Sensors and Actuators B 208 (2015) 339–345

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Approach for quantification of metal oxide type semiconductor gas sensors used for ambient air quality monitoring

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ARTICLE INFO

Article history:
Received 29 June 2014
Received in revised form 4 November 2014
Accepted 7 November 2014
Available online 15 November 2014

Keywords:
Gas sensor
Metal oxide
Metal-oxide quantification
MOx model
Collocation

ABSTRACT

Metal oxide type (MOx) sensors are one of several technologies being employed in low-cost air quality monitors. Their size and cost make them ideally suited for portable and remote monitoring applications. Quantifying the sensor response, however, remains a significant challenge due to sensitivity to ambient temperature and humidity, and interference with non-target pollutant species. Temporal characteristics such as signal hysteresis and sensor drift over time also affect MOx sensor response.

We present a quantification model rooted in principles of semiconductor science and chemistry, yet informed by and simplified using empirical observations. This model predicts concentration from resistance while providing a correction for temperature effects, usually the most significant confounder in ambient air quality monitoring with MOx sensors, and drift due to change in the sensor heating element. The model parameter values are first determined using lab calibrations, then refined using a field collocation with reference instruments. The work thus provides both a quantification model and a means to effectively calibrate sensors for practical applications.

1. Introduction

The use of inexpensive sensor networks and embedded systems [1,2] are quickly emerging as a key player in the monitoring of local and regional air quality as lower cost monitoring equipment enables new spatial resolution of pollutants. Metal Oxide (MOx) type sensors [3,4] are one of several technologies being used in sensing gas phase pollutants. Many varieties of MOx sensors exist for the detection of different gas species. All types, however, function in a similar manner. An oxidation or reduction reaction occurs when species bind to the sensor surface resulting in the removal or injection of free electrical charge into the semiconductor material [5,6]. This process changes the sensor's electrical conductivity, which is measured by external instrumentation.

Unfortunately there are many challenges when trying to convert the sensor response to pollutant concentrations. All MOx sensors suffer from significant interference effects with temperature, humidity [7] and other gas species. Even when these parameters are controlled, the sensor conductivity is non-linear with respect to the gas species of interest. Most MOx sensors also exhibit 'out-of-the-box' variability from the manufacturing process. Finally, sensor signals will also drift over time from both poisoning (permanent bonding to the sensor surface) and changes in the sensor's heating element resistance caused by thermal stress.

Many approaches exist for the quantification of metal oxide gas sensor, yet most practical models are based entirely on experimentation and *a posteriori* knowledge of sensor behavior [8,9]. While these models provide acceptable results, they tend to be specific to sensor type and operating conditions. It would be advantageous to use a model derived entirely from the theory of chemistry and semiconductor physics, yet in practice this proves prohibitively complex. The approach presented here is rooted in the principles of semiconductor science, yet uses experimental observations to make informed assumptions and simplifications. Doing so retains some physical insight as to sensor behavior, yet allows the model to be tailored to sensor specific applications and proves to be effective in real-world implementation of ambient pollutant quantification.

The model derivation process consisted of lab experimentation and ambient collocation measurements. The theoretically derived model was first applied to experimental data, using the Sensortech (formerly e2v) MiCS-5525 as an example of a commercially available MOx type CO sensor. In practice, sensors are often employed in low pollutant concentration environments with significant environmental variability, hence the need to properly

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http://dx.doi.org/10.1016/j.snb.2014.11.032
0925-4005/

address temperature affects. Humidity effects were neglected as they are at least an order less significant than temperature effects, particularly for CO sensors [10].

MOx sensors are operated at elevated temperatures in order to facilitate the surface chemistry reactions of interest. Most commercially available MOx sensors have built in heating elements to keep the sensor surface in the vicinity of a target temperature. The resistance of the heating element and thus the heat output tend to change over time. This complicates the ambient temperature correction term as the relationship between surface temperature and ambient temperature is not constant when the heater output varies over time. To correct for this drift effect, the heater resistance was measured over several months and incorporated into the model as a temporally varying temperature correction term. This differs from other drift correction methods [11,12] as it is based directly on the observed changes in the sensor heater output. No drift due to poisoning was incorporated in the model, as drift of this type can only be accounted for by using periodic calibrations.

The sensors were then collocated with a reference carbon monoxide instrument in an urban environment. An optimization algorithm was used to dynamically fit the reference data to the theoretical model prediction, thus modifying the model parameters determined in lab experimentation.

2. Principles of MOx operation

Barsan and Weimar [13] present an in-depth discussion of the metal oxide semiconductor conduction model in which a sensor's conductivity is analytically attributed to changes in gas-phase species concentrations. Solving for the conductivity entirely from theory, however, requires extensive knowledge of the chemical kinetics and semiconductor electrical properties. Even if all parameters are known, the functional relationship between conductivity and ambient gas concentration requires numerically solving a complex system of several non-linear relations. Doing so is not practical in many applications; for our ambient application this approach is not feasible. It is thus necessary to incorporate simplifications and experimental data in the theoretical model derivation.

First consider the general principles driving MOx sensor operation. Fig. 1 is a simplistic representation of a MOx sensor element in an environment void of surface reactions. Pertinent attributes of the MOx element include the free charge density in the bulk material volume (charge that is free to conduct across the material), and the surface charge density (charge on the surface of the MOx sensor, which is free to react with reducing agents). The surface charge density will change with temperature.

Electrons are added or removed from the surface when the MOx sensor is exposed to reacting species. Chemical reaction theory governs these reactions. When charge is removed from the MOx surface, the bulk semiconductor responds by restoring some of the surface charge from the bulk charge 'reservoir'. This results in "band

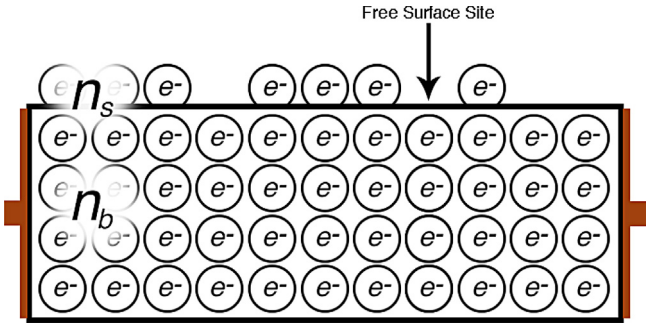

Fig. 1. MOx sensor without surface reaction.

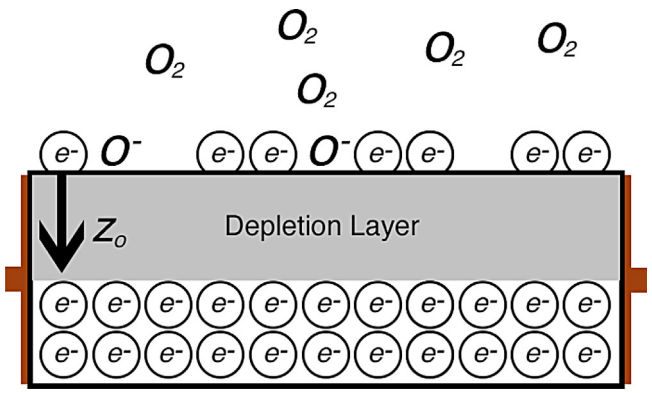

Fig. 2. MOx sensor with surface reaction.

bending" and depletion of some of the bulk charge within the semiconductor volume. As such, the surface charge provides the physical coupling between the semiconductor physics and the gas-phase surface chemistry. Fig. 2 is an example of a sensor element with a depletion layer due to atmospheric oxygen binding in its reduced form to the sensor surface.

Net conduction of electrons within the MOx element occur parallel to the sensor surface, whereas the depletion of charge occurs normal to the surface. It stands to reason then that the conductivity (or resistance) of the MOx sensor is a function of the depletion depth of charge within the bulk semiconductor.

Other important factors include the surface site concentration of chemisorbed species, the temperature dependence of chemical reactions and semiconductor band-bending, and the nature of intermediate and global reaction mechanisms. In this derivation, chemical reaction mechanisms are mostly neglected or generalized while temperature effects are more rigorously accounted for.

3. Model derivation

A usable model can be generated by applying practical simplifications to the theoretical derivation of a MOx sensor model. For our application, simplifications are motivated by a desire to have a closed-form, easily manipulated algebraic equation relating measurable quantities (resistance, ambient air temperature, etc.) with the concentration of target pollutants. The approximations used in this model are not necessarily the best or only approximations adequate for our application. A model derived from a different set of approximations may be equally valid. The model here represents one possible derivation, the quality of which is assessed in the final section. The focus here is on low detection limits where the sensor surface is far from being saturated with the target pollutant. The strong dependence of the sensor signal on sensor surface temperature (thus also ambient temperature) suggests the need for good fidelity between the final equation's temperature term and the governing equations driving the temperature affect.

To begin, it is assumed that the metal oxide semiconductor material is fabricated as a compact layer impermeable to gas-phase species. The metal-oxide crystals thus have tight grain boundaries with uniform imperfections over the volume of the sensing region. This supports the assertion that gas-phase reactions occur only with the exposed sensor surface and bulk charge transport (current in the sensor) traverses parallel to the sensor surface, whereas charge depletion due to surface reactions occurs normal to the semiconductor surface. This would not hold if the semiconductor were permeable to reactive gas species.

The conductivity of the semiconductor will depend on the depletion layer depth and the decrease in free charge density. Following Barsan and Weimar's derivation, the charge removed from the