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 ε-WO_3. While anatase was shown to have unique activities over rutile, ε-WO_3 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 SnO_2 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 envelops 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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http://www.springer.com/978-1-4614-5394-9

Metal Oxide Nanomaterials for Chemical Sensors
Carpenter, M.A.; Mathur, S.; Kolmakov, A. (Eds.)
2013, XX, 548 p., Hardcover
ISBN: 978-1-4614-5394-9