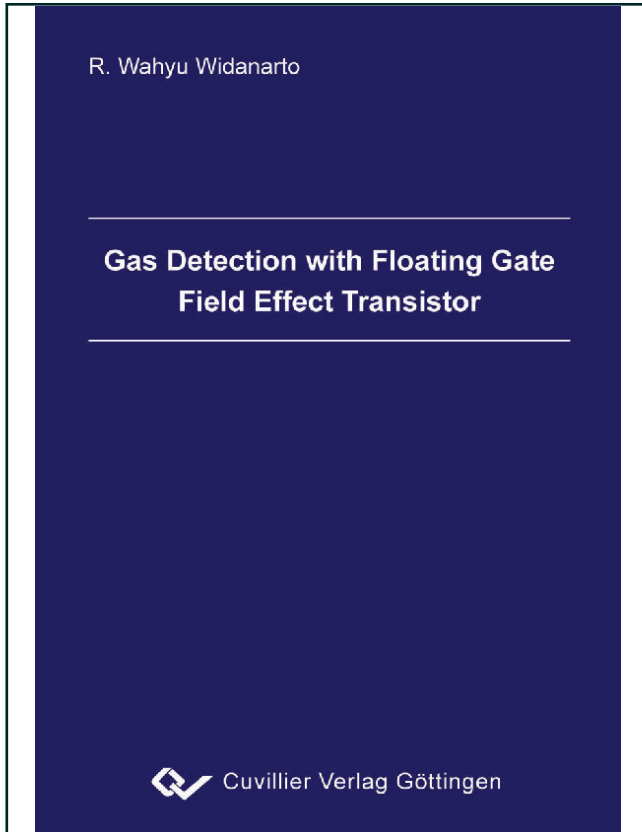




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Gas Detection with Floating Gate Field Effect Transistor



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Introduction

A gas sensor is a device, which allows for the determination of information about the ambient gas atmosphere. It consists of a gas sensitive film and a signal transfer component, which is called transducer. The transducer converts physical and chemical change of the sensitive film into an electrical signal. The sensor's ability to detect certain gas can be optimized by an appropriate choice of gas sensing material and by suitable technology.

Over the past 20 years, a great deal of research effort has been directed towards the development of small dimensional gas sensing devices for practical applications in detection of polluting and inflammable gases as well as manufacturing process monitoring. Detection of polluting and inflammable gases is becoming increasingly important for environmental and human protection.

- Nitrogen dioxide (NO_2) is one of the indicators of poor air quality and can cause photochemical smog and corrosion.
- Hydrogen sulfide (H_2S) is a toxic gas and very dangerous for people, who live in surroundings of volcanoes. H_2S appears in blast furnaces, petroleum-refineries, in gasworks, and also in the viscose-industry, cell-wool-, cell-glass-, and rayon-manufacturing. Already small concentrations of approximately 200 ppm H_2S can cause irritation of the mucous membranes (eyes, breath-ways), nausea, sickness, headaches, diarrhea, breathing difficulty, unconsciousness and cramps.
- Hydrogen (H_2) is predicted to be an alternative energy carrier in the future. It will be used in automotive industry and in local fuel cells. This

energy can decrease the problem related to the green house warming by CO₂. On the other hand, hydrogen is dangerous due to its explosive character. Already a concentration of 4% can cause an explosion. Hydrogen is also a produced gas in the very early stage of fire. It has been shown that hydrogen sensors can detect a fire earlier than the smoke detectors used up to now [1].

Metal oxides like SnO₂, ZnO and TiO₂, which are used as gas sensitive films in sensor systems, are playing an important role in the gas detection. The systems are mostly based on conductivity change measurement of the metal oxides due to reaction between surface of the metal oxides and the ambient gas atmosphere [2-6]. One disadvantage of the systems is that they need high temperature above 200°C to obtain interaction between the material and gas molecule. Since it is necessary to actively heat the sensor for proper operation, it is difficult to use it in mobile systems due to the limited energy supply. Therefore the high operating temperature of the systems is a serious problem to be considered. Intense efforts are being made to reduce it. A well known strategy is to modify the gas sensitive films by doping with metallic catalyst e.g. platinum (Pt), palladium (Pd) and various nano-dimensional architectures [7-10]. However, the temperature can not be decreased yet. Moreover, application of noble metals as gas sensitive films or doping in the systems creates a new problem with selectivity.

Accordingly, it has become very important to develop new gas sensors and sensing materials, which offer high sensitivity, selectivity, stability and reproducibility to certain gas as well as low cost of ownership and power consumption. The sensors should also allow for continuous monitoring of the gas concentration in their environment of application.

For this propose new transducer principles are necessary. One possible approach is to measure surface effects instead of bulk effects. A well known surface effect is work function change due to interactions between the surface and ambient gases. Work function measurements can be carried out with Kelvin Probe (BESOCKE DELTA PHI¹), which however needs a mechanically vibrating electrode or Field Effect Transistor (FET).

¹ BESOCKE DELTA PHI GmbH, Tuchbleiche 8, D-52428 Jülich

The first Gas-FET has been introduced by I. Lundström in 1978 for hydrogen detection in ppm range [11]. A heated Pd gate was used as sensing element. Hydrogen modifies the work function of Pd and modulates in this way the channel conductance. Afterwards the Gas-FET was developed towards more versatile hybrid structures with an air gap from the FET channel. In 1996 the Hybrid Suspended Gate FET (HSGFET) and the Capacitive Controlled Gas FET (CC-FET) have been developed by J.S. Chung [12] and Z. Gergintschew et al [13] respectively in order to improve ability of the Gas-FET principle.

In this thesis, metal and metal oxides are used as gas sensitive films in the Floating Gate Field Effect Transistor (FG-FET) sensor system. The system has been developed from the HSGFET and CC-FET principle. It uses a Field Effect Transistor (FET) as transducer to measure work function change $\Delta\Phi$ of the gas sensitive films and convert it into an electrical signal. The advantages of the system are its sensitivities to work function changes due to physisorption, chemisorption and chemical reaction as well as ionosorption, which are occurring at gas sensitive films [14-18]. The gas sensitive films and the transducer can be separately developed. Additionally this system solves the problem of high power consumption [19].

The goal of the thesis is to develop and characterize new gas sensing materials and optimize sensing materials. This work concentrates on new sensing materials for hydrogen sulfide (H_2S), nitrogen dioxide (NO_2) and hydrogen (H_2) detection. For this propose, silver oxide (Ag_2O), zinc oxide (ZnO), tin oxide/copper (SnO_2/Cu), platinum/tin oxide (Pt/SnO_2) and titanium silicide/platinum (TiSi_2/Pt) were employed in the FG-FET to detect target gases. Different gas sensitive films were used in order to obtain gas sensors with high sensitivity, selectivity and reproducibility as well as well long-term stability.

Chapter 1

Fundamental theory

In this chapter, the fundamental theory and process of gas sensing based on work function change measurement will be discussed. The effects, which lead to gas sensing mechanism is emphasized on gas and metal oxides interface.

1.1 Work function

The work function is the minimum energy (usually measured in electron volts) which is needed to remove an electron from the Fermi energy level in a metal or semiconductor to a point at infinite distance away outside the surface. The work function is also generally defined as the difference between energy of an electron at Fermi energy level E_F and the local vacuum energy level E_l^{Vac} [20].

The local vacuum energy level E_l^{Vac} is defined as the energy of a resting electron at a certain place, so as if it would not be exposed to the solid potential. It is very important to understand the difference between the local (E_l^{Vac}) and the absolute vacuum potential E^{Vac} . E^{Vac} is defined as the reference energy of a resting electron, which is at infinite distance away outside the surface. In Fig. 1.1 the illustration of energetic conditions for an electron in a semiconductor can be seen.

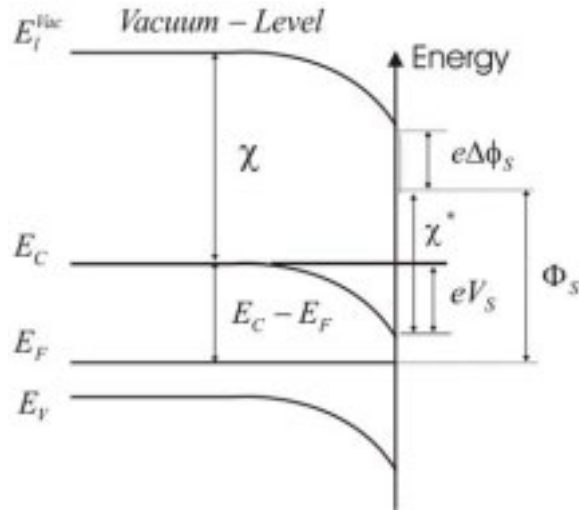


Figure 1.1. Energy band structure of a semiconductor surface.

The electron affinity is defined as energy difference between local vacuum level and conduction band level:

$$\chi = E_i^{vac} - E_C \quad (1.1)$$

The surface dipoles can be present in this case, so that the effective electron affinity χ^* can be differentiated from the bulk affinity. These surface dipoles have atomic size and to become manifest as stage in the local vacuum energy level. Therefore the work function Φ_S can be written as follow

$$\Phi_S = (E_C - E_F)_{bulk} - eV_S + (\chi - e\Delta\phi_S) \quad (1.2)$$

$$= (E_C - E_F)_{bulk} - eV_S + \chi^*$$

with V_S is surface potential or barrier potential.

In metals, the charge carrier density is high enough, so that no space-charge zones can be formed. Therefore, the electron affinity χ and the surface dipole potential $\Delta\phi_S$ determine the work function Φ_S . The Fermi energy level coincides with the conduction energy level E_C .

$$\Phi_S = \chi - e\Delta\phi_S = \chi^* \quad (1.3)$$

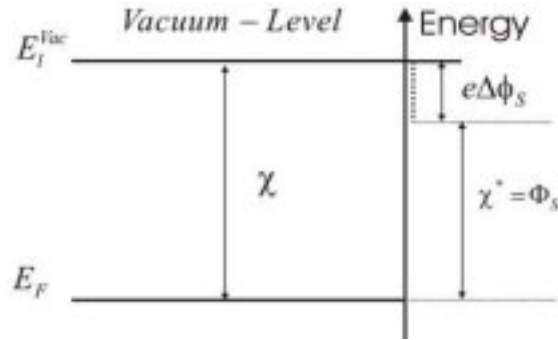


Figure 1.2. Energy band structure of a metal surface.

1.1.1 Adsorption on the surface

There are several ways that the gaseous ambient can change the work function. Some of these are unacceptable for the application of the gas sensors. Physical and chemical adsorption of gas molecules on the surface are famous processes, which can yield the work function change.

Adsorption is the attraction of molecules, atoms or ions of a substance to a solid surface. It is traditionally referred to as either physical or chemical. In discussions of adsorption a distinction has been made between physical adsorption and chemisorption. A set of criteria are often used which hopefully allows a separation to be made. Physical adsorption is considered to be reversible and non-activated while chemisorption is irreversible at one temperature and may also be non-activated and reversible at a high temperature. Furthermore the other difference is energy of bonding at the surface.

The interaction between gases and solid surfaces is a basic process, providing an understanding of the working principle of gas sensors. The adsorption of different gases depends on the surface structure composition and gas molecules. The adsorption can take place in different ways. In the following different types of adsorption are roughly described.

Physical adsorption

Physical adsorption is a weak adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved.

The Lennard-Jones potential-energy diagram, which is shown in Fig. 1.3, has already been used to discuss the adsorption at solid surfaces [21]. Here the energy of the system is plotted against a coordinate related closely to the distance of the adsorbate from the surface. Curve A shows the energy of the adsorbate molecule as a function of the distance. It can be seen that the lowest energy occurs if the molecule has reached a distance d_p from the surface. In this condition the physical adsorption occurred with ΔE_p , whereas curve B confirms the system energy if two atoms are close to the surface. The strong chemisorption occurred at a distance d_c from the surface with ΔE_c whereas ΔE_∞ is the potential energy which is needed to separate the molecule (dissociation of molecule).

ΔE_A is the threshold energy or the activation energy that must be overcome in order to a chemical reaction to occur. Activation energy may otherwise be denoted as the minimum energy necessary for a specific chemical reaction to occur. In generally the activation energy nearly always appears at the adsorption process. Exception is only in van der Waals adsorption.

Chemisorption

Chemisorption (or chemical adsorption) is adsorption in which the forces involved are valence forces of the same kind as those occurring in the formation of chemical compounds. The chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered. In this sense chemisorption may not be reversible and leads to radical changing in the electronic structure of the solid state surface and particles.

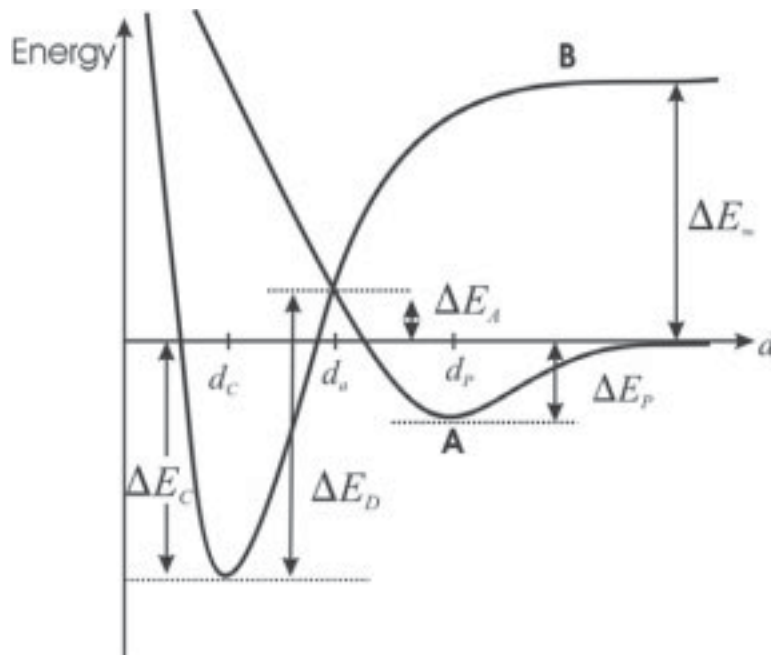


Figure 1.3. Lennard-Jones potential energy of physical adsorption and chemisorption. A). Physical adsorption of molecule. B). Chemisorption of molecule.

The chemisorption may be reversible if the molecule receives again a minimal energy $\Delta E_C + \Delta E_A$, which is called with desorption energy (ΔE_D), as depicted in Fig. 1.3. ΔE_C and ΔE_A are not constant. The both values depend strongly on surface coverage θ (interactions). Mostly ΔE_C decreases and ΔE_A increases with increasing θ [22].

Ionosorption

Ionosorption is a special type of chemisorption. By ionosorption atoms or molecules are ionized through capturing of an electron from the bulk (conduction band) during the adsorption process. Therefore ionosorption can be seen as delocalized chemisorption. As a consequence of the charge transfers between molecules and surface, the chemical reactivity of the molecules, as well as their electronic and geometrical structures, are strongly influenced.

1.1.2 Desorption from the surface

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. However as the temperature of the substrate is increased, there will be reached a point at which the thermal energy of the adsorbed species is high enough that one of several things may occur:

1. A molecular species may decompose to yield either gas phase products or other surface species.
2. An atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid.
3. The species may desorb from the surface and return into the gas phase.

The last of these options is the desorption process. In the absence of decomposition the desorbing species will generally be the same as that originally adsorbed but this is not necessarily always the case.

The rate constant for the desorption process may be expressed in an Arrhenius form [23]

$$k = k_0 \cdot \exp\left(\frac{-E_D}{R \cdot T}\right) \quad (1.4)$$

where k_0 is the frequency factor and E_D is the activation energy for desorption measured in KJ mol^{-1} . The frequency factors are usually calculated on the basis of the theory of absolute reaction rate.

Surface residence times

One property of an adsorbed molecule that is intimately related to the desorption kinetics is the *surface residence time*. This is the average time that a molecule will spend on the surface under given conditions (in particular, for a specified surface temperature) before it desorbs into the gas phase. The surface residence time is expressed by Frenkel equation [24]