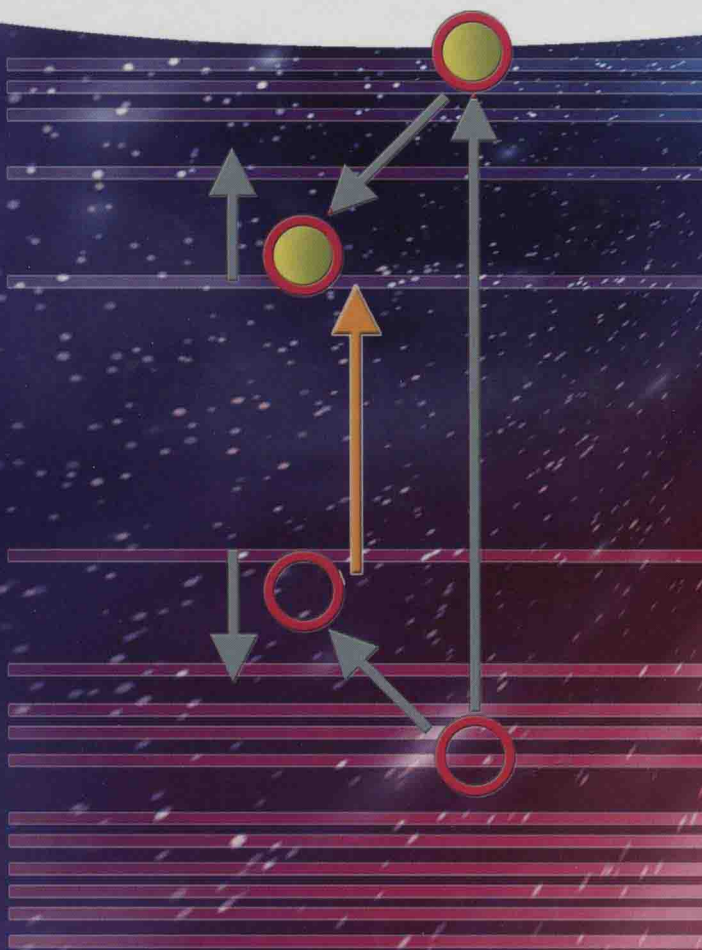


Rüdiger Memming

# Semiconductor Electrochemistry

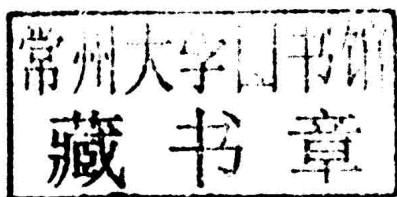
Second Edition



*Rüdiger Memming*

## Semiconductor Electrochemistry

2nd Edition



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## Preface to the Second Edition

The concept of the book has not been changed in the second edition, as it also addresses mainly scientists who are new in the field of semiconductor electrochemistry. In Chapters 1–6, various corrections and small additions were made. Moderate changes occur in Chapters 7 and 8 because of the replacements of some former by more modern results. Substantial additions were made in Chapters 9 and 11. In Chapter 9, fascinating basic research performed with semiconducting particles concerning ionization and carrier multiplication is reported. The application of these phenomena is of interest for producing new types of solar cells (“third generation”) as discussed in Section 11.1.1.3. In addition, the performances of dye-sensitized solar cells and their limitations are described in Chapter 11. The solar  $\text{H}_2\text{O}$  splitting at semiconductor–liquid junctions is also an important topic to produce a storable fuel. New approaches and strategies are extensively discussed in a further subsection. A new insight into the electrochemical reduction of  $\text{CO}_2$  is also presented.

Also, this time several people helped me preparing the second edition of this book. I had many scientific discussions (via email) mainly with Dr. M.C. Beard (National Renewable Energy Laboratory, Golden, CO, USA), Prof. L.M. Peter (Department of Chemistry, University of Bath, Bath, UK), Prof. B.A. Parkinson (Department of Chemistry, University of Wyoming, Laramie, WY, USA), Prof. W. Jaegermann (Institute of Material Science, Darmstadt University of Technology, Darmstadt, Germany), and Prof. P.V. Kamat (Department of Chemistry, University of Notre Dame, IN, USA). I would also like to acknowledge the help of Dr. R. Goslich (Institute of Solar Energy Research, Emmerthal, Germany) in solving computer and software problems. Finally, I wish to thank my wife for her patience and support during the time I used for preparing the second edition.

October 2014

*Rüdiger Memming*



## Preface

Several books on classical electrochemistry had already appeared about 30 to 40 years before the present book was written, for example, *Electrochemical Kinetics* by K. Vetter, in 1958, and *Modern Electrochemistry* by O. Bockris and A. Reddy in 1970. In the latter book a wide-ranging description of the fundamentals and applications of electrochemistry is given, whereas in the former the theoretical and experimental aspects of the kinetics of reactions at metal electrodes are discussed. Many electrochemical methods were described by P. Delahay in his book *New Instrumental Methods in Electrochemistry*, published in 1954. From the mid-1950s to the early 1970s there was then a dramatic development of electrochemical methodology. This was promoted by new, sophisticated electronic instruments of great flexibility. About 20 years ago, in 1980, Bard and Faulkner published the textbook *Electrochemical Methods*, which is an up-to-date description of the fundamentals and applications of electrochemical methods.<sup>1)</sup>

The modern work on semiconductor electrodes dates back to mid-1950s when the first well-defined germanium and silicon single crystals became available. Since then many semiconducting electrode materials and reactions have been investigated and most processes are now well understood. Since charge transfer processes at semiconductor electrodes occur only at discrete energy levels, that is, via the conduction or valence band or via surface states, and since they can be enhanced by light excitation, detailed information on the energy parameters of electrochemical reactions has been obtained. Corresponding investigations had greatly contributed to the understanding of electrochemical processes at solid electrodes in general. In this area, a major role was played by the modern theories on electron transfer reactions, developed by Marcus, Gerischer, Levich and Dogonadze. During the last quarter of the twentieth century, models and experimental results have been described and summarized in various review articles and books. In this context, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*, by S.R. Morrison (1980), and *Semiconductor Photoelectrochemistry* by Y.V. Pleskov and Y. Gurevich (1986), should be mentioned.

Semiconductor electrochemistry has various important applications, such as solar energy conversion by photoelectrochemical cells, photo-detoxification of

1) The second edition is in preparation.



organic waste, etching processes in semiconductor technology and device fabrication, photoplatin and photography. In particular, the first-mentioned application provided a great impetus to research in the field of semiconductor electrochemistry.

Therefore, there is a need for a textbook for teaching the fundamentals and applications of semiconductor electrochemistry in a systematic fashion. This field has interdisciplinary aspects insofar as semiconductor physics and also, in part, photochemistry are involved, as well as electrochemistry. Thus, one can expect that students and scientists with backgrounds in semiconductor physics on the one hand and in metal electrochemistry on the other will become interested in this area. A physicist will have no problem with the concept of band model and little difficulty with the energy concept of electron transfer, but the ion interactions in the solution and at the interface may present obstacles. On the other hand, an electrochemist entering the field of semiconductor electrochemistry may have some problems with energy bands and the Fermi level concept and in thinking of electrode reactions in terms of energy levels. In the present book, these difficulties are taken into account by including appropriate chapters dealing with some of the fundamentals of semiconductor physics and classical electrochemistry. Accordingly, it is the intention of this textbook to combine solid state physics and surface physics (or chemistry) with the electrochemistry and photoelectrochemistry of semiconductors. It is not the aim of the book to cover all results in this field. The references are limited, and are selected primarily from an instructional point of view.

I have been helped by several people in preparing this work. The basic parts of some chapters were prepared during several extended visits to the National Renewable Energy Laboratory (NREL) in Golden, Colorado, USA. I am mainly indebted to Dr. A.J. Nozik and Dr. B.B. Smith (NREL), for many stimulating discussions, essential advice, and support. I would like to thank Prof. B. Kastening, Institute of Physical Chemistry, University of Hamburg and Dr. D. Meissner of the Forschungszentrum Jülich, for discussions and for reading some chapters. I would also like to acknowledge the help of Dr. R. Goslich of the Institute for Solar Energy Research (ISFH), Hannover, in solving computer and software problems. Finally, I wish to thank my wife for her support and for affording me so much time for this work.

October 2000

*Rüdiger Memming*

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## Chapter 1

### Principles of Semiconductor Physics

The understanding of electrochemical processes at semiconductor electrodes naturally depends on the knowledge of semiconductor physics. This chapter presents a brief introduction to this field; only those subjects relevant to semiconductor electrochemistry are included here. For detailed information, the reader is referred to the standard textbooks on semiconductor physics by Kittel [1], Smith [2], Moss [3], and Pankove [4].

#### 1.1

##### Crystal Structure

A crystalline solid can be described by three vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , so that the crystal structure remains invariant under translation through any vector that is the sum of integral multiples of these vectors. Accordingly, the direct lattice sites can be defined by the set

$$\mathbf{R} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c} \quad (1.1)$$

where  $m$ ,  $n$ , and  $p$  are integers [1].

Various unit cells of crystal structures are shown in Figure 1.1. Most of the important semiconductors have diamond or zincblende lattice structures which belong to the tetrahedral phases, that is, each atom is surrounded by four equidistant nearest neighbors. The diamond and zincblende lattices can be considered as two interpenetrating face-centered cubic (f.c.c.) lattices. In the case of a diamond lattice structure, such as silicon, all the atoms are silicon. In a zincblende lattice structure, such as gallium arsenide (the so-called III–V compound), one sublattice is gallium and the other is arsenic. Most other III–V compounds also crystallize in the zincblende structure [5]. Various II–VI compounds, such as CdS, crystallize in the wurtzite structure, and others in the rock salt structure (not shown). The wurtzite lattice can be considered as two interpenetrating hexagonal close-packed lattices. In the case of CdS, for example, the sublattices are composed of cadmium and sulfur. The wurtzite structure has a tetrahedral arrangement of four equidistant nearest neighbors, similar to a zincblende structure. The lattice constants and structures of the most important semiconductors are given in Appendix A.3.



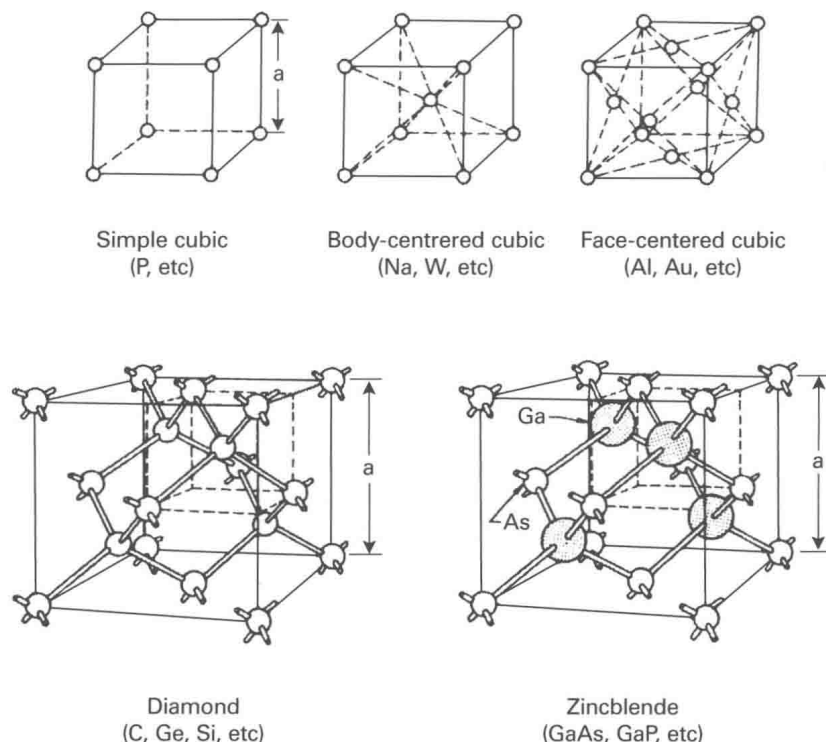


Figure 1.1 Important unit cells (taken from [7]).

It is also common to define a set of reciprocal lattice vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$ , such as

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \cdot \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \cdot \mathbf{c}}; \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \cdot \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \cdot \mathbf{c}}; \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \cdot \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \cdot \mathbf{c}} \quad (1.2)$$

so that  $\mathbf{a} \cdot \mathbf{a}^* = 2\pi$ ;  $\mathbf{a} \cdot \mathbf{b}^* = 0$  and so on. The general reciprocal lattice vector is given by

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (1.3)$$

where  $h, k, l$  are integers.

According to the definitions given by Eqs. (1.1)–(1.3), the product  $\mathbf{G} \cdot \mathbf{R} = 2\pi \times \text{integer}$ . Therefore, each vector of the reciprocal lattice is normal to a set of planes in the direct lattice, and the volume  $V_c^*$  of a unit cell of the reciprocal lattice is related to the volume of the direct lattice  $V_c$  by

$$V_c^* = \frac{(2\pi)^3}{V_c} \quad (1.4)$$

where  $V_c = \mathbf{a} \cdot \mathbf{b} \cdot \mathbf{c}$ .

It is convenient to characterize the various planes in a crystal by using the Miller indices  $h, k, l$ . They are determined by first finding the intercepts of the plane with the basis axis in terms of the lattice constants, and then taking the reciprocals of