

ELECTROCHEMICAL REACTIONS AT SEMICONDUCTOR ELECTRODES

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Electrochemical reactions at semiconductor electrodes have been studied in detail only recently. Beginning with the classic paper of Brattain and Garrett<sup>1</sup> in 1955 which laid down many of the basic principles, our understanding of the subject developed very rapidly. Excellent survey papers and original contributions to semiconductor electrochemistry are attributed to Dewald<sup>2</sup>, Green<sup>3</sup>, and Gerischer<sup>4</sup>. Electrochemical processes are now well understood on single-crystal elemental semiconductors such as Ge and Si<sup>5,6</sup>. Some intermetallic semiconductor compounds such as GaAs have been studied and, while the chemistry of the reactions is different, their electronic behavior is the same as for Ge and Si.

Electrochemical reactions at semiconductor electrodes are unique in electrochemistry in that the kinetics of electrode processes may be determined by phenomena which occur within the electrode itself. In order to understand electrochemical reactions at semiconductor electrodes, it is necessary first to recognize how semiconductors differ from metals in their electrical properties. In metals, there is always a large number of electrons associated with valence bonds which have sufficient energy to become conduction electrons. Another way of saying this is that the valence band of electron energy levels overlap with the conduction band. In semiconductors, there is an appreciable energy gap between the top of the valence band and the bottom of the conduction band. This results in a relatively low electronic conductivity since the number of electrons which have enough thermal energy to bridge the gap and provide current carriers is relatively low. Current carriers in semiconductors are of two types--conduction band electrons (electrons free to move through the crystal lattice) and valence band holes (electrons missing from covalent bonds). Electron motion from bond to bond gives the effect of positive charges moving in the opposite direction. These positive charges are called electron holes or simply holes. Each electron that bridges the energy gap produces one hole and one electron current carrier. The product of the concentrations of holes and electrons is a constant at a given temperature. The analogy between the hydrogen ion--hydroxyl ion equilibrium in water and the hole ( $e^+$ )--electron ( $e^-$ ) equilibrium in semiconductors is often made. Both equilibria are controlled by the law of mass action. Increasing one carrier type depresses the concentration of the other. The relative concentrations of holes and electrons in semiconductors are controlled by doping with small amounts of impurities which provide energy levels lying close to the valence band (these accept electrons from the semiconductor and produce p-type material) or close to the conduction band (these donate electrons to the semiconductor and make n-type semiconductors). The terminology n- and p-type indicates the polarity of the major current carrier in the semiconductor--n signifies negative charges

(electrons) while p is for positive charges (holes). Certain electrochemical reactions require specifically holes or electrons from the semiconductor. Hence, reaction rates may become limited by the supply of holes or electrons when they are the minority current carrier in the semiconductor. A complication in clearly defining the concentration of holes and electrons in the surface region of semiconductors is surface states. These are often ill-defined surface phenomena which give rise to allowed energy levels in the normally forbidden region--the energy gap. Surface states can trap electrons and/or holes. They may also act as a source of current carriers. A comprehensive review of the structure of the semiconductor-electrolyte interface has been prepared by Boddy<sup>7</sup>.

### Electrochemical Techniques

A wide variety of experimental techniques has been used to study electrochemical reactions on semiconductor electrodes. Many of these techniques take advantage of the semiconducting properties of the electrode. Photo effects, capacitance measurements, and solid-state pn junction indicator electrodes give information about the charge distribution and/or the charge transfer mechanism at the semiconductor-electrolyte interface.

### Anode Reactions

The important anodic reactions are semiconductor dissolution, film formation, and oxidation of ions in solution.

#### Dissolution

Germanium is dissolved anodically in most electrolyte solutions whereas silicon may be electrolytically dissolved only in fluoride solutions. Brattain and

Garrett<sup>1</sup> showed that the Ge dissolution reaction consumes holes at the anode surface. The same phenomenon has since been demonstrated for the anodic dissolution of all semiconductors. Saturation anodic currents are observed with n-type semiconductors. The limiting anodic current is increased when the surface concentration of holes is increased by any means. Illumination of the anode surface with light of sufficient energy to excite electrons from the valence to the conduction band thus creating hole-electron pairs is the most effective method of increasing the hole concentration in the semiconductor surface. The Ge dissolution valence is four at low current densities and between two and four holes per Ge atom are consumed in the anodic reaction depending on the surface hole concentration. At high current densities, the Ge dissolution valence becomes two. The anodic solution of Si in fluoride solutions is quite different from Ge. The Si dissolution valence is two at low current densities and becomes about four when the current density exceeds a critical value at which fluoride ions are consumed in the anodic reaction as fast as they reach the

surface by mass transport. Divalent silicon is unstable and disproportionates to tetravalent Si and amorphous Si. A thick film of amorphous Si can be built up below the critical current density. The thick film comes off at the critical current density and Si dissolution valence becomes four. Electropolishing also occurs under the conditions of tetravalent dissolution.

### Film Formation

Stable uniform films of oxides or other materials cannot be formed anodically on Ge in aqueous solutions because of their excessive solubility in water. Non-aqueous solutions may be used to produce films on Ge. Anodically formed oxide films are produced on Si in fluoride-free electrolytes.

### Cathodic Reactions

Cathodic reactions of interest at semiconductor electrodes are reduction of surface films, cathodic dissolution of Ge, and reduction of ions in solution. Many cathodic reactions on semiconductor electrodes require conduction band electrons. Therefore, limiting currents are observed at p-type semiconductors where conduction band electrons are the minority current carrier.

### Film Reduction

Surface films such as oxides may be cathodically reduced on Ge but not on Si. This is of practical interest when metal contacts must be electrodeposited directly on an oxide-free semiconductor surface. The plating solution composition and the method of applying current to the cell is important in determining whether or not an intimate contact between deposited metal and semiconductor is formed.

### Cathodic Dissolution of Ge

The discharge of hydrogen ions on electrodes has been studied more than any other electrochemical reaction. This reaction on semiconductor electrodes is unique in two respects: (1) conduction band electrons are required for the electron transfer process and (2) at very high current densities ( $>100 \text{ A/cm}^2$ ), germane ( $\text{GeH}_4$ ) is formed at nearly 100% current efficiency.

### Redox Reactions

The reduction and oxidation of ions in solution at semiconductor electrodes are especially interesting since the electron transfer process is predominantly with valence band or electron band electrons depending on the potential of the redox system.<sup>4</sup> In general, the stronger the oxidizing agent formed or reduced at the semiconductor electrode, the more likely that the reaction will involve the injection or extraction of holes. Conversely, the stronger the reducing agent produced or oxidized on a semiconductor, the greater

is the fraction of the current from electrons extracted from or injected into the conduction band. Practically all the experimental work concerning redox reactions at semiconductor electrodes has been done with Ge. A pn junction indicator electrode is the most convenient method of determining the relative amount of each kind of electron in the redox reaction.

### Practical Applications

An understanding of the basic electrochemical reactions at semiconductor electrodes has led to improvements of many electrochemical processes for semiconductor materials. The most important of these are: "chemical" etching and polishing, electropolishing, metal deposition, metal displacement plating, and staining pn junctions.

### Oxide Semiconductors

Oxide semiconductors were known long before elemental semiconductors yet the oxide materials are not nearly as well understood. Their semiconducting properties stem largely from structural defects in oxides that would be insulators if the crystals were defect-free. These oxides are of considerable practical significance; for example, many battery electrodes and corrosion films are composed of semiconducting oxides. Attempts have been made in recent years to interpret battery and corrosion reactions in terms of semiconductor phenomena with limited success.

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