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A STUDY ON THE FUNDAMENTAL THEORETICAL ASPECTS OF SEMICONDUCTOR ELECTROCHEMISTRY

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A Study on the Fundamental Theoretical Aspects of Semiconductor Electrochemistry

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Abstract – This paper begins with a brief overview of aspects of semiconductor electrochemistry. The basic principles of semiconductor/electrolyte junctions are then outlined along with their application in different photo electrochemical devices, including solar cells. The special properties of nanostructured semiconductor electrolyte systems are contrasted with those of bulk analogues, and applications of mesoporous semiconductor films in dye-sensitized solar cells and water splitting systems are described. The study concludes with a short survey of a range of experimental methods used in semiconductor electrochemistry.

In the present document energy levels in the bulk of the solid and the electrolyte including their interface are introduced and kinetic parameters defined. In addition a terminology on photo electrochemical cells is recommended. In the latter case, it is distinguished between two modes of operation in these cells, i.e. photovoltaic cells in which radiant energy is converted into electrical energy and photo electrolysis cells in which radiant chemistry causes a net chemical conversion.

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INTRODUCTION

The study of semiconductor-electrolyte interfaces has both fundamental and practical incentives. These interfaces have interesting similarities and differences with their semiconductor-metal (or metal oxide) and metal-electrolyte counterparts. Thus, approaches to garnering a fundamental understanding of these interfaces have stemmed from both electrochemistry and solid-state physics perspectives and have proven to be equally fruitful. On the other hand, this knowledge base in turn impacts many technologies, including microelectronics, environmental remediation, sensors, solar cells, and energy storage. Some of these are discusseelsewhere in this volume.

It is instructive to first examine the historical evolution of this field. Early work in the fifties and sixties undoubtedly was motivated by application possibilities in electronics and came on the heels of discovery of the first transistor. Electron transfer theories were also rapidly evolving during this period, starting from homogeneous systems to heterogeneous metal-electrolyte interfaces leading, in turn, to semiconductor-electrolyte junctions. The 1973 oil embargo and the ensuing energy crisis caused a dramatic spurt in studies on semiconductor-electrolyte interfaces once the energy conversion possibilities of the latter were realized.
Subsequent progress at both fundamental and applied levels in the late eighties and nineties has been more gradual and sustained. Much of this later research has been spurred by technological applicability in environmental remediation scenarios. Very recently, however, renewed interest in clean energy sources that are nonfossil in origin, has provided new impetus to the study of semiconductor-electrolyte interfaces. As we also learn to understand and manipulate these interfaces at an increasingly finer (atomic) level, new microelectronics application possibilities may emerge, thus completing the cycle that first began in the 1950s.

To facilitate a self-contained description, we will start with well-established aspects related to the semiconductor energy band model and the electrostatics at semiconductor-electrolyte interfaces in the "dark". We shall then examine the processes of light absorption, electron-hole generation, and charge separation at these interfaces. The steady state and dynamic aspects of charge transfer are then briefly considered. Nanocrystalline semiconductor films and size quantization are then discussed as are issues related to electron transfer across chemically modified semiconductor-electrolyte interfaces. Finally, we shall introduce the various types of photoelectrochemical devices ranging from regenerative and photoelectrolysis cells to dye-sensitized solar cells.[1]

Widespread interest in the potential applications of semiconductor electrochemistry was sparked by the oil crisis in the early 1970s, when the search for renewable energy sources suddenly became an urgent priority. Although the foundations of the subject had already been laid a decade earlier by the seminal work of Gerischer and others, it was a 1972 paper in Nature by Fujishima and Honda reporting the photoelectroehemical splitting of water using a titanium dioxide electrode that caught the world's attention. The promise of generating hydrogen using sunlight encouraged scientists worldwide to turn their attention to semiconductor photoelectrochemistry. Although further progress on water splitting was slow, the following decade saw the rapid development of highly efficient regenerative solar cells based on single ciystal and polycrystalline semiconductors in contact with redox electrolytes. Unfortunately, one of the main problems with these cells is that they rely on rapid electron transfer to or from the solution redox species to prevent parasitic corrosion reactions involving photo generated minority carriers (e.g. holes in the case of w-type semiconductors). In practice, these side reactions limit the lifetime of photoelectroehemical solar cells to such an extent that they are unable to compete with conventional solid state devices. However, the field of semiconductor photo electrochemistry saw a remarkable resurgence of activity following another Nature paper, this time in 1992. by O'Regan and Gratzel. Who demonstrated that efficient and stable regenerative photo electrochemical cells could be made using a thin porous layer of nanocrystal line titanium dioxide coated with a ruthenium-based sensitizing dye. These dye-sensitized solar cells (DSC) have now achieved efficiencies that are comparable with other low cost thin film photovoltaic devices. Interestingly, the way that the DSC operates differs substantially from its solid state predecessors, since band to band excitation of electrons is not involved. Instead, sunlight is absorbed by the sensitizer dye. and the photo excited dye molecules inject electrons into the conduction band of the nanocrystal line TiCK The injected electrons are collected at the contact by trap-limited diffusion, and the oxidized dye is regenerated rapidly by electron transfer from solution redox species. Since no holes are generated in the TiCb by the illumination, it is generally the stability of the dye and electrolyte that determines the solar cell lifetime.

Semiconductor electrochemistry is also important in other areas besides solar energy conversion. For example, the processing of silicon for electronic devices involves etching processes that can be understood in terms of a combination of chemical and electrochemical reaction steps. Electro- chemical etching of silicon is also used to prepare porous silicon layers, which exhibit unusual optical and electronic properties arising from quantum confinement of electrons and holes within the nanostmctured material. Electrochemical processes are also involved in the deposition of metal contacts during fabrication of electronic devices. Electrochemistry has also been used to grow semiconductor layers for thin film solar cells: the best known example is the BP Solar Apollo® process for the growth of CdTe films for CdS|CdTe cells. More recently, electrodeposition has been used to fabricate layers of Cu(In|Ga)Se2 (CIGS) for thin film solar cells. Finally the area of photo catalysis using semiconductor colloids is closely related to semiconductor electrochemistry.

The development in applied aspects of semiconductor electrochemistry has been paralleled by a steady growth in our understanding of the basic physical and chemical processes taking place at semiconductor electrolyte interfaces. At the same time, a range of experimental methods has been developed to deal with the need to understand the mechanisms and kinetics of electrode reactions taking place at illuminated semiconductor electrodes. These involve measuring not only time- and frequency-resolved currents and voltage responses to illumination but also corresponding changes in properties such as microwave reflectivity or visible/infrared transmission. Methods developed for bulk semiconductor electrodes have been applied successfully to investigate nanostmctured semiconductor electrodes. The objective of this study is to give a reasonably comprehensive and balanced overview of the present state of the art.[2,3]

SEMICONDUCTOR ELECTROCHEMISTRY

Energy levels in semiconductors - The properties of semiconductors can to a large extent be described by their electronic band structure which can be obtained by solving the Schrödinger equation. The solution shows that all semiconductors possess a forbidden energy region termed the bandgap, E_g, in which energy states cannot exist. This region lies between the lowest unoccupied energy band called the conduction band (CB) and the highest occupied energy band called the valence band (VB).

If both the lowest minimum of the conduction band, E_c, and the highest maximum of the valence band, E_v, occur at the same wave vector k, the corresponding energy gap is termed a direct bandgap as illustrated to the left in Figure 1. If on contrary the conduction band minimum is found at a different k-vector the energy gap is termed an indirect bandgap. A transition from the VB to the CB will then require a change in crystal momentum by a phonon ($h\omega$).[4]

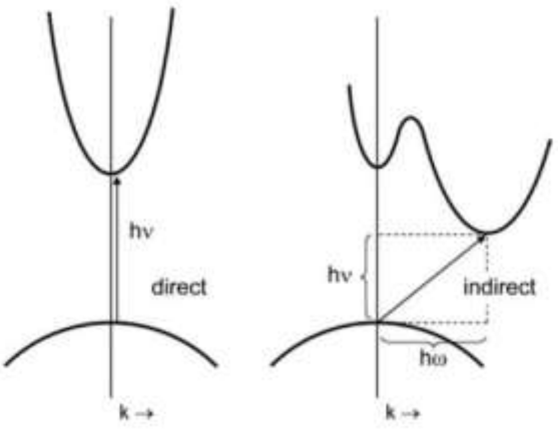


Figure 1 : Direct (left) and indirect (right) bandgap of a semiconductor.

The Fermi energy, *EF*, of a semiconductor is defined as the energy of the topmost filled orbital at absolute zero. At temperatures above absolute zero the distribution of electrons in the semiconductor is describes by Fermi-Dirac statistics. The probability that an energy level *E* is occupied by an electron at an absolute temperature *T* is then given by the Fermi function *f(E)* where *k* is the Boltzmann constant:

$$f(E) = \frac{1}{1+\exp\left(\frac{E-E_F}{kT}\right)} \quad (1)$$

At energy levels slightly below *EF* the occupation probability becomes unity while at energy levels a few *kT* above *EF* it tends towards zero. Thus the probability of occupancy is ½ at the Fermi level for an absolute temperature *T*.

For an intrinsic (i.e. undoped) semiconductor the Fermi energy will be situated close to the middle of the bandgap as shown in Figure 2(a). This is because the last term in below equation will be small when the effective masses of holes and electrons are almost equal $m_h^* \approx m_e^*$.

$$E_F = \frac{1}{2}E_g + \frac{3}{4}kT\ln\left(\frac{m_h^*}{m_e^*}\right) \approx \frac{1}{2}E_g \quad (2)$$

For an extrinsic (i.e. doped) semiconductor energy levels are introduced within the bandgap. A semiconductor doped with electron donors is called n-type and has a Fermi level just below the conduction band edge, Figure 2(b). Doping with electron acceptors yields a p-type semiconductor with a Fermi level just above the valence band edge as illustrated in Figure 2(c).

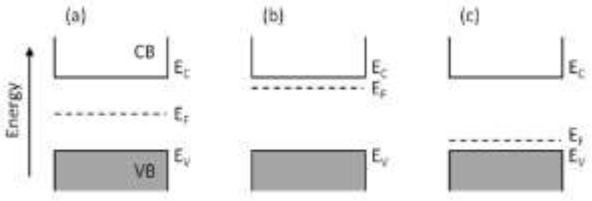


Figure 2 : Energy levels for (a) an intrinsic semiconductor, (b) an n-type semiconductor and (c) a p-type semiconductor.

ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL MEASUREMENTS

A standard three electrode setup was used for the electrochemical measurements with the photocatalyst on a conducting substrate as working electrode (WE), platina as counter electrode (CE) and a reversible hydrogen electrode (RHE) as reference. The reference electrode (RE) was placed as close to the working electrode as possible to reduce ohmic losses in the electrolyte. A sketch of the setup is illustrated in Figure 3.

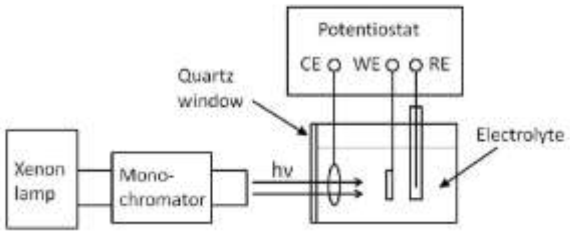


Figure 3 : Experimental setup consisting of a standard 3 electrode setup connected to a potentiostat with a xenon lamp irradiating the working electrode.

The electrodes were connected to a potentiostat (Zahner IM6ex) and placed in a square shaped cell with one side made of quartz. The light was sent through the plane quartz side to reduce the refraction and absorption of light in the cell wall. As electrolyte 0.5M H2SO4 (95- 97%, Sigma-Aldrich) or 0.5M K2SO4 (99.0%, Alfa Aesar) was used. The current and potential were measured and regulated using the program "Thales". All the polarizing potentials reported in this report are referred to the standard hydrogen electrode.

Electrochemical impedance spectroscopy - A potentiostat (Zahner IM6ex) was used to carry out the impedance measurements. The impedance was measured at potentials ranging from 0 to 1.2V by applying a 10mV ACvoltage with frequencies from 100 mHz – 100 kHz onto the constant potential. The amplitude and phase of the corresponding AC-current was measured by the potentiostat. Impedance data were used to determine the capacitance of the space charge region of the photocatalyst by modeling the electrochemical system as a simple equivalent circuit.[5]

ELECTRON ENERGY LEVELS IN SEMICONDUCTORS

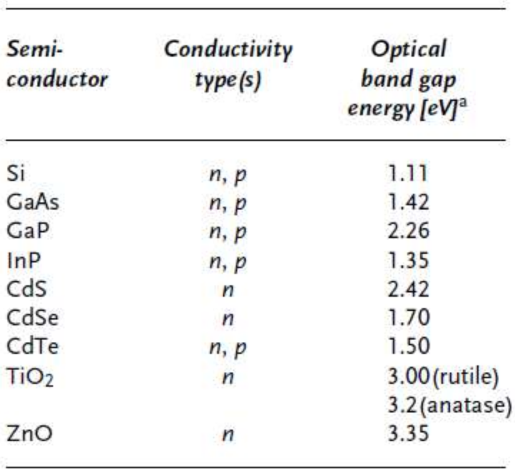
Unlike in molecular systems, semiconductor energy levels are so dense that they form, instead of discrete molecular orbital energy levels, broad energy bands. Consider a solid composed of N atoms.

Its frontier band will have 2-N energy eigenstates, each with an occupancy of two electrons of paired spin. Thus, a solid having atoms with odd number of valence electrons (e.g. Al with [Ne]$3s^2$ $3p^1$) will have a partially occupied frontier band in which the electrons are delocalized. On the other hand, a solid with an even number of valence electrons (e.g. Si having an electron configuration of [Ne]$3s^2 2p^2$) will have a fully occupied frontier band (termed a valence band, (VB)). The situation for Si is schematized in Fig. 4.

As Fig. 5 illustrates, the distinction between semiconductors and insulators is rather arbitrary and resides with the magnitude of the energy band gap (Eg) between the filled and vacant bands.

Semiconductors typically have Eg in the 1 eV-4 eV range (Table 1). The vacant frontier band is termed a conduction band, (CB) (Fig. 5). We shall see later that Eg has an important bearing on the optical response of a semiconductor.[6]

For high density electron ensembles such as valence electrons in metals, Fermi statistics is applicable. In a thermodynamic sense, the Fermi level, (defined at 0 K as the energy at which the probability of finding an electron is 1/2) can be regarded as the electrochemical potential of the electron in a particular phase (in this case, a solid). Thus, all electronic energy levels below $£_F$ are occupied and those above E_f are likely to be empty.[7,8]



Semi-conductor	Conductivity type(s)	Optical band gap energy [eV]^a
Si	*n, p*	1.11
GaAs	*n, p*	1.42
GaP	*n, p*	2.26
InP	*n, p*	1.35
CdS	*n*	2.42
CdSe	*n*	1.70
CdTe	*n, p*	1.50
TiO_2	*n*	3.00(rutile) 3.2(anatase)
ZnO	*n*	3.35

^{a}The values quoted are for the bulk semiconductor.

Table 1 : Some elemental and compound semiconductors for photoelectrochemical applications.

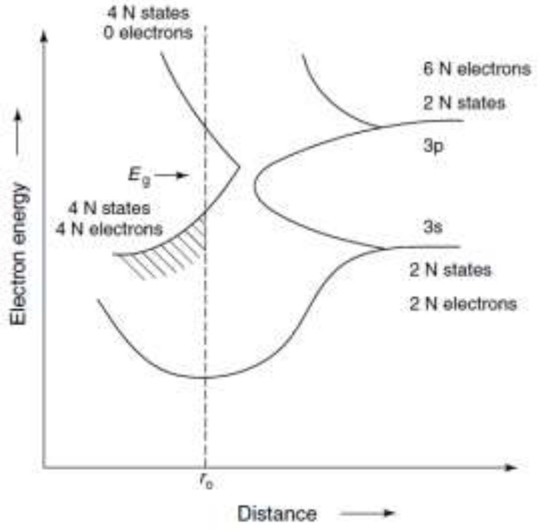


Figure 4 Schematic illustration of how energy bands in
semiconductors evolve from discrete atomic states for the specific
example of silicon.

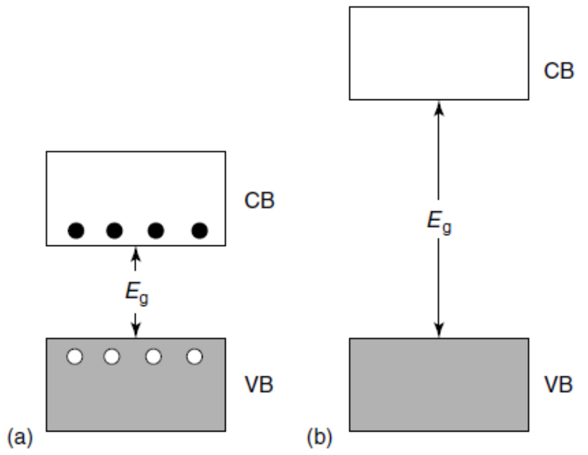


Figure 5 Relative disposition of the CB and VB for a semiconductor (a) and an insulator (b). E_g is the optical band gap energy.

CONCLUSION

In this study, we have discussed the electrostatics of the semi-conductor-liquid interface considering both single crystals as well as their nanocrystalline counterparts. The charge transfer dynamics across both these types of interfaces have been described in the dark and under photoexcitation of the semiconductor. Finally, the various types of photoelectro-chemical devices for solar energy conversion are introduced.

A study of photoelectrochemical and electrical properties of undoped-Fe2O3 was reported. This photoanode showed significantly electron transport limitations, producing a low photocurrent density of about 89.7 mA cm_2 at an applied voltage of 1.23 VRHE. Two different configurations were used to characterize the performance of the photoelectrochemical cell. In both situations, the impedance analysis showed that the charge transfer resistances are significantly reduced under irradiation. With a two-electrode configuration it is difficult to estimate the semiconductor and the electrolyte impedances, due to the overlap between these two components of the PEC cell. Moreover, the phenomena occurring in the electrolyte under illumination and in the dark are different and need to be represented by different electrical analogs.

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