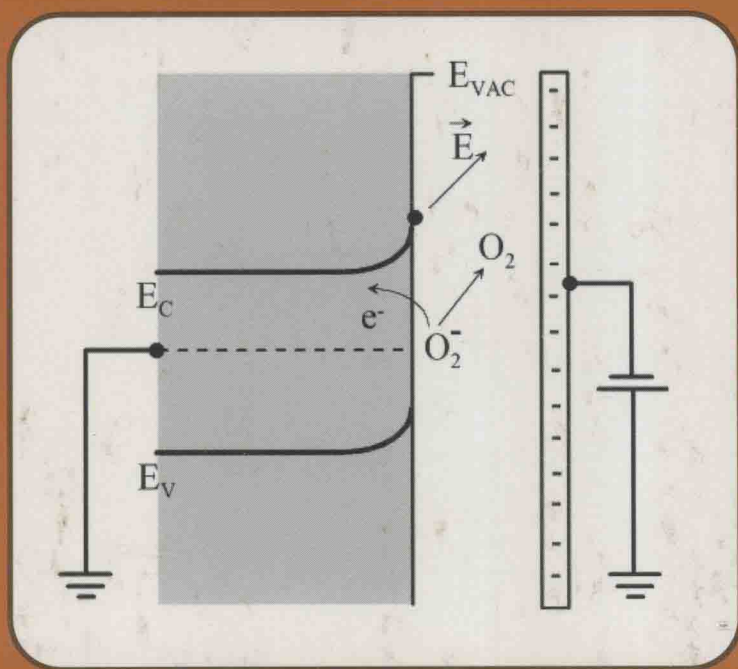


# Advanced Gas Sensing

## The Electroadsorptive Effect and Related Techniques

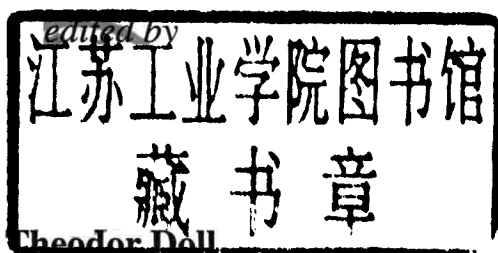
edited by  
Theodor Doll



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**ADVANCED GAS SENSING**  
*The Electroadsorptive Effect and Related  
Techniques*



*California Institute of Technology*  
*U.S.A.*



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**ADVANCED GAS SENSING**  
*The Electroadsorptive Effect and Related  
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## Preface

Chemical sensing searches for specific atoms or compounds that are expected to be present in an environment, that - with the exception of the concentration of this specific component - should always be well defined.

By the use of selectively reacting materials that transform chemical information into an optical, mechanical or electrical one, chemical sensing enables us to have test sticks or even electrical, continuously operating miniaturized sensors. Continuous operation however needs fast, reversible reactions, which seems to be contradictory to other criteria sensor engineering wants to meet. They are namely sensitivity, selectivity and stability (“S<sup>3</sup>”), which especially for sensitivity, refer to the relative strength of chemical binding between detected molecule and sensing material. A simple rule says the stronger the particles are bound, the higher the signal – and the weaker produces the “reversible” return to a sensor baseline. Ways to circumvent this dilemma by using non-steady-state methods are subject of this book.

For the detection of gaseous components semiconductor sensors are widely used, as they directly transform changes of surrounding gas composition into easy-to-measure resistivity changes. In many cases semiconducting Tin oxide serves as a basis, because it is the material most investigated in gas sensing. Some problems remain in the stability of these sensors, and cross sensitivities which are naturally given as the base material have only a general sensitivity to the oxidizing / reducing properties of gases.

What is needed is to enhance a desired selectivity whilst maintaining reversibility and signal height or similar combinations. Ways to achieve this are modifying the metal oxide with additives or using surface catalysts at the sensor level, or, at system level, forming sensor arrays, adding data fusion or varying the working point of the sensor via the temperature.

From a systematic view, these approaches can be regarded as a consequent parametrization of a generalized sensor model and “turning the knobs”. We

change material composition, temperature and use non-steady-state-processes such as temperature modulation. Are there other “knobs” or effects promising for future use?

In this book the authors describe new insights into temperature modulation and the use of light. The emphasis is given to electrical fields in gas sensors, which cause the “Electro Adsorptive Effect”. The effect has long been known by experts working in the field, but has been regarded as too difficult for use until recently because of increasing sensor miniaturization; many groups working in the field “stumbled” onto it.

It was in 1998, when several of those groups met in Munich, Universität der Bundeswehr (Prof. I. Eisele), for a workshop on the electroadsorptive effect, reporting their most recent results and combining the focus on the pure effect with introductory lectures on advanced methods of gas-surface studies as well as the other parametric sensing methods. At that time we decided to work on a book that provides a comprehensive survey of the effects, adds theory where appropriate, shows related surface physics and finally discusses some application aspects.

It took some extra time for completing this book in the midst of a booming period, where improved and more detailed results and better understanding were coming up rather quickly. We gratefully acknowledge the authors’ patience and Kluwer’s enduring interest in publishing this book and thank Mrs. Gisela Müller, TU Ilmenau, for all formatting and graphical work.

In 1999 we lost our mentor and colleague Wolfgang Göpel who tragically died in a car accident. Prof. Dr. Dr. h.c. mult. Wolfgang Göpel was co-organizing the Munich meeting and it was he, who once started out from surface physics with potential measurements of gas adsorption into the field of sensor development. Playing a leading role in the international sensor community, he encouraged more than one generation of young MEMS-, sensors- and sensor signal analysis scientist to always bear in mind the importance of surface physics for our work and that things may be more complicated, even more than we know. May this book, which he wanted to co-edit, provide useful knowledge and, lead to many good new questions to sensor science in honor of him.

Ilmenau, spring 2002

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Chapter 1

INTRODUCTION TO THE  
ELECTROADSORPTIVE EFFECT AND ITS  
APPLICATIONS

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**Abstract:** Strong electrical fields acting on the sensitive layer surfaces of a semiconductor gas sensor can alter its adsorption characteristics for gases and thus its sensing behaviour. Models for the effect are described based on the works of Morrison and of Wolkenstein<sup>1</sup> and simulations for clarifying important parameters are provided. Design aspects of conductivity sensors for proper use of the effect are discussed, also in a comparison to potentiometric FET sensors. Some exemplary experimental results obtained with the latter sensors are shown and possible new operation modes of gas sensing using the electroadsorptive effect are introduced.

## 1. THE VERY BASIC CONCEPT

Recently, the author was asked to give an introduction to gas sensing including the specialty of the electroadsorptive effect in front of non-engineers and non-physicists within five minutes only. It turned out to be the thread of this contribution, using five simple arguments.

The first considers surfaces under normal conditions. There are always gases adsorbed like water vapor as well as oxygen which is the most reactive main constituent of air. Its tendency to “oxidize” physically means that oxygen attracts electrons, for instance from the surface of the solid. It remains then tightly bound as a charged ion at the surface. The bound electron, however is no longer available, i.e. “free” for the solid. This leads us to the second argument.

It leads to building a gas sensor. If we think of a very thin solid layer where an electric current is forced to go through, we can imagine that the layer could be made so thin that adsorbed gases, especially oxidizing species, alter the conductivity of this layer as the number of electrons available for current transport is significantly reduced. This effect has been observed for extremely thin metal layers (e.g. Platinum of 3 nm thickness). For semiconductors, which per se have a low number of charge carriers with respect to surface sites, the layer can be left thicker, which is technically convenient. Therefore gas sensors are typically using semiconductor layers.

The third argument simply remembers the plate capacitor. A voltage applied between the plates creates an electric field inside the capacitor. It is directed towards the surface of the negative plate that carries some electrons in excess whereas the positively charged surface has some electrons lacking. Argument number four combines the previous two. If an ultra thin gas sensing film is put into the electric field of a capacitor, the field might force some electrons to the gas adsorbing side of the film or repel them from there.

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<sup>1</sup> Theodor Wolkenstein, at some places cited as F.F. Volkensthein

It can be easily understood that in the case of excess electrons at the surface adsorption with oxidation might be facilitated, whereas in the reverse situation electrons are rather missing for oxidation. Therefore an electric field may have some influence on the adsorption characteristics of gases at surfaces. This is called the electroadsorptive effect.

Finally, in step number five we learn that the adsorption of many other gases is not a reaction with clean surfaces but is mediated by already adsorbed species, which is oxygen under normal conditions in most cases. For instance, carbon monoxide catches oxygen from the surface forming carbon dioxide. Such processes are called heterogeneous catalysis<sup>1</sup>. For gas sensors, we conclude that the composition of strongly bound adsorbates at a surface rule over the gas reactivity of lots of additional gases. Therefore, if we electrically change the strongly bound states, we change the entire performance of a gas sensor. These five steps are the shortest possible introduction to our topic. It presents the idea without having any scientific depth. That shall be added in the following.

## 2. SEMICONDUCTOR GAS SENSORS

Metal oxides are the best choice for heated semiconductor gas sensors<sup>2</sup>, as they are naturally self-passivated against oxygen. Their wide variety includes nearly metallic ones like ITO, insulators like  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and a wide group of semiconducting materials useful for sensing as  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{NiO}$ . The insulators, having the widest electronic band gaps known, are almost passive against normal gases. Towards the semiconductors, there is a general tendency that gas sensitivity increases with decreasing band gap<sup>3</sup>, or, in the case of transition metals, goes with the reactivity of d-electrons<sup>4</sup>.

The basic concept of semiconductor gas sensing is explained in **Figs. 1a, b**. Let us assume flat band conditions (horizontal conduction and valence band energy levels  $E_C$  and  $E_V$ ) for the semiconductor surface and a gas molecule that is free in front of it. The distance between both  $E_C$  and  $E_V$  and the Fermi level  $E_F$  is a statistical measure for the amount of charge carriers that may serve for electrical conductivity. As the gas adsorbs, it may collect an electron from the semiconductor bulk and localize it at the surface (chemisorption). The adsorbed gas molecule will then be called a surface acceptor. **Fig 1b** depicts the reaction of the semiconductor towards that. The semiconductor valence and conduction bands will locally bend underneath the surface so that the horizontal Fermi level  $E_F$  comes closer to the adsorption energy level  $E_{SS}$  of the surface molecule. It is important to know that these electronic surface states  $E_{SS}$  only exist in the presence of adsorbed

gas molecules. Their levels are gas specific, always fixed with respect to  $E_C$  and  $E_V$ , and the probability of charge transfer into  $E_{SS}$  is governed by  $E_F$  just like the other levels. Furthermore we note that upward band bending moves the energy levels of the semiconductor bulk downward with respect to the vacuum reference level by  $e\Delta V_s$  and vice versa.

Band bending, however, changes the electron concentration and thus alters the semiconductor conductivity where it occurs. In the mostly observed case of depletion, this semiconductor zone is called a space charge region (SCR). At this point we have to introduce the polycrystalline structure of metal oxides. The layer consists of three-dimensional subunits, the grains, with individual gas/solid interfaces and space-charge regions, as sketched in the inserts. Given their typical size of some ten nm to few hundred nm the SCR will surround the whole grain.

The next **Figs. 1c and d** are using this model of depleted grains to explain the two common ways of realizing metal oxide gas sensors: For conductivity (**1c**) a thin, closed layer of these grains is deposited between two electrodes for simple conductivity measurement. The current may split between surface and bulk paths, but there is a must for it to go through two adjacent surface regions during the transition from one grain to the next one<sup>5</sup> (grain boundaries). Therefore we have at least one region where the whole sensor conductivity is governed by chemisorption-induced space charge modulations and a simple electrical gas sensor is obtained.

If we want to avoid the sometimes critical influence of the grain boundaries, we could try a pure potential measurement perpendicular above a metal oxide layer. Only some backside contacting is required for that. Capacitive methods have been developed for these potential measurements like the Kelvin probe, which is for laboratory use. Miniaturized sensors can be fabricated using the principle of Airgap - Field Effect Transistors (FET) as depicted in **Fig. 1d**. Analogous to the MOSFET, which is completely potential-controlled via its gate, the metal oxide layer with its backside contact is brought close to the channel region of a MOSFET whose gate has been omitted (similar to ISFET<sup>6</sup>). In this case the metal oxide layer serves as the gate and controls the FET channel conductance. The electric potentials are transmitted towards the FET via the vacuum level  $E_{VAC}$  whilst the surrounding gas will be able to mechanically reach the metal oxide through the airgap. Such gas sensitive FETs are almost insensitive to grain boundary effects. There is ongoing development on these devices<sup>7</sup>, but they are clearly more difficult to fabricate in comparison to conductivity sensors.

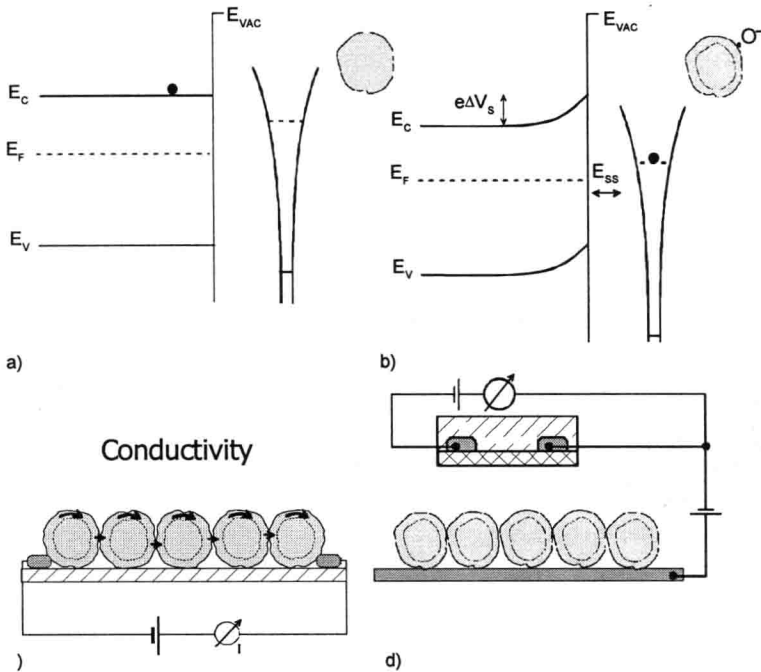


Figure 1. Semiconductor Gas Sensing a) Simple Semiconductor Surface Model with Surface State b) Adsorption Induced Band Bending (Insert: Grains) c) Conductivity Gas Sensor with Idealized Metal Oxide Grains d) Surface Potential Measurement with a Transistor Device Facing Down to the Same Metal Oxide. The Real Dimension in c) and d) are for the Grains 100 nm, for the Devices few mm, and the Airgap Height in d) is few  $\mu m$ .

### 3. PRINCIPLES OF THE ELECTROADSORPTIVE EFFECT

One of the major problems in chemical sensing is related to the reversibility of chemical reactions. Reversibility means that, in terms of gas sensors, an adsorbed layer should leave the surface rather fast after the end of a gas exposure bringing the sensor signal back to its base line. This is influenced by transport processes (charge carriers and gas diffusion), but mainly depending on reaction enthalpies (binding energies) not exceeding several  $kT$  which is the thermal energy of the bound gas molecule. On the other hand, for significantly high responses of the sensor a large amount of adsorbed species is desired under gas exposure, which requires higher

binding energies. Additional problems arise from very strong binding sites that are present on real surfaces causing stable, preadsorbed or memory layers as will be discussed in a following paragraph.

Up to now, changing the sensor operating temperature has been the common way to tradeoff with these problems. Temperature modulation techniques have been developed for this despite higher power consumption for such devices and decreasing sensor baseline stability caused by possible morphological changes in the layer. However, from a solid state physics view, changing the temperature is equivalent to changing the statistic equilibriums of transport and adsorption processes as mentioned above.

There is little difference towards chemistry except adding Fermi statistics to Boltzman where necessary: The Fermi level governs the surface states, which themselves lead to sensor signals according to alterations of the relative position of these states towards the Fermi level. Conversely, if one artificially changed these relative positions this would result in a change of the probability that adsorption at a sensor surface can occur. This means that sensing itself gets under control.

The most powerful tool to do this is using the electrical field effect in semiconductor surfaces, being just the physical basis of most modern electronics including the silicon part of the gas sensitive MOSFET mentioned above.

An electrical field perpendicular to a semiconductor surface induces some alteration of the band bending and will move the whole scheme of surface bands and surface states in their relative positions to the Fermi level, and thus changes the adsorption statistics of the surface. As given as an example in **Fig. 2a**, oxygen molecules in chemisorbed  $O_2^-$  surface sites will become energetically unfavoured by upward band bending in an external field. They will loose their electron and might desorb as free oxygen into the gas phase. Other oxygen molecules approaching the surface will not be adsorbed so much under this field. In terms of gas sensors, the electric field provides a pure electrical modulation of the gas sensitivity of the surface. This is the basic idea of the electroadsorptive effect as firstly described by Wolkenstein<sup>8</sup>. If a distribution of several surface sites for different gases would be assumed, the effect could be used to modulate the adsorption balance for gas mixtures and ultimately lead to an electrical surface spectroscopy.

In **Fig. 2b** an electrode arrangement has been added to the conductivity sensor of **Fig. 1c**. It allows for perpendicular high electric fields above the most sensitive gas / semiconducting layer interface and will lead to a general thin film transistor control of the sensor. Thus one has to expect a strong variation of the sensor baseline with its "gate" electrode voltage and

potentially superimposed changed gas sensitivities according to band bending and surface state distribution.

The following sections are providing a theoretical approach to estimate the fields required for making use of the electroadsorptive effect. They lead to the result that microstructures are a basic prerequisite for its practical application.

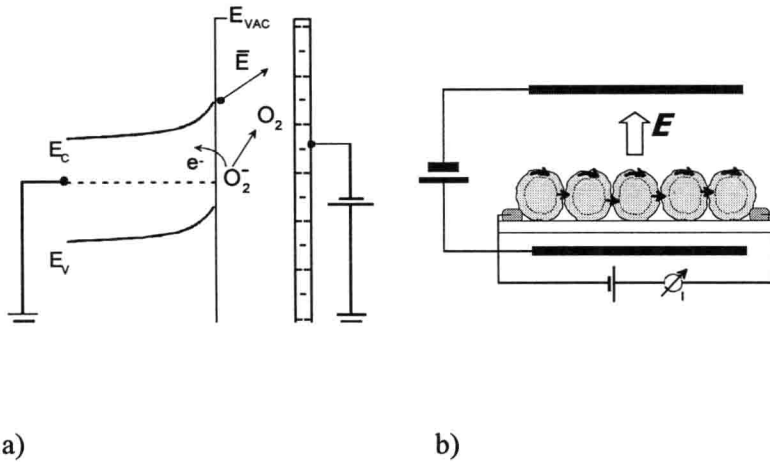


Figure 2. Introduction to the Electroadsorptive Effect a) Basic Idea of an Electric Field (Charged Capacitor Plate) Acting on a Surface with Adsorbed, Negatively Charged Species b) Virtual Arrangement of a Freely Suspended Electrode.

#### 4. THEORETICAL APPROACH AND MODELING

If a gas molecule is free in front of a surface, its energetic reference is given by the vacuum level  $E_{VAC}$  that is commonly used as a reference. Both systems, i.e., molecule and solid, are described by an electron affinity  $\chi$  which is the difference between the vacuum level and the lowest unoccupied energy level (LUMO). The difference between  $E_{VAC}$  and the highest occupied level of the molecule (HOMO) is called the electrochemical potential  $\tilde{\mu}$  for many molecules and this corresponds to the bulk work function  $\phi$  of the semiconductor, i.e., the difference of the Fermi level  $E_F$  towards  $E_{VAC}$ .

If molecules bind at the surface, both levels  $\tilde{\mu}$  and  $E_F$  will adjust and, in the simplest case, their energy difference is yield in the heat of adsorption  $Q$ . Due to that adsorption the energy of the whole system is changed towards an altered work function  $\phi + \Delta\phi$  with contributions from an altered band

bending  $V_s'$  and a change in the mean electron affinity<sup>2</sup> of that covered surface by  $\Delta\chi$ :

$$\phi' = \chi' + eV_s' + (E_c - E_F) \quad \text{or} \quad \Delta\phi = \Delta\chi + e\Delta V_s \quad (1)$$

An altered band bending means that the charge density at the surface has been changed and that a surface charge  $Q_{ss}$  has been built up. In a quantum mechanical view this must be a number of electrons that moved into surface states  $E_{ss}$ .  $Q_{ss}$  is formally described as an integral

$$Q_{ss} = e \int_{-\infty}^{+\infty} D_{ss}(E) f_{ss}(E) dE \quad (2)$$

over the density of surface states  $D_{ss}$  and their distribution function  $f_{ss}$ . As the bulk of the semiconductor must be free of an electric field, the surface charge  $Q_{ss}$  is compensated by a space charge  $Q_{sc}$  per unit area

$$Q_{ss} + Q_{sc} = 0 \quad (3)$$

which, for a uniform adsorbate coverage and using the approximate Schottky solution of the one dimensional Poisson equation

$\rho(z) = -\epsilon_{se}\epsilon_0(d^2V/dz^2)$ , causes the band bending by  $\Delta V_s = V_{Surface(z=0)} - V_{Bulk}$

$$\Delta V_s = \frac{Q_{ss}^2}{2 \cdot e \cdot \epsilon_0 \epsilon_{se} \cdot n_{se}} \quad (4)$$

with  $\epsilon_{se}$  and  $n_{se}$  being the dielectric constant and the charge carrier density of the semiconductor.

It has already been noted that under band bending the surface density of states  $D_{ss}(E)$  remains tied towards the surface semiconductor energy levels. Then the distribution function as a function of the Fermi level must be transformed according to band bending<sup>3</sup>:

$$f_{ss}(E, E_F) \rightarrow f_{ss}(E, E_{F,bulk} + e\Delta V_s(\Theta)) \quad (5)$$

<sup>2</sup> Electron affinity is defined via a surface and its adsorbates. Thus it is a microscopic local measure.

<sup>3</sup> For clarity it may be noticed that in the bulk region  $\Delta V_s$  affects both  $D(E)$  and  $f(E)$  and thus referencing to  $E_{vac}$  is of no influence.

Thus any increasing fraction of the maximum number of available surface sites (increasing coverage  $\Theta$ ) that involves a charge localization towards the adsorbed molecules, hinders itself. This is known in particular as the Weisz<sup>9</sup> limit. It describes the limitation of charging adsorbed oxygen at a metal oxide surface. A typical value for a reasonable density  $N_s$  per unit area is  $10^{11}$  or  $10^{12} \text{ cm}^{-2}$  what corresponds to a coverage  $\Theta$  of a few  $10^{-4}$ .

If we now apply a perpendicular electrical field  $E_{el}$  to the surface, Eq. 3 can be written to

$$Q'_{ss} + Q'_{sc} = Q_{s,el} = \varepsilon_{air} \cdot E_{el} \quad (6).$$

For a metal oxide with dominating charged surface acceptors, an applied negative electric field will alter the surface band bending upwards. Electrons from surface states will be repelled,  $Q_{ss}$  will be reduced, and  $Q_{sc}$  will increase to an amount so that the sum  $Q_{s,el}$  will form a positive charge that balances the electric field. It is reasonable to assume charged oxygen as the dominant surface constituent for many gas sensing materials that are operated in ambient air. Their Fermi levels will be expected to be already readjusted close to the oxygen levels, where “close” means a few kT where the Fermi distribution changes from 1 to 0 almost entirely. The electric fields necessary to shift  $f_{ss}(E)$  by one  $kT \approx 26 \text{ meV}$  are normally only available in FET devices.

A simple calculation with  $D_{ss}(E) = 0$  yields

$$\Delta V_s = \varepsilon_{air}^2 \cdot E_{el}^2 / (2 \cdot e \cdot \varepsilon_{se} \cdot n_{se}) \quad (7)$$

which, for  $n_{se}$  ranging from  $10^{16} \text{ cm}^{-3}$  to  $10^{18} \text{ cm}^{-3}$  and  $\varepsilon_{se} \approx 10 \cdot \varepsilon_0$  results in a necessary field strength of  $5 \cdot 10^5 \text{ Vcm}^{-1}$ , which comes close to dielectric breakthrough of air and requires for a dedicated design even in micro sensors.

For nonzero  $D_{ss}(E)$  there are two cases. If a monoenergetic surface level is assumed, an external electrical field will only change the amount of charged adsorbed species but does not alter the band bending (pinning). In this case the sensing effects of excess adsorption or desorption due to the field can only be found in  $\chi'$ . In the other case there is a band of surface energies and the change in signals may reflect  $e\Delta V_s$  as well as  $\chi'$ .

Due to the possible change in  $V_s$  the electroadsorptive effect must be calculated selfconsistently by combining Eqs. 2, 4, 5 and 6. The quality of simulation results will strongly depend on the assumptions made on  $D_{ss}(E)$ . Moreover, it may be necessary to treat  $n_{se}$  in Eq. 4 as depending on the



depth within the space charge region because of a variation of oxygen vacancy concentrations underneath the surface due to instantaneous or field effect induced  $V_S(z)$ <sup>10</sup>. The general electroadsorptive effect is given by

$$\varepsilon_{gas} \cdot E_{el} = \int_{SCR}^{z=0} e \cdot n_{SE}(z) dz + e \int_{-\infty}^{+\infty} D_{SS}(E, \Theta) \cdot f_{SS}[E, E_F + e\Delta V_S(E_{el}, \Theta)] dE \quad (8).$$

The density of states is changed under the presence of gas, and furthermore its occupation is controlled by the electrical field. Its functional shape is depending on the surface properties as will be shown the next section.

For the distribution function  $f_{SS}$  two approaches are known. Both refer to the Lennard-Jones model of adsorption with its increasing binding energy the closer the particles comes to the surface and a possible energetic separation of those binding states via activation energies  $E_a$ . All models think of the weaker bound particles as forming the reservoir for the stronger bound, “part of the adsorbed layer”. S.R. Morrison’s classical ‘Charge Transfer Model’ explains the weaker bound part with physisorption and the stronger with chemisorption. The latter includes the formation of a charged, localized surface adsorbate complex<sup>11</sup>. The specific heat of physisorption  $\Delta H_{phys}$  is seen almost smaller than 100 meV whilst chemisorption should involve energies of  $\Delta H_{phys} \geq 500$  meV. The model describes the mechanisms of band bending with surface charge and surface state shifts completely and may be used for the calculation of the electroadsorptive effect for conductivity sensors. For oxygen and assuming for simplicity only one of the two ionosorbed forms ( $O_2^-$ ), the total surface charge density  $N_S$  is, idealized, equal to the surface concentration  $[O_2^-]$

$$N_S = [O_2^-], \quad (9)$$

which in turn depends on the oxygen surface concentration  $[O_2]$  by

$$\frac{[O_2^-]}{[O_2]} = e^{-(E_{O_2} - E_F)/kT} \quad (10).$$

This Nernstian equation uses a mean surface energy level  $E_{O_2}$  for the chemisorbed oxygen similar to a standard potential, assuming that the Franck Condon split of occupied from unoccupied energy levels can be taken into account by an intermediate value<sup>12</sup>. For a simple Henry-type