Metal Oxide Nanomaterials for Chemical Sensors
Integrated Analytical Systems

Series Editor
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Series Preface

In my career I’ve found that “thinking outside the box” works better if I know what’s “inside the box.”

Dave Grusin, composer and jazz musician

Different people think in different time frames: scientists think in decades, engineers think in years, and investors think in quarters.

Stan Williams, Director of Quantum Science Research, Hewlett Packard Laboratories

Everything can be made smaller, never mind physics;
Everything can be made more efficient, never mind thermodynamics;
Everything will be more expensive, never mind common sense.

Tomas Hirschfeld, pioneer of industrial spectroscopy

Integrated Analytical Systems
Series Editor: Dr. Radislav A. Potyrailo, GE Global Research, Niskayuna, NY

The field of analytical instrumentation systems is one of the most rapidly progressing areas of science and technology. This rapid development is facilitated by (1) the advances in numerous areas of research that collectively provide the impact on the design features and performance capabilities of new analytical instrumentation systems and by (2) the technological and market demands to solve practical measurement problems.

The book series Integrated Analytical Systems reflects the most recent advances in all key aspects of development and applications of modern instrumentation for chemical and biological analysis. These key development aspects include: (1) innovations in sample introduction through micro-and nano-fluidic designs, (2) new types and methods of fabrication of physical transducers and ion detectors, (3) materials for sensors that became available due to the breakthroughs in biology, combinatorial materials science and nanotechnology, (4) innovative data processing and mining methodologies that provide dramatically reduced rates of false alarms, and (5) new scenarios of applications of the developed systems.

A multidisciplinary effort is required to design and build instruments with previously unavailable capabilities for demanding new applications. Instruments with more sensitivity are required today to analyze ultra-trace levels of environmental pollutants, pathogens in water, and low vapor pressure energetic materials in air. Sensor systems with faster response times are desired to monitor transient in-vivo events and bedside patients. More selective instruments are sought to analyze specific proteins in vitro and analyze ambient urban or battlefield air. Distributed sensors for multiparameter measurements (often including not only chemical and biological but also physical measurements) are needed for surveillance over large terrestrial areas or for personal health monitoring as wearable sensor networks. For these and many other applications, new analytical instrumentation is urgently needed. This book series is intended to be a primary source on both fundamental and practical information of where analytical instrumentation technologies are now and where they are headed in the future.

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Radislav A. Potyrailo
Metal Oxide Nanomaterials for Chemical Sensors
Preface

Metal oxide materials due to their unique combination of redox chemistry, optical, electrical and semiconductor properties, have for many years played a key role in the successful implementation of chemical sensor technology. Given the intrinsic advantages of confinement effects and fundamentally new material properties of nanoscopic materials, there is a strong drive to exploit the potential of nanosized metal oxide materials and their new morphologies for chemical sensing applications. However, the multi-dimensional interplay among interfacial interactions, chemical composition, preparation method, and end-use conditions of metal oxide nanomaterials strongly affects the sensor functionality, which often makes device integration and development for real-world applications very challenging.

Research efforts to improve the performances of present metal oxide sensor technology through the variation of both surface chemistry, morphology and microstructure via combinatorial and chemically directed design and novel synthetic methods has begun to yield libraries of materials for use and development as chemical sensing materials. Interestingly, while the general reaction mechanism for both oxidizing and reducing gases on metal oxides is thought to be understood, there are many details within the reaction mechanism which induces the subsequent sensing signal that are not definitively characterized and points out the need for further development.

The contents of this book present a state-of-the-art collection and critical survey of recent developments in the implementation of metal oxide nanomaterial research methodologies for the discovery and optimization of new sensor materials, methods and sensing systems. The book should be of interest to a diverse and broad readership belonging to both academia and industrial research units as it provides a detailed description and analysis of (i) metal oxide nanomaterial sensing principles (ii) advances in metal oxide nanomaterial synthesis/deposition methods, including liquid and vapor processing techniques (iii) advances, challenges and insights gained from the in situ/ex situ analysis of reaction mechanisms and (iv) technical development and integration challenges in the fabrication of sensing arrays and devices.
Chapter 1 describes the generally accepted reaction mechanism of both oxidizing and reducing gases with metal oxides. In many ways this reaction mechanism is thought to be well understood. However, a direct measurement of the surface species produced via the myriad of interfacial reactions taking place, both during active gas exposure and while sensing signal measurement is taking place, i.e. operando conditions, has been difficult and in many cases inconclusive with respect to the proposed reaction mechanism. This first chapter provides a very detailed review of this topic and its associated measurement challenges.

As a follow-on to the first chapter’s discussion of reaction mechanisms, Chap. 2 details many of the classic methods used in studying the oxidation or reduction reactions on metal oxides. These ultra-high vacuum surface science experiments are able to produce and characterize perfectly clean model metal oxide surfaces for study. Surface science methods that are working on closing the gap between model UHV and real sensor exposure conditions are described with respect to the methods and their limitations. Lastly, unique TiO$_2$ metal oxide surfaces prepared using grazing incidence low energy ion sputtering are described, which provide new insight for some unique sensor applications. These illustrations are also an example for expanding the use of surface science techniques to include unique surface preparation as well as its characterization and study.

The design and synthesis of metal oxides for sensing applications can benefit from a chemical principles approach as detailed in Chap. 3. Specifically, the redox reactions of metal oxide materials with a variety of gases is examined from a determination of the acidity and basicity of the metal oxide surface. Current concepts of interrelationships between metal oxide chemical composition, crystal and surface structure and its activity in the reaction with gas phase components are considered. Details are provided on how these calculations are made and applied towards the doping of SnO$_2$ nanomaterials with a range of dopants with varying acidic/basic character. The variation in response of these materials with respect to the selectivity and the overall sensor response to both oxidizing and reducing target gases is detailed.

Chapter 4 begins with an introduction into the use of metal oxides for chemical sensing applications both from a materials development standpoint as well as a description of the generally accepted reaction mechanism for oxidizing and reducing gases. The chemistry of metal oxides is rich with possibilities, even more so when one considers the range of dopants that can be added to a given metal oxide material. Such a variation modifies the reactive properties of the metal oxide towards the target gases as well as modifying its corresponding thermal dependence. To develop libraries of materials, Chap. 4 includes a description of a combinatorial synthesis and testing methodology for a wide variety of metal oxide nanomaterials. A series of experimental approaches are described with a range of sensing examples provided.

The characteristic sensing dependence as a function of control of the crystalline character is developed in Chap. 5 with studies pertaining to selected microstructures. The synthesis and characterization of these selected microstructures are described for TiO$_2$ (anatase) and dopant-stabilized $\varepsilon$-WO$_3$. While anatase was
shown to have unique activities over rutile, ε-WO₃ shows a high sensitivity and unique selectivity to polar gas molecules. Such unique dependencies can be particularly useful in the development of both sensitive and selective sensing arrays. The need of developing materials with an increasing level of control is continued in Chap. 6. Molecular beam epitaxial (MBE) growth of metal oxide thin films is a method enabling the development of nanomaterials with a higher level of crystalline ordering than that achievable by physical vapor deposition methods. Such a high level of ordering has been found to be beneficial, for instance, in increasing the oxygen ion conductivity of metal oxide films and can provide interesting characteristics from a chemical sensors perspective. The MBE deposition method and its associated materials characterization techniques are described and examples of the use of MBE grown metal oxide materials for sensing applications are provided.

Chapter 7 outlines a methodology to provide atomic level control over the chemistry of the metal oxide as well as the ability to coat geometries and structures with angstrom levels of film thickness control. Atomic layer deposition (ALD) methods have been well developed for a variety of needs related to the integrated circuit (IC) industry. However, many of the properties of this technique which are so attractive for the IC industry are also of interest for the development of metal oxide nanomaterials for chemical sensors. The characteristics of the ALD method are outlined and applications for coating both thin films on flat and very porous substrate materials are described in the context of a series of sensing applications.

While the chemistry available for producing a variety of metal oxides is rich with possibilities there are also a number of new methods, beyond the well known colloidal wet chemistry or vapor phase processing methods that are available for production of unique metal oxide nanomaterials. Chapter 8 details one of the more recent efforts which utilizes microwave irradiation processing methods for production of a rich array of metal oxides and composites as well as microstructures. The experimental processes used to achieve this library of materials is outlined and sensing applications of a subset of the materials is provided.

Part II of the book is concentrated on describing novel morphologies and the signal transduction principles in metal oxide-based sensors. Chapter 9 provides a detailed introduction into the synthesis and characterization of metal oxide nanowires as well as their currently accepted general reaction/sensing mechanism. Both conductometric and field effect device structures are introduced. The benefits of using nanowires with diameters on the size scale of the Debye screening length are discussed with respect to both the enhanced sensitivity as well as their reactive properties.

Chapter 10 continues the discussion of metal oxide nanowire-based sensors with a focus on the most commonly used ZnO and SnO₂ nanowires. These types of sensors are discussed with respect to both gas phase and biochemical sensor device development and applications. Furthermore, the possibility of using ZnO-based nanowire materials for optical detection schemes as well as integration into wireless structures are detailed as well, which provides strong evidence for the ubiquity of metal oxide nanomaterials in sensing devices.
In many cases the improvement of a sensing material can be realized by increasing its surface area. While for nanowire-based devices the benefit for a reduction in the nanowire diameter is realized by the creation of a depletion layer that envelopes the entire wire and is significantly modulated upon reaction with the target gases, thus creating a more sensitive sensor. Furthermore, increasing the surface area of the nanowire through the creation of complex morphologies such as a fish-bone type structure as well as many other 3-D structures can lead to unique adsorption sites for reaction and transduction. Chapter 11 describes the synthesis and characterization of a variety of metal oxide chemistries with complex morphologies. The benefits with respect to both sensitivity and selectivity, operation temperature reduction, enhanced response times and stability are described.

While the use of the optical properties of ZnO for sensing applications was briefly introduced in Chap. 9, a detailed description of the optical properties of metal oxides is provided in Chap. 12. An optical transduction method can be advantageous given that it can be considered a wireless technique and is thus compatible with harsh environment conditions. Furthermore, in the development of multi-transduction sensing array platforms, combining both electronic and optical techniques may offer unique selectivity measurement opportunities. In this chapter the intrinsic and extrinsic photoluminescence of metal oxides and their dependence on target gas exposures are shown to be used for the detection of oxidizing and reducing gases. The size dependence of photoluminescence with regards to both quantum effects as well as changes in surface dominated processes is discussed with respect to sensing applications. While photoluminescence has proven to be useful for the detection of target gases, changes in the absorption properties of noble metals (Cu, Ag and Au) embedded in metal oxides have also proven to be optical beacons for the development of harsh environment compatible chemical sensors.

Part III of the book is focused on new device architectures and integration challenges of metal oxides into sensing device structures. Chapter 13 begins by outlining the unique possibilities that metal oxides with hetero-contacts and phase boundaries offer as a design platform for sensing applications. These details are highlighted with examples of engineered nanostructures of various compositions (pure, doped, composites, heterostructures) and forms (particles, tubes, wires, films). In addition the system architecture can be further enhanced through surface functionalization and the addition of a pre-concentrator system to promote enhanced transduction.

While both changes in the metal oxide chemistry as well as morphology can have pronounced effects on the sensing properties of a particular nanomaterial, the reaction temperature is also a dominating factor in the sensing characteristics. Chapter 14 provides a detailed description of a sensing device structure which uses temperature not only to affect the reaction properties of the target species, but through the collection of the sensing signals as a function of both temperature and time, a sensitive and selective sensing device can be achieved. Interpretation of these multi-parameter data sets using statistical algorithms provides both a characterization of the sensitivity as well as the selectivity of these sensing arrays.
Sensor arrays based on metal oxide nanowires for the so called “electronic nose” applications are the focus of Chap. 15. Details with respect to nanowire growth and integration onto sensor array platforms are described. The benefits and implications of such nanowire sensor arrays for a range of sensing applications is provided. Finally, the interpretation of sensing array data using pattern recognition algorithms to provide the necessary sensitivity and selectivity performance factors for electronic nose applications is detailed.

Chapter 16 begins this discussion with integration of metal oxide nanomaterials onto MEMS device structures such as microhotplates. These challenges include functionalization of the microhotplate with metal oxides formed using both liquid and vapor phase methods. A series of examples are provided for acquisition of sensing data as a function of temperature, sensor array integration as well as multiparametric data acquisition and interpretation.

To summarize, the last decade was famous due to the appearance of new paradigms for the development of metal oxide nanomaterials-based chemical sensors leading to new principles in receptor and transduction principles. This book reviews only a beginning of this exciting journey as it is clear that there will be many years of exciting discoveries ahead.

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Introduction

Modern chemical sensors can be defined as a transducer, which is comprised of, or coated with, a chemically responsive layer. The transducer converts forms of energy such as electrical, optical, or mechanical into a measurable signal. The chemically responsive layer, however, is what makes chemical sensors unique from physical sensors. This layer is needed as there are nearly an infinite number of detectable chemicals that are important for a variety of applications including automotive, mining, pharmaceutical and many other industries as well as personal safety and homeland security. In order for the chemical sensor to respond to the target chemical of interest, the chemically selective layer needs to preferentially interact with the target chemical. This interaction causes a change in the transducer’s properties, which produces a change in the sensor signal. If these target chemicals could be detected using chemical sensors with the required detection limit, sufficient selectivity as well as an acceptable cost factor, the industrial and personal applications of chemical sensors would penetrate a variety of markets. These basic chemical sensing concepts are not new, and no doubt were envisioned with some of the very first chemical sensor demonstrations. The earliest of which may be likened to nineteenth and early twentieth century miners who were certainly grateful for their “hand held” air quality monitor, the canary. Once their canaries stopped singing (acoustical transduction) and fell off their perch (observed signal), the miners would immediately evacuate the mine as this was an indication of a buildup of combustible gases (methane) or carbon monoxide. Either of which could cause a fatal condition for the miners and unfortunately for the canary, it was nearly always a fatal condition.

With the passage of time and the industrial revolution a tremendous amount of development work has been completed over the years in the field of chemical sensors and thankfully it appears that the industry has moved beyond the use of canaries. While air quality monitoring is one application of chemical sensors, monitoring of our other natural resources, water and soil quality are also of vital importance. Chemical sensors, or their need, can also be found in a variety of technological areas including: combustion, agricultural, industrial processing, food
industry, medical, public safety, among many others. As the technology and processes in each of these individual areas mature the sensor required typically becomes more challenging to develop with regards to their reliability, detection limits, sensitivity, selectivity and cost.

Recently there have been several new publications that have described the history and fundamental operating principles of a variety of chemical sensors [1–3] and these details need not be included in this book. For the current work we will focus on the use of metal oxide nanomaterials for chemical sensors. One of the first landmark demonstrations, which in hindsight is a precursor to modern metal oxide-based chemical sensors was the Nernst lamp developed in the late nineteenth century [4]. Nernst’s studies on the electrolytic conduction of metal oxides showed that while they were non-conductors at room temperature, at high temperatures, upwards of 700 K, these metal oxides became conductors and in being resistively heated they also produced a brilliant white light. Furthermore, they could be reliably operated in the presence of air and did not need to be encapsulated in a non-oxidizing environment, as did its incandescent predecessors. Thus in 1904 the Nernst lamp replaced those comprised of carbon filaments, but this was short-lived as the Nernst lamp was eventually replaced by the tungsten lamp [5]. Interestingly though, the Nernst lamp used yttria-stabilized zirconia (YSZ) as its incandescent source and as such is closely related to Lambda oxygen sensors which are used in automobiles even today. YSZ has over time been shown to be stable in oxidizing atmospheres at temperatures even as high as 1,200 K and is an excellent oxygen ion conductor, leading to its widespread use as an electrolyte in solid oxide sensors and fuel cells. Lambda sensors typically have a hollow cylinder of YSZ, with the outer wall exposed to the exhaust gas and the inner wall exposed to the ambient atmosphere. At elevated temperatures (700 K) oxygen is reduced on the YSZ electrolyte and the gradient of oxygen ions at elevated temperatures induces an ionic potential across the electrodes placed on the inner and outer walls of the YSZ cylinder.

The Lambda oxygen sensor developed during the late 1960s by the Robert Bosch GmbH Company used a very similar design as described above. This device was first used in cars as part of an emissions control system in 1976. The use of this device allowed for optimization of the fuel to air mixing ratio for more efficient combustion of fuel and in doing so reduces the concentrations of unburnt fuel and oxides of nitrogen (NOx) that are emitted into the atmosphere. The reduction in these emissions have been critical in the improvement of tropospheric air quality over the last three decades, making the integration of O2 sensors in cars a key enabling technology for the improvement of vehicular emissions.

The Taguchi gas sensor, sold by Figaro Engineering, is another example of a very successful chemical sensor and these devices have been mass-produced since 1968. This sensor was developed out of research conducted by Mr. Naoyoshi Taguchi and uses the chemiresistive properties of semiconductor metal oxides as the transduction mechanism. Tin oxide is the most popular metal oxide used in these sensors and by functionalizing them with various catalytically active materials (Pd, Pt, Au, etc.) an entire product line of sensors which detect common
combustible and reducing gases such as H₂, CO, CH₄ as well as gases of interest to various industrial applications can be purchased.

What kind of properties makes metal oxides so attractive for their use in gas sensors? Metal oxides in general have proven to be resistant to high temperatures, often are catalytically active, are optically transparent in the visible wavelengths, and are wide band gap materials that are often used as electrical insulators or semiconductors in a variety of electrical devices [6]. The electrical and optical properties and the chemical reactive characteristics of metal oxides are the key attributes for chemical sensing applications. Metal oxides such as YSZ, SnO₂, TiO₂, ZrO₂, CeO₂, ZnO, CuO and many others commonly undergo oxidation and reduction cycles under appropriate conditions. Metal oxides exposed to oxidizing gases, such as O₂ or NO₂ as an example, will typically result in reactions of the following general form:

(1) \( \text{O}_2 + 2e^- \rightarrow 2\text{O}^- \)
(2) \( 2\text{O}^- + 2e^- \rightarrow 2\text{O}_2^- \)
(3) \( \text{NO}_2 \rightarrow \text{NO} + \text{O} \)
(4) \( \text{O} + e^- \rightarrow \text{O}^- \)
(5) \( \text{O}^- + e^- \rightarrow \text{O}_2^- \)

While this is a greatly simplified reaction scheme, as it does not show all of the possible intermediates, the common theme for oxidizing gases is that they tend to form \( \text{O}^- \) and/or \( \text{O}_2^- \) ions. The formation of oxygen ionic species at the surface leads to buildup of the depletion (accumulation) region in \( n^- (p^-) \) type of semiconducting metal oxides, which effectively modulates their conductance. On the other hand, in order for the doubly ionized oxygen anion to be stabilized it needs to diffuse into an oxygen vacancy site formed at a lattice defect. These modifications of the defect sites will in turn affect the optical (luminescent, color) properties of oxide.

Reducing gases such as H₂ or CO are thought to react readily with the aforementioned oxygen anions along the following simplified reaction paths:

(6) \( \text{H}_2 + \text{O}^- \rightarrow \text{H}_2\text{O} + e^- \text{ or } \text{H}_2 + \text{O}_2^- \rightarrow \text{H}_2\text{O} + 2e^- \)
(7) \( \text{CO} + \text{O}^- \rightarrow \text{CO}_2 + e^- \text{ or } \text{CO} + \text{O}_2^- \rightarrow \text{CO}_2 + 2e^- \)

A few logical questions can be raised at this point: how are these electrons donated from/to the sensing material, how does this produce a measurable affect on the transduction mechanism of choice and how does size as well as morphology of the sensing element influence the transduction function? For chemical sensors that rely on the change in resistance of an \( n^- \)-type (\( p^- \)-type) metal oxide semiconductor as the transduction mechanism, a decrease in valence band electrons used for production of oxygen anions with the accompanying formation of the depletion (accumulation) regions in the sensing material will cause an increase (decrease) in resistance. Likewise upon exposure to reducing type gases, there will be a reduction in the number of ionosorbed oxygen species and the electrons will be donated back to the metal oxide semiconductor causing a decrease (increase) in resistance. For systems that rely on the modulation of optical properties as a
transduction mechanism the change in oxygen anions upon reaction with the target gases produces a strong signal as well. This has been most commonly observed with ZnO and TiO$_2$ [7, 8]. In both of these cases there are oxygen defect states that are a source of photoluminescence upon excitation with a UV photon. If the defect states (or oxygen vacancy) are not populated with oxygen anions, this channel is available for photoluminescence, and likewise it turns off when oxygen anions occupy the defect state. Therefore in the presence of an oxidizing gas, photoluminescence is reduced, while in the presence of a reducing gas, photoluminescence increases. The interaction mechanism is slightly different for Lambda type sensors. In this case oxygen still follows the simplified reactions noted in schemes (1) and (2) above, however, the transduction mechanism is dictated by the diffusion of the incorporated O$^{2-}$ bulk ions. This is driven by a concentration gradient of O$^{2-}$ ions between the ambient and emission side of the YSZ component, and the quantity measured is the change in ionic conductance. It is interesting to note that the details of the above reaction mechanisms are strongly material and materials processing specific and in many cases are an active area of research in the optimization of these materials for enhanced sensitivity and selectivity characteristics.

While the use of metal oxides has provided many useful chemical sensing results, it is quite common to add either dopants or catalytically active materials to the metal oxide to modify its reactive/sensing properties. As an example: the addition of yttria (Y$_2$O$_3$) dopants to zirconia creates the commonly used yttria-stabilized zirconia metal oxide that is used in the Lambda sensors as well as in solid oxide fuel cells. Catalytically active materials such as Pt, Pd, Au, Fe$_2$O$_3$ among many others are also added to metal oxides to modify the reaction paths and rates with the aim of increasing the detection limits as well as enhancing the selectivity towards detection of specific target gases.

For over 40 years the most visible application of chemical sensors was employment of O$_2$ sensors in automobiles and CO detectors in households. Currently there exists a strong demand in chemical sensors for bio-medical applications, homeland security, environmental control as well as in appliances within our homes, or in our portable electronics. To meet these needs improvement of selectivity, sensitivity, power consumption along with reduction in cost and size for the chemical sensing systems has to be realized. It is here where over the last 10–15 years, advances in the areas of nanoscale science and engineering of metal oxide composite materials have shown promise for their incorporation and potentially disruptive advancement of chemical sensor technologies. Advantages that are realized by nanoscale materials include a number of new functional opportunities as well as financial aspects. In the simplest case, the surface area to volume ratio of a spherical particle increases by a factor of $1/r$ with a reduction in particle size. Particles with diameters below 10 nm contain a significant fraction of their material in the surface layer of the particle. This is important as the catalytic reactions responsible for sensing action take place at the surfaces of these metal oxide materials. The reduction in size will not only reduce costs but may also provide novel opportunities in realization of new receptor/transduction principles in chemical sensing. Specifically, the reduction in size of metal oxides often
contributes to emerging catalytic reaction characteristics, which can be taken advantage of during the design of an optimized material for detection of the target gases. As the catalytic properties of metal oxides also typically are tailored by decorating the metal oxide with metallic particles, this reduction in size is also beneficial for modifying the catalytic properties of nanocomposite materials comprised of both metal and metal oxide nanoparticles [9]. Further yet, the metal oxide nanocomposites can be processed to include 3-D assemblies of either particles or nanowires. The porosity of these assemblies can be highly beneficial for enhanced adsorption of the target gases, and with this 3-D heterostructures can be developed with individual components within the heterostructure designed for particular interactions. However, a balance here clearly needs to be struck, as highly porous materials can have enhanced adsorption properties, but for use in a chemical sensor this property does not want to be enhanced to the point where it acts like a chemical sieve or trap for the target chemicals, as an optimal chemical sensing material must have both a fast response and recovery time.

While optimizing the chemistry, size and microstructure of metal oxide and metal doped metal oxide composite materials for catalytic chemical reactions is at the forefront of the design of materials for chemical sensors, the reduction in size to the nanoscale also allows for enhanced transduction properties. As noted above chemiresistor-based sensing devices operate under the principle that upon adsorption and or reaction of gases the resistance across the conducting channel changes in a characteristic fashion. When the metal oxide composite material which coats the electrodes is comprised of either a bed of percolating nanoparticles or nanowires the resistance change can be dictated both by the individual contact resistances between particles or wires, but also through the formation of a depletion layer inside the individual nanoparticle (nanowire) [10]. As electrons are donated from the conduction band to enable chemical reactions an electron depletion layer is formed, and resistance across an $n$-type material will increase. As this layer approaches the respective materials Debye length the conductance changes can be quite significant. This is more clearly relevant when the Debye length, which is typically on the order of several nanometers, is on the order of the size of the nanoparticle or nanowire. In these cases the depletion layer envelops the whole nanoparticle or nanowire and resistivity changes should be the largest and most beneficial for sensitive analyte detection. In metal oxides composed of nanosized grains almost all the carriers are trapped in surface states and only a few thermally activated carriers are available for conduction. In this configuration the transition from activated to strongly de-activated carrier density, produced by reactions with the target gas species, has a huge effect on sensor conductance. Thus, the technological challenge has moved to the fabrication of metal oxide-based sensors with crystallite sizes as small as possible which maintain their stability over long-term operation at high temperature.

To decouple and better understand the contribution of the interconnects and individual nanoparticles (nanowires) in the sensing process, recent work has been focused on using single particles or single nanowires between two electrodes as model sensing devices. This is easiest to visualize for a single chemiresistor pinned
between two electrodes [10]. In this approach, the nanowires are usually placed between two electrodes, and biased at constant voltage, reading the change in resistance (RES). This approach works on the same principle with thin film conductometric gas sensors. Sensors based on single crystalline nanowires may be advantageous over their planar counterparts as almost all of the adsorbed species are active in producing a surface depletion layer compared with a thin surface. If the nanowire diameter is on the order of its Debye length, then reactions which deplete electrons from the conduction band will form a depletion layer that spans the entire core of the nanowire, resulting in a dramatic increase in resistivity for this nanowire. These features together with transport of charge carriers in one-dimensional channels are responsible for enhanced sensitivity and thus ultra low detection limits. There are other benefits as well, in that one can not only measure the change in resistance of the nanowire, but by applying a constant voltage to the wire, the wire itself is resistively heated [11]. This is an important point because most metal oxide-based materials need to be operated at elevated temperatures in order for them to function as a chemical sensing material. Typically these temperatures range between 100 and 500 °C. By integrating the heater into the very design of the nanowire-based chemiresistor, a component required for integration into a chemical sensing platform has been removed and therefore simplifies its production and minimizes the sensor power consumption to record low levels in the micro-watt range. While the use of individual nanowires is proving to enhance the sensing properties of these materials, it is still challenging and expensive to produce this kind of sensor, as the nanowire is still most often “picked up” and “pinned” in place on electrodes to ensure good electrical contact. However, this single nanowire approach is clearly not a scalable method yet. While work is in progress to develop methods to grow or align the individual wires of a given size and composition between electrical contacts, this is still an area of research with much work to be done to ensure that this is a scalable method which can be compatible with modern device integration paradigms.

In order to find new principles of analyte detection and to enhance the selectivity as well as sensitivity limits by miniaturization of active sensing elements, heterostructured sensor devices utilizing multiple transduction techniques are currently being explored. An example of this type of device structure using an integrated RES and surface ionization (SI) approach has recently been proposed. In this device a metal oxide is electrically contacted directly opposite a counter electrode. Resistive measurements are performed between the two electrodes making contact with the nanowire, whereas SI recordings are carried out between the nanowire and the counter electrode. Surface ionization is an alternative method of gas detection, which was studied in the past by several groups mostly for noble and refractory metals, whereby ionosorbed analyte ion species are extracted into free space by a counter electrode positioned at a short distance above the hot emitter surface [12–14]. In contrast to earlier reports on metals, the recent developments have demonstrated that the SI principle can be applied to SnO₂ nanowires as the emitter surface which is the most widely employed material in the fabrication of RES metal oxide gas sensors [15].
In closing, while metal oxide nanomaterials have many promising attributes that are pushing the state of the art in chemical sensor development, system integration is a major challenge. For metal oxide-based chemical sensors these include incorporation of a variety of ancillary components including heaters, gas sampling mechanisms (active or passive), power sources, and the associated electronics for signal processing and data analysis. While the use of nanomaterials allows for reduced requirements for power consumption, this nanomaterial still needs to be incorporated into a bulk device for all current applications of chemical sensors. Again, this is a common integration problem for many types of devices and if the market requires bulk quantities of units, a process which uses parallel manufacturing paradigms is inevitably a requirement in order to drive down production costs. A solution to this problem would be integration onto a platform such as silicon, which allows one to take advantage of the parallel processing methods, which have been developed over the past decades for the MEMS and integrated circuit (IC) industries. While not every process step utilizing metal oxide nanomaterials is compatible with the strict material and processing protocols used in the IC industry, there are components, which can likely be coupled post-processing. Therefore it is not surprising that modern device fabrication methods using a combination of MEMS and silicon IC processing techniques are currently being explored to probe this next step in the development of chemical sensors for pervasive use across a variety of applications. The development of novel metal oxide nanomaterials and new sensing paradigms in combination with integration strategies for production of scalable chemical sensors promises to lead to a variety of new research directions as well as sensors which will satisfy the needs of a range of technological fields for many years to come.

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References

Part I

Understanding, Characterization and Synthesis of Modern Metal Oxide Nanomaterials
Chapter 1
Insights into the Mechanism of Gas Sensor Operation

Aleksander Gurlo

Abstract Since the development of the first models of gas detection on metal-oxide-based sensors much effort has been made to describe the mechanism responsible for gas sensing. Despite progress in recent years, a number of key issues remain the subject of controversy; for example, the disagreement between the results of electrophysical and spectroscopic characterization, as well as the lack of proven mechanistic description of surface reactions involved in gas sensing. In the present chapter the basics as well as the main problems and unresolved issues associated with the chemical aspects of gas sensing mechanism in chemiresistors based on semiconducting metal oxides are addressed.

“Sensors have a ‘life cycle’ consisting of preparation, activation, operation with deactivation and, possible, regeneration. Thus understanding the performance in terms of reaction and conductance mechanisms is only a part of the total understanding of a sensor.”

1.1 Chemiresistors: From Semiconductor Surfaces to Gas Detectors

Since the early 1920s numerous investigations have demonstrated the influence of the gas atmosphere on conductivity, free carrier mobility, surface potential, and work function on a number of semiconductors (see summary of early works in [1–13]). This led to the understanding that the surface of semiconductors is highly sensitive to chemical reactions and chemisorptive processes [3, 14–20] and resulted finally in the “theory of surface traps” (Brattain and Bardeen [21]), “boundary layer theory of chemisorption” [10, 22, 23] (Engell, Hauffe and Schottky) and “electron theory of chemisorption and catalysis on semiconductors” (Wolkenstein [5–7, 24]). They laid also the theoretical foundations for the subsequent development of metal-oxide-based gas sensors.

Although from this understanding to the use of semiconductors as gas sensors “was, in principle, a small step” [25], the idea of using the changes in conductivity of a semiconducting metal oxide for gas detection was not conceived until the middle of the 1950s. The earliest written evidence came in 1956, in the Diploma Thesis performed in Erlangen under supervision of Mollwo and Heiland and entitled “Oxygen detection in gases changes in the conductivity of a semiconductor (ZnO)” [26], the results discussed later in [1, 27]: “If one exposes a zinc oxide layer which has been given a previous heating at 500 K in a high vacuum to oxygen at a constant pressure, the conductivity falls very rapidly initially and more slowly later. If one then increases the oxygen pressure suddenly, the current of the conductivity exhibits a kink when plotted as a function of the time. In this change the slopes immediately before and immediately after the kink point are proportional to the partial pressure of oxygen. One can use this effect to relate a known and an unknown concentration of oxygen often even under conditions in which one has a mixture of gases...” (cited from Ref. [1]). In 1957, Heiland showed that the “wellconducting surface layer on zinc oxide crystals provides a new, very sensitive test for atomic hydrogen” [28] and Myasnikov demonstrated that ZnO films can be used as a highly-sensitive oxygen-analyzer [29]. Later he developed this “to the method of semiconductor probes”, which allows for “studying free radical processes” and for detecting “free active particles and to measure their concentration under stationary and non-stationary conditions in gases and liquids” [30]. However, the conditions under which ZnO was able to operate as a “sensing device” were far from the real ambient conditions (and, accordingly, from a practical application); the “sensitive” effects were observed: (i) in vacuum conditions, exposed to oxygen or hydrogen, (ii) after “activation” or “sensitization” of the surface by heating in H$_2$ and in UHV.

The practical use of metal-oxide-based gas sensors in normal ambient conditions was not considered until 1962, when Seiyama et al. reported that a ZnO film can be used as a detector of inflammable gases in air [31] (see also [32]), and Taguchi claimed that a sintered SnO$_2$ block can also work in the same way [33] (for the history of TGS (Taguchi Gas Sensor) sensors, see [34]). The latter
approach became very successful, leading to the foundation of the first sensor company (Figaro Engineering Inc.), which established mass production and started selling the TGS sensors in 1968.

Since then, many different metal oxides have been investigated as sensing materials (see, for example, Ref. [35] for a comprehensive review), however, tin dioxide (SnO₂)—alone or “activated” with small quantities of noble metals/their oxides (Pd, Pt, Au)—has remained the most commonly used and the best-understood prototype material in commercial gas sensors [36] as well as in the basic studies of the gas sensing mechanism [35–43].

1.2 Characterization Methodology: From Prototype Surfaces to Operating Sensors

The detailed characterization of metal oxide sensors requires the “simultaneous measurement of the gas response and the determination of molecular adsorption properties for a better understanding of gas sensing mechanisms” [44]. This measurement can be done either on clean and well-defined surfaces in ultrahigh vacuum (UHV) conditions or at temperatures and pressures that mimic real sensor operating conditions (“in situ” [45]). Continuous progress has been made during the past few years for the latter strategy, i.e. toward the use of in situ and operando spectroscopic techniques.

The “crossing of interests” [46] and “bridges of physics and of chemistry across the semiconductor surface” [47] determined experimental methodology applied for the gas-semiconductor studies in general and gas sensing studies in particular in the course of the last 50 years.

The first systematic methodological approach (“design concept for chemical sensors”) in gas sensing-studies was explicitly formulated in 1985, in a series of papers entitled “Development of chemical sensors: empirical art or systematic research?” ([48–50], see also [51]).

The underlying concept was that by “studying the surface of single crystals under well-defined conditions, one might try to achieve a better separation of parameters influencing the properties of gas sensors” [52]. The reactions were addressed by surface spectroscopic methods under ultra-high-vacuum (UHV) conditions on well-defined “prototype” structures while the sensor performance was tested under realistic measuring conditions on the structures of practical importance (“sensors”).

This “comparative approach” advanced the basic understanding of surface reactions and the corresponding conduction mechanism responsible for gas sensing. However, it showed also the limits of surface science in gas-sensing studies and led to the understanding that if spectroscopic and electrical data are not obtained simultaneously, they must be obtained (i) under the same conditions and (ii) on identical samples. A comprehensive description of surface reactions on SnO₂ published in 1989 resulted from simultaneous thermal desorption
spectroscopy (TDS; i.e. reactive scattering of a molecular beam) and conductance measurements [52]. These measurements were applied to SnO$_2$ single crystals and thin evaporated films exposed to a certain dose of CH$_3$COOH, CO or CH$_4$ in UHV conditions while at the sensor operating temperature.

As an alternative to sensing studies on single crystals or thin films, sensing characterization studies have focused on a combination of electrical measurements with spectroscopic investigations of catalysis reactions on polycrystalline, high surface-area materials with the aim to “link semiconductor studies with catalytic studies” [9]. However, most of the studies were performed under conditions far from the real working conditions of sensors (for the summary of numerous studies on semiconducting metal oxides, see references [4, 13, 53]). Besides spectroscopic and catalytic (kinetic) investigations (SnO$_2$: kinetic studies of CO oxidation [54], IR spectroscopic studies of water, CO$_2$ and CO adsorption [55], (summarized in Ref. [56]), EPR investigations of oxygen adsorption, [57], (reviewed in references [58, 59])), the improvements were concentrated on devising systems and in situ cells for combined (i.e., performed under the same conditions on “identical” samples) and simultaneous electrical, catalytic and spectral investigations.

These activities, however, were overlooked by the sensor community at that time, as in situ electrical characterization of realistic (“polycrystalline”) samples, namely, the Hall effect measurements (1982 [60]), changes in work function (CPD) by the Kelvin method (1983 [61]), ac impedance spectroscopy (1991 [62, 63]), simultaneous work function change and conductance measurements (1991 [64]) were preferred for studying the mechanism of operating sensors [99].

Later, this approach was followed systematically in the number of works (reviewed in references [38, 65], recent works in references [66–70] and references therein) to elucidate a mechanism of gas detection on SnO$_2$-based sensors. Local electronic properties (e.g., the density of states in the region near the band gap) of a sensing material were determined by scanning tunnelling microscopy and spectroscopy (STM-STS) in vacuum conditions [71–73] or under N$_2$, CO and NO$_2$ (at room temperature) [74].

By the end of the 1990s, the spectroscopic techniques for gas-sensing studies were differentiated according to conditions under which they can be applied: those that may be applied “under in situ real operation conditions of the sensors” and those that may be applied “under ideal conditions far away from real practical world” [75]. This differentiation subsequently resulted in the systematic combination of phenomenological and spectroscopic measurement techniques under working conditions of sensors [38], and thus lead to the in situ and operando methodology.

Continuous progress has been made during the past few years for the latter strategy, that is, the use of in situ and operando spectroscopic techniques (see [76, 77]):

- **In situ spectroscopy**: spectroscopic characterization of sensing materials under operation conditions or conditions relevant to operation conditions; herein, the sensing performance of this material may be not characterized or may be characterized in a separate experiment,
Operando spectroscopy: spectroscopic characterization of an active sensing element in real time and under operating conditions with the simultaneous read-out of the sensor activity and simultaneous monitoring of gas composition.

These definitions determine the boundary conditions under which an “operando” experiment is performed:

1. on a sensing element, which itself is a complex device and consists of several parts: in solid-state devices with an electrical response, for example, the sensing layer is deposited onto a substrate to which electrodes for an electrical read-out are attached (“transducer”); therefore the assessment of their interfaces is of paramount importance for understanding the overall sensing mechanism;
2. in real time: a sensor is devised to respond to the changes in the gas atmosphere as fast as possible; accordingly, it demands a fast spectroscopic response;
3. under operating conditions: these can vary from ambient conditions (RT and atmospheric pressure) to high temperatures and pressures;
4. with simultaneous read-out of sensor activity: the gas concentration to be measured is transduced by the sensor into an electrical or other convenient output, depending on the modus operandi of sensor (optical, mechanical, thermal, magnetic, electronic, or electrochemical) and the transducer technology;
5. with simultaneous monitoring of gas composition: on-line gas analysis in gas sensing plays a twofold role: (i) the output compositions and concentrations provide data about reaction products and possible reaction paths and (ii) the input concentration verifies the sensor input data (concentration of the component to be detected).

The operando methodology couples electrical (“phenomenological”) and spectroscopic techniques and, aims to correlate the sensor activity with the spectroscopic data obtained under the same conditions on the same sample (Fig. 1.1). In an ideal case, one would obtain four types of information: (i) gas-phase changes (and reaction products) from on-line gas analysis, (ii) species adsorbed on the surface, (iii) changes in the oxide surface and lattice, and (iv) sensor activity.

1.3 Mechanism of Gas Detection: Never Ending Story About Oxygen

Epigraph

Due to the electron affinity of oxygen, the electron can be transferred to the chemisorbed oxygen and, consequently, there will be no chemisorbed oxygen atoms, but ions, in the surface

Since the development of the first models of gas detection on metal-oxide-based sensors [78, 79] much effort has been made to describe the mechanism responsible for gas sensing (see, for example, [80–82]). Despite progress in recent years, a number of key issues remain the subject of controversy; for example, the disagreement between electrophysical and spectroscopic investigations, as well as the lack of a proven mechanistic description of surface reactions involved in gas sensing.

Nowadays, the influence of the gas atmosphere on the electrical transport properties of semiconductors and, accordingly, the operation of metal-oxide-based gas sensors is currently described by the combination of two different models; they are the ionosorption and the reduction-reoxidation mechanisms (Table 1.1). The ionosorption model considers only the space-charge effects/changes of the electric surface potential that results from the “ionosorption” of gaseous molecules. The reduction-reoxidation model explains the sensing effects by changes in the oxygen stoichiometry, that is, by the variation of the amount of the (sub-) surface oxygen vacancies and their ionization. The latter involves explicitly the diffusion of oxygen (or oxygen vacancies) from/in the bulk of the sensing material.

1.4 Oxygen Ionosorption

The electrical conductivity and work function can be described as collective physical properties of semiconductors which are changed by an ionosorption process and are accessible to measurement. The key in the mechanistic description of gas sensing is “oxygen ionosorption” and reaction of reducing gases with ionosorbed oxygen ions.

Fig. 1.1 Methodological approach for simultaneous spectroscopic and electrical (“phenomenological”) characterisation of metal-oxide-based gas sensors. Modified from ref. [76]
<table>
<thead>
<tr>
<th>Gas detection</th>
<th>Ionosorption model</th>
<th>Oxygen vacancy model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>$O_2^{\text{ads}} + e^- (\text{CB}) \leftrightarrow O_2^{-} (\text{ads})$</td>
<td>$2V_0^* + O_2 \text{ (gas)} + 2e^- (\text{CB}) \leftrightarrow 2O_0^*$</td>
</tr>
<tr>
<td></td>
<td>$O_2^{-} (\text{ads}) + e^- (\text{CB}) \leftrightarrow O_2^{2-} (\text{ads}) \leftrightarrow 2O^- (\text{ads})$</td>
<td></td>
</tr>
<tr>
<td>CO/presence of oxygen</td>
<td>$\text{CO (gas)} + O^- (\text{ads}) \leftrightarrow \text{CO}_2 (\text{gas}) + e^- (\text{CB})$</td>
<td>$\text{CO (gas)} + O_0^- \leftrightarrow \text{CO}_2 (\text{gas}) + V_0^*$</td>
</tr>
<tr>
<td></td>
<td>$\text{CO (gas)} \leftrightarrow \text{CO}^+ (\text{ads}) + e^- (\text{CB})$</td>
<td>$V_0^* \leftrightarrow V_0^{**} + e^- (\text{CB})$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$\text{NO}_2 (\text{gas}) + e^- (\text{CB}) \leftrightarrow \text{NO}_2^{-} (\text{ads})$</td>
<td>$\text{NO}_2 (\text{gas}) + V_0^* \leftrightarrow \text{NO}_2^{-} (\text{ads}) + V_0^{**}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2\text{NO}_2 (\text{gas}) + O_0^{-} (\text{ads}) + V_0^* \leftrightarrow 2\text{NO}_3^{-} (\text{ads}) + V_0^{**}$</td>
</tr>
<tr>
<td>Water vapour</td>
<td>$\text{H}<em>2\text{O (gas)} + O^- (\text{ads}) + 2\text{Sn}^{x}</em>\text{Sn}^{-} \leftrightarrow 2(\text{Sn}^{x}_\text{Sn}^{-} - \text{OH}) + e^- (\text{CB})$</td>
<td>$\text{H}<em>2\text{O (gas)} + 2\text{Sn}^{x}</em>\text{Sn}^{-} + O_0^{-} \leftrightarrow 2(\text{Sn}^{x}_\text{Sn}^{-} - \text{OH}) + V_0^* + e^- (\text{CB})$</td>
</tr>
<tr>
<td></td>
<td>$\text{H}<em>2\text{O (gas)} + \text{Sn}^{x}</em>\text{Sn}^{-} + O_0^{-} \leftrightarrow (\text{Sn}^{x}<em>\text{Sn}^{-} - \text{OH}) + \text{OH}^*</em>\text{Sn}^{-} + e^- (\text{CB})$</td>
<td></td>
</tr>
</tbody>
</table>
The oxygen influence on the electrical conductivity and work function is very well documented. For SnO$_2$, for example, exposure of single crystals (Ref. [83] and refs therein), polycrystalline samples (porous films [84], powders [57], pressed bars[85]) as well as one dimensional nanostructures [86, 87] to oxygen leads to the (i) decrease in the electrical conductivity and in the concentration of conduction electron density (Hall effect measurements [57]), (ii) increase in the work function observed in UHV conditions (XPS/UPS [88]) and under atmospheric pressure (simultaneous Contact Potential Difference, CPD, and conductance measurements [84]). Similar effects have been also observed on TiO$_2$ and ZnO (see early publications on TiO$_2$ [89, 90][91] and on ZnO [3, 92–95]).

The magnitude of the changes depends strongly on the oxide temperature (see for example [85] and [84]), particle size and pre-treatment (history). On high-surface area and reduced samples the changes are much higher in comparison to single crystals and oxidised samples. The reduced samples show activity at temperatures as low as room temperature (r.t.), for oxidised samples higher temperatures (>100 °C) are needed. This difference between oxidised and reduced samples is usually ignored by the “ionosorption theory”.

Because the detailed mechanism of oxygen adsorption cannot be derived directly from electrophysical investigations[96], the chemistry of adsorbed surface oxygen on SnO$_2$ was adapted from the “ionosorption model” [97–100]. It was assumed that the thermally stimulated processes of oxygen adsorption, dissociation and charge transfer involve only conduction electrons [4, 81]:

\[
\begin{align*}
\text{O}_2(\text{gas}) & \leftrightarrow \text{O}_2(\text{ads}) \\
\text{O}_2(\text{ads}) + e^- (\text{CB}) & \leftrightarrow \text{O}_2^-(\text{ads}) \\
\text{O}_2^- (\text{ads}) + e^- (\text{CB}) & \leftrightarrow \text{O}_2^{2-}(\text{ads}) \leftrightarrow 2\text{O}^-(\text{ads}) \\
\text{O}^- (\text{ads}) + e^- (\text{CB}) & \leftrightarrow \text{O}^{2-}(\text{ads}) \\
\text{O}^{2-}(\text{ads}) & \leftrightarrow \text{O}^{3-}(1\text{st bulk layer})
\end{align*}
\]

**Fig. 1.2** The simulated equilibrium coverages of the oxygen species. The transition from O$_2^-$ to O$^-$ is calculated to be around 700 K (intersection at 427 °C). Copyright Elsevier, reproduced with permission from Ref. [100]
The nature of the ionised oxygen species is assumed to depend on the adsorption temperature (Fig. 1.2). At low temperatures (150–200 °C) oxygen adsorbs on SnO₂ non-dissociatively in its molecular form (as charged O₂<sub>ads</sub>⁻ ions). At high temperatures (between 200 and 400 °C or even higher) it dissociates to atomic oxygen (as charged O<sub>ads</sub>⁻ or O<sub>ads</sub>²⁻ ions) [4, 37, 75, 80, 81, 98, 99, 101]. Neutral oxygen species such as physisorbed oxygen, O₂<sub>phys</sub>, are assumed not to play any role in gas sensing. The same holds for the lattice oxygen ions, O<sub>lat</sub>²⁻, in bulk materials at temperatures not high enough for fast oxygen exchange reactions (see detailed discussion below).

At this point, a problem of semantics starts to bring additional confusion, especially in the operational use of the terms “charged” species and the “charge transfer” at the surface. In semiconductor physics, the charge transfer implies by definition the transfer of free charge carriers, that is, conduction electrons or holes. Accordingly, the species that influence the electrical conductivity are regarded as “charged” or “ionized”. They are represented by free oxygen ions. The species that do not influence the conductivity are regarded as “neutral”. They are represented by physisorbed oxygen molecules.

The phenomenological model describes the oxygen ionosorption on an n-type semiconductor as follows:

- ionosorbed oxygen species are formed due to the transfer of conduction electrons from the semiconductor;
- they can be regarded as free oxygen ions which are electrostatically stabilized in the vicinity of the surface;
- there are no other adsorbed oxygen species besides physisorbed oxygen and oxygen ions;
- physisorbed oxygen is electrically neutral and oxygen ions are electrically active (“charged”) species.

The simplified picture showing the influence of adsorption on surface conductivity and work function is as follows. An oxygen molecule becomes physisorbed at the surface. In the next step, an electron from the oxide’s conduction band is trapped at the adsorbed oxygen molecule. The adsorbed oxygen molecule and surface itself become negatively charged. The flow of electrons from the semiconductor into the chemisorbed layer, without any diffusion of ionic species at the same time, induces a space charge between the interior of the semiconductor and its surface. The negative surface charge is compensated by a positive charge and a space-charge layer forms below it. This positive space-charge layer has reduced electron densities as compared to the bulk and is called an “electron-depleted layer or a charge depleted layer”. As a result the energy band, pertaining to the surface, bends upwards with respect to the Fermi level. This causes the creation of barriers on the surface, (qΔV₅ > 0), due to the increasing work function, (qΔV₅ > 0), and decreasing surface conductance (G = Gexp(–qΔV₅/kT)) (Fig. 1.3). The process of charge transfer continues until equilibrium is reached and a steady state is achieved. To prevent very high double-layer potentials, the total amount of the “charged” species is limited to 10⁻⁵–10⁻³ monolayer which corresponds approximately to 1 V of the surface potential V₅ (this is the so-called