (1982) 963.
27 K Rajeshwer, J Electrochem Soc 129 (1982) 1003.
28 RH Wilson, J Appl Phys 48 (1977) 4292.
29 JJ Kelly and R Memming, J Electrochem Soc 129 (1982) 730.
30 F Cardon, WP Gomes, F Vanden Kerchove, D Vanmaekelbergh and F Van Overmeire, Faraday Disc Chem Soc 70 (1981) 155.
31 JO'M Bockris, T Uosaki and H Kita, J Appl Phys 52 (1981) 808.
32 J O'M Bockris, SUM Khan, OJ Murphy and M Szklarczyk, Int J Hydrogen Energy 9 (1984) 243.
33 M Skhlarczyk and J O'M Bockris, J Phys Chem 88 (1984) 1808.
34 FRF Fan, B Reichman and AJ Bard, J Am Chem Soc 102 (1980) 1488.
35 LB Wheeler, G Nagasubramanium, AJ Bard, J Electrochem Soc 131 (1984) 1038.
36 AJ Bard, FRF Fan, AS Gioda, G Nagasubramanian and HS White, Faraday Discussions of the Chemical Society 70 (1980) 19.
37 S Chandra, p. 184 in ref 13.
38 H Morisaki, H Ono and K Yazawa, J Electrochem Soc 131 (1984) 2081.
39 OV Romanov and MA Sokolov, Elektrokhimiya 20 (1984) 1346.
40 T Yamase, H Harada, T Ikawa, S Ikeda, and H Shirakawa, Bull Chem Soc Japan 54 (1981) 2417.
41 JA Baglio, GS Colobrese, E Kamieniecki, R Kershow, CB Kubliak, AJ Ricco, A Wold, MS Wrighton and GD Zoski, J Electrochem Soc 129 (1982) 1461.
42 JA Baglio, GS Calabrese, DJ Harrison, E Kamieniecki, AJ Ricco, MS Wrighton and D Zoski, J Am Chem Soc 105 (1983) 2246.
43 A Aruchamy and MS Wrighton, J Phys Chem 84 (1980) 2848.
44 LF Schneemeyer and MS Wrighton, J Am Chem Soc 101 (1979) 6496.
45 A Aruchamy, JA Bruce, S Tanaka and MS Wrighton, J Electrochem Soc 130 (1983) 359.

46 RE Malpas, K Itaya and AJ Bard, J Amer Chem Soc 101 (1979) 2535.

47 M Herlem, D Guyomard, C Mathew J Belloni and JL Solfort, J Phys Chem 88 (1984) 3826.

48 R Parsons, G Picq and P Vennereau, J Electroanal Chem 181 (1984) 281.

49 PA Kohl and AJ Bard, J Electrochem Soc 126 (1979) 59, 603.

50 FRF Fan, HS White, B Wheeler and AJ Bard, J Electrochem Soc 127 (1980) 518.

51 AJ Bard, AB Bocarsly, FRF Fan, EG Walton and MS Wrighten, J Am Chem Soc 102 (1980) 3671.

52 AB Bocarsly, DG Bookbinder, RN Dominey, NF Lewis and MS Wrighten, J Am Chem Soc 102 (1980) 3677.

53 FRF Fan, TV Shea and AJ Bard, J Elecrrochem 131 (1984) 828.

54 G Nagasubramanian, BL Wheeler, FRF Fan and AJ Bard, Photoelectrochemistry Fundamental Processes and Measurement Techniques (WL Wallace, AJ Nazik and SK Deb, Ed) Electrochem Soc Inc, Pennington NJ (1982) p 372.

55 RN Dominey, NS Lewis and MS Wrighton, J Am Chem Soc 103 (1981) 1261.

56 H Gerischer, Discussions relating to ref 36 in the first discussion section of the same proceedings.

57 CD Talger, H Gerischer ane W Kautek, Ber Bunsenges Phys Chem 86 (1982) 20.

58 G Nagasubramanian, BL Wheeler and AJ Bard, J Electrochem Soc 130 (1983) 1680.

59 JB Bolts, AB Bocarsly, MC Palazzotto, EG Walton, NS Lewis and MS Wrighton, J Am Chem Soc 101 (1979) 1378.

60 G Horowitz, P Allongue and H Cachet, J Electrochem Soc 131, 11 (1984) 2563.

61 F Decker, B Pettinger and H Gerischer, J Electrochem Soc 130 (1983) 1335.

62 S Nakabayashi, S Miyabe, A Fujishima and K Honda. J Electroanal Chem 157 (1983) 135.

63 H Gerischer, Faraday Disc Chem Soc 70 (1980) 137.

64 PA Kohl, C Wolowodink and FW Ostermayer, J Electrochem Soc 130 (1983) 2288.

65 MM Faktor, T Ambridge, CR Elliott and JC Regnault in Current Topics in Materials Science, Vol. 6 (E Kaldis, Ed) North-Holland, Amsterdam (1980) p1.

66 MP Dare Edwards, JB Goodenough, A Hamnett and PR Travellick, J Chem Soc Faraday Trans 79, 9 (1983) 2027.

67 B krazysztof, Electrochim Acta 28, 12 (1983) 1767.

68 M Dimitrov, K Kochev and D Pavlov, J Electroanal Chem 183, (1985) 145.

69 JS Buchanan, NP Freestone and LM Peter, J Electroanal Chem 182 (1985) 383.

70 LM Abrautes, LM Castillo, C Norman and LM Peter, J Electroanal Chem 163 (1984) 209.

71 S Chandra, p. 163 in ref 13.

72 P Allongue, H Cachet and G Horowitz, J Electrochem Soc 130 (1983) 2352.

73 J Reichman and MA Russak, J Electrochem Soc 131 (1984) 796.

74 JH Reeves and M Cocivera, J Electrochem Soc 131 (1984) 2042.

75 G Hodes, in Energy Resource through Photochemistry and Catalysis (M Onatzel, Ed) Academic Press, N York (1983) p. 421

76 H Tributsch, Faraday Disc Chem Soc 70 (1980) 189.

77 H Tributsch, J Photochem 29 (1985) 89.

78 GS Calabrese and MS Wrighton, J Am Chem Soc 103 (1981) 6273.

79 A Heller, J Vac Sci Technol 21 (1982) 559.

80 SR Morrison, MJ Madou and KW Frese, in Photoeffects at Semiconductor-Electrolyte interfaces (AJ Nozik, Ed) ACS Symp Series No. 146 American Chemical Society, Washington (1981) p. 179.

81 A Heller, B Miller and FA Thiel, Appl Phys Lett. 38 (1981) 282.

82 DJ Harrison, GS Calabrese, AJ Ricco J Dresner and MS Wrighton, J. Am Chem Soc 105 (1983) 4212.

83 GS Calabrese, MS Lin, J Dresner and MS Wrighton, J Am Chem Soc 104 (1982) 2412.

84 S Tanaka, JA Bruce and MS Wrighton, J Phys Chem 85 (1981) 3778.

85 HS White, AJ Ricco and MS Wrighton, J Phys Chem 87 (1983) 5140.

86 AJ Frank in Energy Resources through Photochemistry and Catalysis (M Gratzel, Ed) Academic Press, N York (1983) p. 467.

87 G Hodes, SJ Fonash, A Heller and B Miller, Adv Electrochem Electrochem Eng 13 (1985) 113.

88 MS Wrighton, J Vac Sci Technol A 2 (1984) 795.

89 D Miller, S Mamicke-Afara, MJ Dignam and M Moskovits, Chem Phys Lett 100 (1983) 236.

90 T Kobayashi, H Yoneyama and H Tamura, J Electrochem Soc 130 (1983) 1706).

91 P Salvador, C Gutierrez, G. Campet and P Hagenmueller, J Electrochem Soc 131 (1984) 550.

92 R Nonfi, J Electrochem Soc 130 (1983) 2126.

93 A Heller, Science 223 (1984) 1141.

94 A Heller in Energy Resources through Photochemistry and Catalysis (M Gratzel, Ed) Academic Press, N York (1983) p. 385.

95 E Aharon-Shalon and A Heller, J Electrochem Soc 129 (1982) 2865.

96 A Heller, WJ Leamy, B Miller and W Johnston, J Phys Chem 87 (1983) 3239.

97 RN Dominey, NS Lewis, JA Bruce, DC Bookbinder and MS Wrighton, J Am Chem Soc 104 (1982) 467.

98 N Katuta, KH Park, MF Finlayson, A Veno, AJ Bard, A Campion, MA Fox, SE Weber and JM White, J Phys Chem 84 (1985) 732,

99 JH Kennedy and D Dunnwald, J Electrochem Soc 130 (1983) 2013,

100 GS Calabrese, TJ Sobieralski and MS Wrighton, Inorg Chem 22 (1983) 1634.

101 J Li and LM Pter, J Electroanal Chem 182 (1985) 399.

102 M Halmann in Energy Resources through Photochemistry and Catalysis (M Gratzel, Ed), Academic Press, N York (1983) p 507.

103 AE Shilov in Energy Resources through Photochemistry and Catalysis (M Gratzel, Ed) Academic Press, N York (1983) p 535.

104 M Szklarczyk, JO'S Bockris, V Brusie and G Spanon, Int J Hydrogen Energy 9 (1984) 707.

105 KD Legg, AB Ellis, JW Bolts and MS Wrighton, Proc Nat Acad Sci USA 74 (1977) 4116.

106 MS Wrighten, RG Austin, AB Bocasly J Bolts, O Haas, KD Legg, L Nadjo and M Polozzotto, J Am Chem Soe 100 (1978) 1602.

107 JM Bolts and MS Wrighton, J Am Chem Soc 100 (1978) 5257.

108 JM Bolts and MS Wrighton, J Am Chem Soc 101 (1979) 6179.

109 DR Rolison and RW Munay, J Electrochem Soc 131 (1984) 337.

110 JM Bolts, AB Bocarsly, MC Polazzotto, EG Walton, NS Lewis and MS Wrighton, J Am Chem Soc 101 (1979) 1378.

111 DC Bookbinder and MS Wrighton, J Am Chem Soc 102 (1980) 5123.

112 NS Lewis, AB Bocarsly and MS Wrighton, J Phys Chem 84 (1980) 2033.

113 HD Abruna and AJ Bard, J Am Chem Soc 103 (1981) 6898.

114 RN Dominey, NS Lewis, JA Bruce, DC Bookbinder and MS Wrighton, J Am Chem Soc 104 (1982) 467.

115 M Zafir, M Ulman, Y Zuckerman and M Halmann, J Electroanal Chem 159 (1983) 373.

116 GS Calabrese and MS Wrighton, J Electrochem Soc 128 (1981) 1014.

117 R Naufi, AJ Frank and AJ Nozik, J Am Chem Soc 103 (1981) 1849.

118 AR Simon and SM Wrighton, Appl Phys Lett 44 (1984) 930.

119 N Kakuta, JM White, A Campion, AJ Bard, MA Fox and SE Webber. J Phys Chem 89 (1985) 48.

120 FA Sammells and GPP Ang, J Electrochem Soc 131, 3 (1984) 617.