Principles of Gas Sensing Application of Metal Oxide Semiconductor Devices

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Abstract: This Paper gives the briefly idea about the basic type of chemical gas sensor and the gas sensing principles. It describes regarding surface chemistry of Diffusion of reactants to the active region, Adsorption of reactants onto the active region, Surface reaction, Desorption of products from the active region, Diffusion of products away from the active region and the application of this surface chemistry over the gas sensing principles of Metal Oxide Semiconductor Devices.

Keywords: Chemical gas Sensors, Adsorption, Desorption, Metal Oxide Semiconductor

Introduction

Chemical gas sensors:

Sensors are important components in quality control as well as for online control of different processes in industry. Physical sensors, measuring parameters like temperature, pressure, and flow, have been used very long. For some parameters, like gas molecules in odours, chemical sensors are needed. A chemical gas sensor can be described as a device, which upon exposure to a gaseous chemical compound or a mixture of chemical compounds, alters one or more of its physical properties (e.g. mass, electrical conductivity, or capacitance) in a way that can be measured and quantified directly or indirectly. Single gas sensors can, for examples, be used as fire detectors, leakage detectors, controllers of ventilation in cars and planes, alarm devices warning the overcoming of threshold concentration values of hazardous gases in the work places. The detection of volatile organic compounds (VOCs) or smells generated from food or household products has also become increasingly important in food industry and in indoor air quality, and multisensor systems (often referred to as electronic noses) are the modern gas sensing devices designed to analyze such complex environmental mixtures. gas sensors, based on a variety of principles and materials, are the best candidates to the development of commercial sensors for a wide range of applications. The great interest of industrial and scientific world on gas sensors comes from their numerous advantages, like small sizes, high sensitivities in detecting very low concentrations (at level of ppm or even ppb) of a wide range of gaseous chemical compounds, possibility of on-line operation and, due to possible bench production, low cost. On the contrary, traditional analytical instruments such as mass spectrometer and chromatography are expensive, complex, and large in size. In addition, most analysis requires sample preparation, so that on-line, real-time analysis is difficult. Chemical sensors have been widely used, but they also suffer from limited measurement accuracy and problems of long-time stability. However, recent advances in nanotechnology, i.e. in the cluster of technologies related to the synthesis of materials with new properties by means of the controlled manipulation of their microstructure on a nanometer scale, produce novel classes of nanostructured materials with enhanced gas sensing properties providing in such a way the opportunity to dramatically increase the performances of gas sensors.

Gas Sensing Principles

The characteristics of semiconductor gas sensors is based upon changes in their electrical properties in the presence of a gas. Depending on the material, this change can be due to either bulk effects, surface conductance effects or a combination of both [1, 2]. Most stoichiometrical metal oxide materials are insulators, but by using common deposition techniques, such as sputtering, there is almost always a process-related oxygen surplus (p-type metal oxides). Consequently, oxygen has free valences, which result in a basic electrical conductivity when in a vacuum. The gas dependent conduction behaviour of metal oxide semiconductors relies upon the presence of oxygen in an ambient gas (the use of air for example). If the oxygen concentration in the ambient gas is different from the oxygen equilibrium concentration in the bulk metal oxide, oxygen diffusion takes place and the conductivity of the metal oxide changes. This is termed the "bulk effect". At room temperature in air, oxygen is adsorbed at any surface (including the metal oxide surface). Therefore, oxygen molecules react with electrons from the metal oxide surface and so decreasing the concentration of the free electrons. This leads, in the case of n-type materials, to a reduction in their conductivity.
The amount of adsorbed $O_2$ depends strongly on the oxygen partial pressure.

If there is a reducing or oxidizing gas present in the ambient gas, which is able to react with the adsorbed oxygen, the surface concentration of the adsorbed oxygen will be altered. Normally energy must be applied externally to overcome internal activation energies. Common operation temperatures of SMO gas sensors are therefore in the range of 50 °C to 900 °C. The reaction will take place only at the surface of the heated sensor part. In order to understand this surface reaction it is necessary to consider some surface chemistry concepts. The gas dependent change in the electrical conductivity of SMO materials is controlled through the following processes:

- altering the concentration of the sensing gas leads to a change in the oxygen surface coverage ("surface chemistry")
- the oxygen surface concentration affects the charge carrier distribution in the material ("charge transfer model")
- the electrical conductivity depends directly on the concentration of free charge carrier ("electrical conductivity of metal oxide semiconductors")

**Surface Chemistry**

The gas sensing principle of SMO gas sensors depends on the adsorption/desorption behavior between gas molecules and surfaces. In case of semiconductor gas sensors, the whole gas reaction process can be simply split into five consecutive steps:

1. Diffusion of reactants to the active region
2. Adsorption of reactants onto the active region
3. Surface reaction
4. Desorption of products from the active region
5. Diffusion of products away from the active region

The surface concentration ($C_{surf}$) of molecules is defined as

$$C_{surf} = \frac{\text{molecules}}{\text{area}}$$  \hspace{1cm} (1)

In order to describe adsorption/desorption processes it is conventional to consider the surface coverage ($\theta$), which depends upon the surface concentration and the saturation surface concentration ($C_{sat}$). It is defined as

$$\theta = \frac{C_{surf}}{C_{sat}}$$  \hspace{1cm} (2)

The surface coverage of an adsorbed gas depends on the pressure of the gas above the surface at a fixed temperature and can be described, in the simplest case, by the Langmuir isotherm. Adsorption, desorption and the Langmuir isotherm are hereby described:

**Adsorption**

The state of adhesion between a species (adsorbate) and a surface (adsorbent) is termed "adsorption". There are two kinds of adsorption - namely physisorption and chemisorption. In the case of physisorption the species are bonded only by weak physical forces (van der Waals-type forces) to the surface. Chemisorption bondings have a rearrangement of the electron density between the adsorbed gas and the surface. The rate of adsorption of a molecule is mainly affected by the rate at which molecules arrive at the surface and the fraction of which are adsorbed at the surface. It is therefore possible to describe the rate of adsorption ($R_{ads}$) by the product of the molecular flux ($F$) and the probability of adhesion ($S$).

$$R_{ads} = S \cdot F$$  \hspace{1cm} (3)

The flux is defined by the Hertz-Knudsen equation:

$$F = \frac{P}{\sqrt{2\pi m RT}}$$  \hspace{1cm} (4)

Where $P$ is the gas pressure, $m$ is the mass of one molecule, $k$ is the Boltzmann constant and $T$ is the temperature. The probability of adhesion ($S$) is defined by an Arhenius law:

$$S = f(\theta) \cdot e^{-\frac{E_{ads}}{RT}}$$  \hspace{1cm} (5)

Where $f(\theta)$ is a function of the surface coverage, $E_{ads}$ is the activation energy for adsorption (which may depend upon the surface coverage), $R$ is the universal gas constant and $T$ is the temperature. Thus, the rate of adsorption ($R_{ads}$) with respect to the change of the surface coverage by adsorption of a molecule on a surface can be expressed with

$$R_{ads} = f(\theta) \cdot \frac{P}{\sqrt{2\pi m RT}} \cdot e^{-\frac{E_{ads}}{RT}}$$  \hspace{1cm} (6)

**Desorption**

The disengagement of an atom or molecule from a surface is termed "desorption". At low temperatures a molecule adsorbed on a surface could remain for an indefinite time. However, as the surface temperature increases the molecule will receive energy, and so one of the following processes can occur:

- the molecules can react with the surface
- the molecules can break down to two or more other molecules (either in gaseous or solid state)
the molecules can desorb

The last option is the desorption process, which could also occur in the second option if one of the products is a gas. The rate constant of the desorption process with respect to the change of the surface coverage by desorption is given by the Arrhenius formula:

\[ R_{\text{des}} = v \cdot f(\theta) \cdot \exp \left( -\frac{E_{\text{des}}}{RT} \right) \] (7)

Where \( E_{\text{des}} \) is the activation energy for desorption and \( v \) is a pre-factor that can be considered as the frequency of the molecule-surface bonding (in effect, a function that depends on the surface coverage).

**Langmuir Isotherm**

Whenever a gas comes in contact to a surface there is an effort to reach an equilibrium state between the molecules in the gas phase and the molecules adsorbed onto the surface. The position of the equilibrium depends on different factors such as the stability of the adsorption process, temperature of both the substrate and gas, and the partial pressure of that gas. The Langmuir isotherm describes the surface coverage (\( \theta \)) of an adsorbed gas and is dependent upon the pressure (\( P \)) at a fixed temperature. It results from the adsorption and desorption rates defined in equation 6 and 7 and is given by

\[ \theta = \frac{E}{1 + EP} \] (8)

Where \( E \) is a function of \( R_{\text{ads}} / R_{\text{des}} \).

The Langmuir isotherm makes use of three assumptions [2, 3]:

- adsorption cannot proceed beyond the point at which the adsorbates are one layer thick on the surface (monolayer)
- all adsorption sites are equivalent
- the adsorption and desorption rate is independent of the population of neighboring sites.

Figure 1 shows the characteristics of several Langmuir isotherms for different values of \( h(T) \). A surface with high desorption relative to the adsorption rate has a small surface coverage (\( h(T) \) is small). With an increase in desorption rate (and thus \( h(T) \)) the surface coverage will rise.

When considering an adsorption process of two gases (gas A and gas B) on a surface it is necessary to modify equation 2.8 to

\[ \theta_A = \frac{E_{A}F_A}{1 + E_{A}F_A + E_{B}F_B} \quad \text{and} \quad \theta_B = \frac{E_{B}F_B}{1 + E_{A}F_A + E_{B}F_B} \]

These equations allow to express the surface coverage of two gases, which react with each other on the surface [4, 5, 6] in the following way:

\[ A_{g} + B_{g} \rightarrow AB_{g} \rightarrow AB \] (9)

This model suitably describes the surface coverage of oxygen in terms of oxygen partial pressure and the concentration of gaseous co-reactants. Examples of such reactions are:

\[ CO + O^- \rightarrow CO_2 + e^- \quad \text{and} \quad NO + O^- \rightarrow NO_2 + e^- \]

**Charge Transfer Model**

The Charge Transfer Model (CTM) describes the interaction at the gas/metal oxide interface. It describes the interaction at the gas/metal oxide interface.

Figure 1: Characteristics of several Langmuir isotherms for different \( h(T) \).

The chemisorption of gas molecules in terms of "ionsorption", where molecules are free to accept or donate electrons from the bulk material. This is equivalent to a generation of surface states with an underlying space charge region. Whether these surface states can act as surface acceptors or surface donors depends on the nature of both the adsorbed gas (whether reducing or oxidizing) as well as the type of semiconductor (whether n-type or p-type). Thus, the gas adsorption leads to a band deflection near the surface [9]. In order to understand the CTM it is necessary to know the band model, the Fermi distribution and the influence of doping, an example of which is described in [10]. A common classification of layers considers whether the injected type of the charge carrier is of the same type as the major charge carrier (termed "accumulation layer")
or visa versa (termed "depletion layer") [11]. For example:

- donors on the surface of an n-type material, which inject electrons into the conduction band, or acceptors on the surface of a p-type material, which inject holes into the valence band, form an accumulation layer
- acceptors on the surface of an n-type material, which extract electrons from the valence band, or donors on the surface of a p-type material, which inject electrons into the conduction band, can form a depletion layer

Figure 2 shows the influence of an adsorbed electron acceptor (e.g. O$_2$) on an n-type and a p-type semiconductor. Owing to such charge transfer, a positive space charge region in the surface region is generated [7, 8].

![Figure 2](image)

Figure 2: The figure shows the space charge at the surface of an n-type semiconductor (left) and of a p-type semiconductor (right) due to the adsorption of an electron acceptor. a) Distribution of the charge carrier. b) Band deflection at the semiconductor surface. c) Charge carrier concentration in the conductor resp.

**Calculation of the Charge Carrier Concentration**

In order to obtain information about the electrical conduction it is necessary to know the concentration of free carriers in the space charge region. In non-degenerated semiconductors the electron concentration ($n$) and the hole concentration ($p$) can be assumed by the Maxwell-Boltzmann statistic:

$$n = N_C \cdot e^{-\frac{E_C - E_F}{kT}}$$  and  $$p = N_V \cdot e^{-\frac{E_V - E_F}{kT}}$$

where $E_C$ is the lowest energy of the conduction band, $E_V$ is the highest energy of the valence band, $N_C$ is the effective density of states in the conduction band, $N_V$ is the effective density of states in the valence band, $k$ is the Boltzmann constant and $T$ is the temperature [12].

In order to obtain the carrier concentration in a space charge region it is necessary to calculate the bending of $E_C$ and $E_V$, respectively. Therefore the Poisson equation 10 has to be solved:

$$\nabla \cdot (\varepsilon \frac{\partial \varphi}{\partial z} \varepsilon) = -q \cdot (N_D - N_A + p - n)$$  \hspace{1cm} (10)

Here $\varepsilon$ denotes the material permittivity, $\varphi$ the electrostatic potential, $q$ the elementary charge and $N_D$ and $N_A$ the fully ionized impurity distribution [13].

![Figure 3](image)

Figure 3: Schematic band deflection under the influence of a surface potential $V_S$.

Here a one dimensional model for a metal oxide gas sensor is considered [11]. Figure 3 schematically shows the dependence of the conduction and valence bands on the surface potential using the relationship $q_0 = E_F - E_F(z)$ and $V(z) = \varphi(z) - \varphi_0$. In order to present this derivation in a clear way the non dimensional potentials $u$ and $v$

$$u \equiv q_0 \cdot \varphi/kT \hspace{1cm} v \equiv q \cdot V/kT$$

are introduced. In doing so $u_b$, $v_b$ are the values for the surface and $u_b$, $v_b$ are the values for the bulk material. Now the carrier concentration $n(z)$ and $p(z)$ have to be transformed into a function relating to the difference between the Fermi level ($E_F$) and the
intrinsic level \((E_I)\) in the bulk material using \(n_i^2 = n \cdot p\) (invoking the law of mass action).

\[
\begin{align*}
    m(z) &= n_i \cdot e^{\mu(z)} = n_p \cdot e^{\nu(z)}, \\
    p(z) &= n_i \cdot e^{\mu(z)} = p_p \cdot e^{\nu(z)}
\end{align*}
\]

(12)

Using non-dimensional potentials and the carrier concentrations, defined in equation 12, the one-dimensional Poisson equation yields the equation:

\[
\frac{d^2 \varphi}{dz^2} = -\frac{1}{\varepsilon_0 \varepsilon_r} \left( n_p - p_p + p_p e^{-\varphi} - n_p e^{\varphi} \right)
\]

(13)

Where \(\varepsilon_0\) is the field constant and \(\varepsilon_r\) the relative dielectric constant.

After some conversions and one integration with the boundary conditions the Debye-length is a quantum value for the distribution of the space charge region. It is defined as the distance to the surface at which the deflected band is decreased to the \(1/e\) -th part of the surface value.

\[
L \equiv \frac{e}{\sqrt{2 \pi n_i}}
\]

(14)

Then the charge carrier concentration \(n(z)\) and \(p(z)\) can be calculated using the computed potential \(\varphi(z)\) and the equations defined in 12.

Conclusion

We have described the basic surface chemistry for the charge transfer principles of the metal oxide semiconductor. In future we will describe regarding the electrical conduction of metal oxide semiconductor and poly crystalline metal oxides.

References