Advances in Electrochemical Science and Engineering

Volume 10
Electrochemical Surface Modification
Thin Films, Functionalization and Characterization

Edited by
Richard C. Alkire, Dieter M. Kolb, Jacek Lipkowski, and Philip N. Ross
Advances in Electrochemical Science and Engineering

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Advances in Electrochemical Science and Engineering

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Series Preface

This tenth volume continues the merger of two well-established monograph series. One point of origin began in 1961 with the editorial collaboration of Paul Delahay and Charles Tobias, and which continued in 1976 with Heinz Gerischer and Charles Tobias. Their efforts led in 1987 to the series “Advances in Electrochemical Science and Engineering”, which was continued in 1997 by Richard Alkire and Dieter Kolb. The second point of origin is the series “Frontiers in Electrochemistry” established in 1992 by Jacek Lipkowski and Philip N. Ross. With this volume the concept of topical volumes is introduced to the new series of Advances that resulted from the merger. The favourable reception of the Frontiers in Electrochemistry and the first eight volumes of Advances, and the steady increase of interest in electrochemical science and technology provide good reasons for the continuation of these editions with the same high standards. The purpose of the series is to provide high quality advanced reviews of topics of both fundamental and practical importance for the experienced reader.

Richard Alkire
Dieter Kolb
Jacek Lipkowski
Philip Ross
The purpose of the series is to provide high quality advanced reviews of topics of both fundamental and practical importance for the experienced reader. This volume focuses on spectacular recent developments in electrochemical surface modification for the purpose of forming thin films and surface regions that have unique functional properties and that can be well-characterized by multi-scale mathematical models.

Michaelis reviews the application of valve metals in electronics based on the dielectric properties of ultra-thin films. Following presentation of fundamental principles and experimental details, the discussion of valve metal systems includes thin film oxide behavior of Ti, Zr, Hf, Nb, Ta, and Al. The application of these valve metal systems in electrolytic capacitor manufacturing is discussed with emphasis on current development trends and research issues. In addition, special emphasis on SiO₂ dielectric films is provided for integrated circuit applications associated with dynamic random access memory chip fabrication.

Moffat, Wheeler and Josell review electrodeposition systems in which superconformal film growth results in progressive reduction of surface roughness. Special emphasis is given to quantitative studies on the relation between electrochemical reaction phenomena and morphological evolution during filling of micro- and nanometer scale features. The complex interplay between electrolyte additives and the metal electrodeposition process is covered in detail. Quantification of additive behavior in order to predict interface motion and morphology evolution is treated with special emphasis on fabrication of on-chip copper interconnects.

Scherson, Palenscar, Tolmachev and Stefan provide a critical review of transition metal macrocycles, in both intact and thermally activated forms, as electrocatalysts for dioxygen reduction in aqueous electrolytes. An introduction is provided to fundamental aspects of electrocatalysis, oxygen reduction, and transition metal macrocycles. Since the theoretical and experimental tools used for investigation of homogeneous and heterogeneous electrocatalysis are considerably different, these topics are given separate discussion. The influence of the electrode surface on adsorbed macrocycles, and their influence on mechanism and rates of O₂ reduction is treated in detail. Issues related to pyrolyzed macrocycles are also described.
Braatz, Seebauer and Alkire discuss recent developments in molecular simulation, multiscale simulation, and multiscale systems engineering, and how these developments enable the targeted design of processes and products at the molecular scale. They point to the need to model electrochemical phenomena at the molecular scale, and to link such models to the macroscopic level where engineering control and optimization strategies are implemented. Following a summary of continuum and molecular-scale simulation approaches, they outline the key challenges of multiscale modeling and its integration with experimental data. Also covered is the use of multiscale models for engineering design and optimization of processes and products where quality is determined by events at the molecular scale.

Urbana, Illinois, May 2008

Richard Alkire
List of Contributors

Richard C. Alkire
Department of Chemical and Biomolecular Engineering
University of Illinois
Urbana, IL 61801
USA

Richard D. Braatz
Department of Chemical and Biomolecular Engineering
University of Illinois
Urbana, IL 61801
USA

Daniel Josell
Materials Science and Engineering Laboratory
National Institute of Science and Technology
Gaithersburg, MD 20899
USA

Alexander Michaelis
Fraunhofer Institute for Ceramic Technologies and Systems
Winterbergstraße 28
01277 Dresden
Germany

Thomas P. Moffat
Materials Science and Engineering Laboratory
National Institute of Science and Technology
Gaithersburg, MD 20899
USA

Attila Palencsár
Ernest B. Yeager Center for Electrochemical Sciences
Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078
USA

Edmund G. Seebauer
Department of Chemical and Biomolecular Engineering
University of Illinois
Urbana, IL 61801
USA

Daniel A. Scherson
Ernest B. Yeager Center for Electrochemical Sciences
Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078
USA
List of Contributors

**Ionel Stefan**
Ernest B. Yeager Center for Electrochemical Sciences
Department of Chemistry
Case Western Reserve University
Cleveland, OH 44106-7078
USA

**Yuriy Tolmachev**
Kent State University
Kent, OH 44242
USA

**Daniel Wheeler**
Materials Science and Engineering Laboratory
National Institute of Science and Technology
Gaithersburg, MD 20899
USA
Valve Metal, Si and Ceramic Oxides as Dielectric Films for Passive and Active Electronic Devices

Alexander Michaelis

1.1 Introduction

Owing to their low electrochemical potential the group IVB and VB valve metals Ti, Zr, Hf, V, Nb and Ta readily react with water or oxygen to form a dense, protecting passive layer. This also holds for Al. Because of these protecting oxide films, the valve metals show an exceptional resistance towards corrosion in many aggressive environments. This explains why valve metals are widely used in the construction of chemical apparatus. An extensive number of papers and reviews exist that focus on the corrosion resistance of valve metal oxides [e.g. 1, 2].

In this treatise however another field is covered, namely the application of valve metals in electronics. The valve metal oxides show outstanding dielectric properties, which make them a key component in many passive and active devices such as capacitors, resistors and ICs (integrated circuits). Nevertheless, the most important oxide system in electronics is still Si/SiO₂, which can be considered the benchmark system. Consequently, one chapter of this book is dedicated to Si/SiO₂ with special emphasis on its use in DRAM (dynamic random access memory) microchip fabrication, which can be considered the most advanced and demanding technology in microelectronics, as will be explained in Chapter 4. Electrochemically, p-Si/SiO₂ also behaves like a valve metal. Regarding their electronic properties, the valve metal oxides are related to another class of oxides, namely the perovskite structured ferroelectrics: BaTiO₃, (Ba,Sr)TiO₃ (BST), Pb(Zr,Ti₃₋ₓ)O₃ (PZT), SrBi₂Ta₂O₉ (SBT). These advanced electroceramics outperform the simple valve metal oxides in many respects, such as, by their exceptional high relative dielectric constant ($\varepsilon_r$) (sometimes also called relative permittivity). Therefore, both the valve metal and the perovskite oxides compete in many applications. For example, in passive component capacitor manufacturing Al/Al₂O₃ and Ta/Ta₂O₅ electrolyte capacitors share the market with multilayer ceramic capacitors (MLCC) that are BaTiO₃ based. However, owing to their more complex chemistry, the integration of perovskite layers into devices is difficult when ultra-thin nano-dielectric films are needed.
Therefore, this treatise focuses on the less complex valve metal oxides as ultra-thin nano-dielectrics (<100 nm). Some relevant oxide systems are summarized in Table 1.1. In anticipation of the results presented later, some parameters that are important for electronic applications are also given. For application as a capacitor dielectric material, for example, a high relative dielectric constant \( \varepsilon_r \) is important but not sufficient. As indicated in Table 1.1 the anodically formed valve metal oxides differ in structure (some are amorphous, some crystalline), electronic behavior (some oxides behave like an n-type semiconductor), and some oxides show a pronounced texture dependence of oxide growth, that is the oxide properties vary with the crystallographic orientation of the substrate surface. Depending on the desired application of the oxides, an optimum combination of these properties has to be found. As will be discussed in the following chapters, Table 1.1 has to be used carefully, that is, it has to be kept in mind that the given parameters hold for certain ‘typical’ experimental conditions only. For instance, in the case of Ti/TiO\(_2\) the texture dependence can be reduced by switching from potentiodynamic to potentiostatic oxide formation conditions. Therefore, Table 1.1 only gives a first, rough orientation of the electronic properties and behavior of the oxides. Depending on the experimental formation conditions a wide range of properties can often be obtained. This also explains why literature data often show a huge variation for almost all relevant parameters. Consequently, if data are to be compared, the experimental conditions have to be carefully considered.

1.1.1 Experimental Approaches

For the study of the oxide systems, electrochemical and optical methods can be applied. Valve metal oxides are formed conventionally electrochemically, with the important exception of SiO\(_2\), which is usually formed by thermal processing or chemical/physical vapor deposition (CVD/PVD). Conventional electrochemical methods show an excellent vertical resolution for the fundamental study of ultra-thin nano-oxide films on solid surfaces, but their application to micro- and nano-systems, which are of special importance in electronics, is limited because of the poor lateral resolution, with typical electrode areas in the mm\(^2\) to cm\(^2\) range. In order to gain deeper insight into local electrode reactions, microscopic in situ methods must be developed and employed that feature both high lateral and vertical resolution. Here an important new approach to address and solve this issue, that is the combination of conventional electrochemistry with optical and new electrochemical micro-methods, is presented. This enables one to characterize or/and modify solid surfaces at high lateral resolution, which is only limited by refraction of light in the \(\mu\text{m}^2\) range. This is especially important for electronic applications as the critical dimensions of relevant structures are extremely small (sub-micron range) and the effect of structural heterogeneities on the film properties is essential for the reliability of the devices. Some fundamental aspects of optical methods employing focused light and their application to electrochemistry are discussed with emphasis on laser light sources. To allow for a high lateral resolution, even by conventional
<table>
<thead>
<tr>
<th>System</th>
<th>$\varepsilon_r$</th>
<th>$m$ (nm V$^{-1}$)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$E_g$ (eV)</th>
<th>$t_+$</th>
<th>Bias dep. Electronic behavior</th>
<th>Structure</th>
<th>Texture dep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/TiO$_2$</td>
<td>56 (anodic) [3]</td>
<td>1.4–2.2</td>
<td>3.9</td>
<td>3.4</td>
<td>0.35</td>
<td>Yes, n-type SC</td>
<td>a</td>
<td>Yes</td>
</tr>
<tr>
<td>Rutile</td>
<td>110 powder 90°, 170°</td>
<td></td>
<td>[6, 7]</td>
<td>4.25</td>
<td>3.0</td>
<td>[3]</td>
<td>No, dielectric</td>
<td>a</td>
</tr>
<tr>
<td>Anatase</td>
<td>48 (powder)</td>
<td>3.99</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brookite</td>
<td>[4, 5]</td>
<td>4.13</td>
<td>3.0</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Zr/ZrO$_2$</td>
<td>27</td>
<td>2.6–3.3</td>
<td>5.7</td>
<td>5</td>
<td>0</td>
<td>No, dielectric</td>
<td>c</td>
<td>Yes</td>
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<tr>
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<td>[9]</td>
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<td>[10]</td>
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<tr>
<td>Ta/Ta$_2$O$_5$</td>
<td>25</td>
<td>1.8</td>
<td>8.5</td>
<td>5.2</td>
<td>0.5</td>
<td>No, dielectric</td>
<td>a</td>
<td>No</td>
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<tr>
<td>[11, 12]</td>
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<td>[14]</td>
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<td>Nb/Nb$_2$O$_5$</td>
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<td>2.9</td>
<td>4.4</td>
<td>3.4</td>
<td>0.5</td>
<td>Yes, n-type SC</td>
<td>a</td>
<td>No</td>
</tr>
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<td>[19]</td>
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<td>[20]</td>
<td></td>
<td></td>
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<tr>
<td>Al/Al$_2$O$_3$</td>
<td>9</td>
<td>1.3</td>
<td>3.1</td>
<td>7</td>
<td>0.5</td>
<td>No, dielectric</td>
<td>a</td>
<td>No</td>
</tr>
<tr>
<td>[21]</td>
<td>[22–24]</td>
<td></td>
<td>[25]</td>
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<tr>
<td>Hf/HfO$_2$</td>
<td>16</td>
<td>2.0</td>
<td>10</td>
<td>5.1</td>
<td>0</td>
<td>No, dielectric</td>
<td>c</td>
<td>Yes</td>
</tr>
<tr>
<td>[28]</td>
<td>[29]</td>
<td></td>
<td>[30]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si/SiO$_2$</td>
<td>3.8</td>
<td>0.7</td>
<td>2.2</td>
<td>9</td>
<td>0</td>
<td>No, dielectric</td>
<td>a</td>
<td>Yes</td>
</tr>
<tr>
<td>[32, 33]</td>
<td>[34, 35]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>≈2000</td>
<td>1.8</td>
<td>6.5</td>
<td>3.1</td>
<td>0.5</td>
<td>Ferroelectric</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>WO$_3$</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

1.1 Introduction
electrochemistry itself, the nl-droplet method first introduced by Kudelka [6] is applied. Depending on the input/output signals, the micro-methods used throughout this text can be divided into three different classes:

1. Optical/optical methods (exciting and measured signal = light beam). Examples are the application of well established optical methods, such as ellipsometry, reflection spectroscopy, beam deflection, interferometry, Raman-spectroscopy, etc., along with electrochemistry [40–45]. The incident light beam is focused on a microscopic portion (e.g. a single substrate grain) of a macroscopic electrode and the optical information in the reflected or deflected light beam is analyzed and correlated with the simultaneously recorded electrochemical signals. For instance, micro-ellipsometry can be performed during cyclovoltammetric formation of a passive layer to record film thickness growth on a particular grain of a polycrystalline macroscopic electrode. Examples of this important application will be discussed in full detail later (Section 1.3). In order to allow for an accurate correlation of the signals to the deliberately chosen electrode areas, microscopic control is essential. Figure 1.1 shows a typical experimental setup for this purpose. SAME (spectroscopic anisotropy micro-ellipsometry) is introduced as the most important spectroscopic method. This newly developed method allows for the determination of structural properties such as the crystal orientation of the surface film along with conventional parameters, for example, the film thickness. In

![Figure 1.1](image-url)
the case of electroceramics such as YBCO even the chemical composition can be determined by SAME [308].

2. Optical/electrical or optical/chemical methods [measured signals such as electric current (photocurrent $i_{ph}$), voltage, reaction rates, etc.]. A characteristic for this class is that the light beam is used to locally induce a reaction [46–51]. The type of reaction depends on thermal and electronic properties of the solid, the neighboring phase and energy or power density of the light beam. In metals, energy dissipation is very fast. Consequently, most of the energy is transformed into heat resulting in melting or even evaporation of the substrate. In dielectric materials bond breaking with subsequent reactions dominates. In semiconductors dissociation and ionization, reactions are often observed if high power densities are used. However, at low power densities electron/hole pair formation with an associated change of the potential distribution at the interface dominates. Both electron transfer (ETR) in addition to ion transfer (ITR) reactions can be induced. For instance, hole accumulation can cause redox reactions and film growth or removal (corrosion, etching) as will be discussed later. Laser-induced reactions under electrochemical conditions at low power densities, that is at quasi-isothermal conditions will be emphasized.

3. Electrical/electrical microelectrode methods under optical (microscopic) control. This class covers the conventional electrochemical methods, that is, application of an electrical signal (e.g. potential) to the electrode to induce a reaction. The role of optics here is twofold:

– Samples are prepared by means of photolithography, that is, the local resolution of the electrical measurement is determined by focused laser radiation. In this context it has to be kept in mind that the high lateral resolution achieved in modern device and micro-system technology and research is mainly due to optical processing, that is, photolithography. Detailed examples for application of photoresist microelectrochemistry, namely the new photoresist nl-droplet method, will be given.

– In order to measure on defined areas the electrode must be microscopically controlled (see Figure 1.1).

1.2 Fundamentals and Experimental Details

In this section some fundamentals of the methods used later are summarized. In particular, electrochemistry and photocurrent measurements (optical/electrical) are treated here.

1.2.1 Electrochemical Oxide Layer Formation on Valve Metals

Valve metals bear this name due to the fact that they pass current in only one direction (rectifying effect), that is, the anodic current is low for potentials lower than the
formation potential but a strong cathodic evolution of hydrogen is possible. Experimentally the following behavior is found for the anodic oxide formation [52, 295]:

\[ i = i_0 e^{\beta E} \]  \hspace{1cm} (1.1)

where \( i \) is the oxide formation current, \( i_0 \) and \( \beta \) are material-dependent constants and \( E \) is the electric field strength in the oxide. This equation is called the high field equation. The corresponding high field model assumes an \( E \)-field supported, thermally activated ion movement (hopping) along the distance \( a \), with \( a \) typically being the lattice parameter. There are many papers on this subject where the above equation is derived assuming specific mechanisms [e.g. 52–61]. Depending on the details in the used models, the rate determining step may be located within the oxide (Verwey, Güntherschulze and Betz), the oxide/electrolyte (Sato) or metal/oxide (Cabrera–Mott) interface. A detailed discussion and derivation of the high field equation can be found in Ref. [20]. An equation of the following form can be derived:

\[ i = n \alpha a e^{-\frac{W}{RT}} e^{\alpha z FaE} \]  \hspace{1cm} (1.2)

with \( n \) = hopping frequency, \( \alpha = \) transfer coefficient, \( \rho = \) concentration of mobile charge, \( a = \) hopping distance, \( W = \) activation energy for hopping, \( R = \) gas constant, \( T = \) temperature and \( F = \) Faraday’s number.

This equation is identical to the experimental Equation 1.1 using the equalities:

\[ \beta = \frac{\alpha a z F}{RT} \hspace{1cm} \text{and} \hspace{1cm} i_0 = n \alpha a e^{-\frac{W}{RT}} \]  \hspace{1cm} (1.3)

The parameters occurring in these equations are illustrated in Figure 1.2.

For homogeneous oxide layers the field strength \( E \) can be determined from the potential drop \( \Delta \phi_{\text{ox}} \) across the oxide and the layer thickness \( d_f \).

\[ i = i_0 e^{\beta E} = i_0 e^{\frac{\Delta \phi_{\text{ox}}}{d_f}} \]  \hspace{1cm} (1.4)

**Figure 1.2** Illustration of the high-field model: (a) adjacent lattice planes in the oxide and (b) effect of the \( E \)-field on the activation energy \( W \) (source Ref. [20]).
For galvanostatic oxide growth \((\log i = \text{const})\) the \(E\) field has to be constant resulting immediately in the proportionality:

\[
d_f \propto \Delta \Phi_{\text{ox}} \Rightarrow d_f = m \cdot \Delta \Phi_{\text{ox}}
\]  

(1.5)

This equation defines the oxide formation factor: \(m \text{ (nm V}^{-1}\text{)}\), that is, the layer thickness increases linearly with the applied potential.

Equation 1.4 directly implies the time behavior (rate) of oxide growth. An inverse logarithmic growth law according to the following expression can be derived to a good approximation (Cabrera and Mott [55]):

\[
\frac{1}{d_f} = A - \frac{1}{\beta \cdot \Delta \Phi_{\text{ox}}} \cdot \ln t
\]

(1.6)

with \(A\) being a constant.

1.2.2 The \(C(U)\) Curve of a Valve Metal Electrode

The total potential drop \(\Delta \Phi_{\text{tot}}\) across an electrode is made up of four parts: the potential drop at the metal/oxide interface, the potential drop in the oxide, the potential drop in the Helmholtz layer and the potential drop in the electrolyte (diffuse double layer):

\[
\Delta \Phi_{\text{tot}} = \Delta \Phi_{\text{Me/ox}} + \Delta \Phi_{\text{ox}} + \Delta \Phi_{\text{H}} + \Delta \Phi_{\text{el}}
\]  

(1.7)

The potential drop \(\Delta \Phi_{\text{tot}}\) correlates with the applied electrode voltage \(\Delta U\) by: \(\Delta \Phi_{\text{tot}} = \Delta U - \text{const}\). For high electrolyte concentrations (>0.1 M), the last part \(\Delta \Phi_{\text{el}}\) can be neglected. In addition, the first part \(\Delta \Phi_{\text{Me/ox}}\) is normally small. The potential drop in the Helmholtz layer is usually determined by the reaction of adsorption of protons and hydroxyl groups. The corresponding reaction rate is high, that is, equilibrium is reached almost instantaneously. Therefore, the corresponding potential drop is constant resulting in a constant double layer capacitance of about 20 \(\mu \text{F cm}^{-2}\).

The potential drop \(\Delta \Phi_{\text{ox}}\) can be calculated using the Poisson equation \(\nabla E = \rho_c/\left(\varepsilon \varepsilon_0\right)\) with \(\rho_c\) being the charge density given by the defect state concentration \(N_0\). This is:

\[
\Delta \Phi_{\text{ox}} = \Delta \Phi_{\text{ox, scl}} + \Delta \Phi_{\text{ox, isol}} = -\frac{eN_0 d_{\text{scl}}^2}{2\varepsilon \varepsilon_0} + \Delta \Phi_{\text{id, isol}}
\]  

(1.8)

where \(\Delta \Phi_{\text{id, isol}}\) describes the potential drop in the ideal insulator part, \(\varepsilon\) is the electronic charge, \(d_{\text{scl}}\) is the extension of the space charge layer \(\text{scl}\). Inversion of the \(\Delta \Phi_{\text{ox,scl}}\) semiconductor part of this equation yields the following expression for the extension of the space charge layer:

\[
d_{\text{scl}} = \sqrt{\frac{2\varepsilon \varepsilon_0 \Delta \Phi_{\text{ox, scl}}}{eN_0}}
\]  

(1.9)

Hence a potential (bias) dependent capacitance \(C_{\text{scl}}\) can be defined with use of the simple capacitor equation \(C_{\text{scl}}/A = \varepsilon \varepsilon_0/d_{\text{scl}}\). (As the \(E\) field is completely shielded
inside the scl region, the potential drop $\Delta \varphi_{\text{cd,isol}}$ vanishes for small applied voltages.)

Linearized with respect to the potential drop this yields the so called Schottky–Mott relationship [62, 310] (for $T > 0$, a $(K_B T/e)$ part has to be subtracted, which describes the thermal discharging of defect states into the conduction band):

$$\frac{1}{C_{\text{scl}}^2} = \frac{2}{\varepsilon_r \varepsilon_0 e N_D} \left( \Delta \varphi_{\text{ox,scl}} - \frac{K_B T}{e} \right) \quad (1.10)$$

This equation holds for the case of small applied voltages when the extension of the scl is smaller than the oxide thickness. Evaluation of the slope of the $1/C_{\text{scl}}^2$ ($\Delta \varphi_{\text{ox,scl}}$) curve allows for the determination of the product $\varepsilon_r N_D$. Once the scl reaches completely through the oxide film, the capacitance is determined by $d_f$, again yielding the conventional potential independent capacitance $C/A = \varepsilon_r \varepsilon_0 / d_f$. A schematic representation of the relevant potential drops as well as the band structure is shown in Figure 1.3 for the case of the Ti/TiO$_2$ system. An example of an illuminated surface (induced photocurrent) is also shown here, which is required later.

1.2.3 Application of Lasers in Electrochemistry

As laser radiation plays an important role in some of the experimental methods employed later, some fundamental aspects of lasers are discussed briefly here. The fact that lasers are more and more replacing conventional light sources in all types of optical applications can be understood by considering their fundamental advantages. Perhaps the most striking feature of laser radiation is its directionality due to a very
low angle of divergence, typically in the order of 1 rad. This has basically two important implications:

1. Laser radiation can be focused down to dimensions of the wavelength of light.
2. A large amount of energy can be concentrated into small spots, yielding high power densities.

In fact, the focusability of laser radiation is the most applied feature. Optimum focusing of laser radiation demands a high mode quality of the laser beam. The best suited mode is the TEM$_{00}$, which shows a Gaussian spatial intensity distribution. This fundamental mode can always be obtained by using intra-cavity apertures, which are small enough to suppress the higher modes. For lasers operated in the TEM$_{00}$ mode, the minimum obtainable spot diameter $s$ (diffraction limit) is given by Airy’s formula:

$$s = \lambda \frac{f}{D\pi}$$

where $f$ is the focal length of the focusing system used, $\lambda$ is the wavelength of the laser and $D$ is the maximum effective beam diameter (aperture) of the focusing system (beam expanders are an advantage).

However, it is not only the spot size $s$ that governs the final spatial resolution of the electrode reaction, but illumination of the sample is just the first step in a whole series of induced processes resulting in the final state of the system. For instance, in semiconductor interfaces the lateral hole drift causes an extension of the reaction zone. For the thermally activated processes, the heat conductivity of the sample determines the reaction zone. Therefore, both optical and physical effects determine the final spatial resolution of optical/electrical laser methods.

Other important properties of laser radiation are its narrow spectral bandwidth, coherence and polarization. These features are used in numerous spectroscopic and interferometric applications, such as Raman, polarization, interference spectroscopy, spectroscopic ellipsometry, holography. Moreover, the possibility to create very short light pulses by Q-switching or mode-locking should be mentioned. Pulses below fs-duration are possible and allow for the elucidation of fast transient phenomena such as short spontaneous lifetimes or fast relaxation processes. Laser illumination results in thermal heating, chemical reactions and/or potential changes. In the following experiments laser-induced reactions under electrochemical conditions at low power densities, that is, at quasi-isothermal conditions, are emphasized. Thermal processes are discussed briefly below.

1.2.3.1 **Thermal Effects**

With the assumption of a Gaussian temperature distribution (TEM$_{00}$-mode) on the laser affected zone, the temperature increase $\Delta T$ can be estimated by the following equation [63]:

$$\Delta T = \frac{A}{2\kappa \sqrt{\pi/2}} \cdot P \cdot r \cdot \arctan \left( \frac{8\kappa r}{\rho cr^2} \right)$$

(1.12)
where \( A \) is absorption, \( \rho \) is density, \( c \) is specific heat, \( \kappa \) is heat conductivity, \( r \) is spot radius \( = s/2 \) and \( P \) is power density.

For times \( t \gg \pi^2 \rho_\lambda c_k / (8 \kappa) \) \((t \gg 10^{-2} s)\) the temperature becomes time independent, a continuous wave (cw) condition. The local temperature is then given by:

\[
\Delta T = \frac{APr}{2\kappa} \cdot \sqrt{\frac{\pi}{2}}
\]

(1.13)

The temperature effect often disturbs precise measurements if isothermal conditions cannot be maintained and if it leads to damage of the sample. Equation 1.12 shows that at constant power density the temperature effect decreases with decreasing pulse times. Therefore, the application of short pulses may be of advantage to avoid damages. If, however, the modification of the surface requires a large amount of total energy, it should be delivered with low power density. On the other hand, there are numerous applications of the thermal heating. It can be used to evaporate or to dissociate the substrate (LAMMA) [64], to enhance reaction rates at the surface or the convection of the electrolyte [65–67]. Finally, it can be employed to study electrode reaction rate constants and the dynamics of the double layer [68].

1.2.4 Electrochemical Photocurrent Measurements (Optical/Electrical Method Class), Introduction of a New Model

The theoretical formalisms for the interpretation of the pure optical (optical/optical) and the pure electrochemical methods are well established and can be found in numerous publications. It is far beyond the scope of this treatise to review the corresponding models. However, the quantitative interpretation of optical/electrical measurements (photoelectrochemistry) is still incomplete and will be discussed here. For instance, multiple internal reflections within the thin films must be considered, causing \( i_{ph} \) to depend on the layer thickness. This experimental fact has already been described by Schultze \textit{et al.} [69] and later by Di-Quarto and coworkers [70, 71]. However, no quantitative analysis or model were given. The quantitative optical model was independently derived by Smyrl and coworkers [72, 73], Gärtner [75] and Michaelis and Schultze [74]. This optical model has to be combined with the Butler–Gärtner model [75, 76], which itself holds only for crystalline bulk materials. The extended model describes \( i_{ph} \) as a function of the layer thickness \( d \), the optical constants of the substrate and layer, the extension of the space charge layer \( d_{scl} \), and such electronic properties as the defect state concentration \( N_D \) and the relative dielectric constant \( \varepsilon_r \). However, this model is still not accurate for an exact description of the \( i_{ph} \) behavior of amorphous oxide layers, but another, \( E \)-field depending term, taking the recombination efficiency \( r(E) \) into account, must be coupled to the model. This yields a further dependence of \( i_{ph} \) on the film thickness and on the applied anodic potential. This complete photocurrent model consisting of three different parts, namely the Gärtner-, optics- and \( r(E) \)-parts, was first introduced by Michaelis and Schultze [74] and allows for a complete description of the
experimental results presented later. Consequently, both electronic and optical film properties can principally be determined allowing for a mutual confirmation of the pure optical and electrical methods. We will discuss in which potential and film thickness ranges the different parts of the model dominate and whether a quantitative evaluation of optical and electronic properties is really possible.

1.2.4.1 Photocurrent Model for Ultra-thin, Amorphous Films With TiO$_2$ as an Example

Illumination of anodically polarized n-type semiconductor oxide films such as TiO$_2$ with photon energies above the band gap energy ($E_g \approx 3.5$ eV for TiO$_2$) results in electron/hole pair formation. These charges are separated within the space charge layer (scl) causing a photocurrent $i_{ph}$. According to the Butler–Gärnter model, the main contribution to $i_{ph}$ can be attributed to electron/hole pairs, which are generated directly within the space charge layer, namely $i_{scl}$. Another contribution is due to charges diffusing into the scl that is, $i_{ph} = i_{scl} + i_{diff}$. The generation of $i_{ph}$ is in competition with recombination processes throughout the entire layer. These recombination processes are not considered explicitly in the Gärnter approach. The electronic layer parameters enter into the Gärnter model only because of their effect on the extension of the scl ($d_{scl}$) (see Equation 1.9):

$$d_{scl} = \sqrt{\frac{2e_0 \epsilon_0 (\Delta \phi_{ox})}{eN_D}}$$  \hspace{1cm} (1.14)

However, the optical film properties describing the absorption of light, that is, the number of photons $g$ generating the electron/hole pairs have not yet been considered. This generation number $g$ is plainly given by the change in the light intensity $I$ per unit length $z$, that is:

$$g(z) = -\frac{d}{dz}I$$  \hspace{1cm} (1.15)

In the classical Butler–Gärnter model, light absorption is simply described in terms of Lambert–Beer’s law, containing just one optical constant, the extinction coefficient $k$. However, this approach holds for bulk semiconductors only. In the case of ultra-thin semiconducting layers dealt with here, multiple internal reflections must be considered [74–76] if the penetration depth $\delta$ of the light is larger than the film thickness $d_f$. This is illustrated in Figure 1.4. The light energy flux $I$ into the volume now has to be described by the Poynting vector $\vec{I}$. A detailed description of the derivation of this quantity can be found in Ref. [74]. In this case, $n$ and $k$ of both the layer and substrate enter into the expression for $i_{ph}$ and, even more importantly, the layer thickness $d_f$ is now considered quantitatively. In principle, this optical model can be coupled to any electronic model. Here, the Butler–Gärnter approach will be kept, yielding

$$i_{ph} = -e \int_0^{d_{scl}} \left( \frac{d\vec{I}(z)}{dz} \right) dz$$  \hspace{1cm} (1.16)
if only the contribution of electron/hole pairs generated within the scl is considered. It can be shown that the neglection of the diffusion contribution is small [75, 80]. More severe and decisive is the complete neglection of recombination processes in Equation 1.16. Recombination processes are of particular interest for amorphous semiconductors because of the large number of recombination centers. The recombination, that is the efficiency of the electron/hole pair separation, must clearly depend on the E-field gradient, which itself is a function of the applied potential and the layer thickness. Therefore, a recombination factor \( r(E) \) must be coupled to the above equation. For \( r(E) \) the following approach obeying the boundary conditions of \( r(E) = 0 \) for vanishing E-fields and \( r(E) = 1 \) for high fields can be chosen:

\[
r(E) = \left(1 - \frac{1}{\text{const} \cdot E + 1}\right)
\]

yielding

\[
i_{ph} = -\varepsilon \left(1 - \frac{1}{\text{const} \cdot \frac{\Delta \varphi_{ox}}{d_{scl}} + 1}\right) \cdot \int_0^{d_{scl}} \left(\frac{d \bar{T}(z)}{dz}\right) dz
\]

with a linear E-field approximation. The unknown constant in this equation can be determined by fitting of the experimental \( i_{ph}(U_{tot}) \) curves. The function used for \( r(E) \) is a good approximation of the expression for the recombination efficiency derived by Pai and Enck [77] for amorphous materials, which has already been discussed in this
The comparison of both equations shows that the constant has to be a function of the thermalization length, which itself depends on the mobility of the charge carriers and the photon energy of the exciting light.

In Table 1.2 the contributions of the three different parts of the model to the experimental output signals are summarized for various cases. The three parts are:

- The classical Gärtner part describing the effect of the extension of the space charge layer $d_{\text{scl}}$, which itself depends on the electronic properties $\varepsilon_r$ and $N_D$.

- The exact optical model describing multiple internal reflections, which are important for thin films where the penetration depth of the light $\delta$ is larger than the layer thickness. Because of this part, $i_{\text{ph}}$ depends on the layer thickness and the optical constants of both substrate and layer. This optical part mainly explains the observed variation in $i_{\text{ph}}(d_{\text{f}})$ found in the photocurrent spectra.

- The third part describes the electron/hole pair recombination efficiency $r(E)$ which causes a further dependence of $i_{\text{ph}}$ on the layer thickness for very thin films, high potentials, respectively ($d_{\text{scl}} = d_{\text{f}}$), and superimposes on the thickness dependence due to the optical part.

The ‘up arrow’, ‘down arrow’ symbols in the table denote an increase or decrease in the applied potential $U_{\text{tot}}$ and $d_{\text{f}}$ or $i_{\text{ph}}$, respectively. For example, the $i_{\text{ph}}$ thickness

<table>
<thead>
<tr>
<th>Case</th>
<th>$d_{\text{scl}}$</th>
<th>$U_{\text{tot}}$</th>
<th>$d_{\text{f}}$</th>
<th>$r(E)$</th>
<th>Multiple reflections</th>
<th>Lambert–Beer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$d_{\text{scl}} &lt; d_{\text{f}}$</td>
<td>↑</td>
<td>const</td>
<td>const</td>
<td>↑↓</td>
<td>not valid</td>
</tr>
<tr>
<td>2</td>
<td>and</td>
<td>const</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>3</td>
<td>$d_{\text{f}} \ll \delta$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>4</td>
<td>$d_{\text{scl}} &lt; d_{\text{f}}$</td>
<td>↑</td>
<td>const</td>
<td>const</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>5</td>
<td>and</td>
<td>const</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>const</td>
</tr>
<tr>
<td>6</td>
<td>$d_{\text{f}} &gt; \delta$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>7</td>
<td>$d_{\text{scl}} = d_{\text{f}}$</td>
<td>↑</td>
<td>const</td>
<td>↑↓</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>8</td>
<td>and</td>
<td>const</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>const</td>
</tr>
<tr>
<td>9</td>
<td>$d_{\text{f}} \ll \delta$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>n.v.</td>
</tr>
<tr>
<td>10</td>
<td>$d_{\text{scl}} = d_{\text{f}}$</td>
<td>↑</td>
<td>const</td>
<td>↑↓</td>
<td>n.v.</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>and</td>
<td>const</td>
<td>↑</td>
<td>↑</td>
<td>n.v.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$d_{\text{f}} &gt; \delta$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑↓</td>
<td>const</td>
</tr>
</tbody>
</table>
dependence in cases 1 and 4 \((d_{sc} < d_l)\) is given solely by the effect of multiple internal reflections or the Lambert–Beer law, depending on whether the penetration depth \(\delta\) of the light is larger or smaller than \(d_l\). Therefore, these cases can be used to judge the optical model and to determine the optical parameters. In the case of the ultra-thin films only \(d_l \ll \delta\) applies. The experiments for the valve metal oxides presented later can be understood by referring to particular cases of this table.

Figure 1.5 shows \(i_{ph}(d_l)\) simulations according to the model for two different wavelengths (280 and 375 nm) under potentiostatic conditions (applied potential 2 V). The optical constants used for these calculations were determined by ellipsometry (isotropic approximation) and are given in the insets of the figures. Owing to the strong light absorption at 280 nm \((k = 1.4)\) no interference is observed at this wavelength. The decrease in the photocurrent at high film thicknesses is due to the