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Thick-film gas microsensors based on tin dioxide

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Abstract. Semiconductive — resistive sensors of toxic and explosive gases were fabricated from nanograins of SnO_2 using thick-film technology. Sensitivity, selectivity and stability of sensors working in different temperature depend on the way the tin dioxide and additives were prepared. A construction also plays an important role. The paper presents an attitude towards the evaluation of transport of electrical charges in semiconductive grain layer of SnO_2, when dangerous gases appear in the surrounding atmosphere.

Keywords: thick film, gas sensor, tin dioxide, catalyst, selectivity, sensitivity, conduction mechanism.

1. Introduction

The air is a mixture of gases. Depending on the environment, it may contain various chemical pollutants, e.g. SO_x, NO_x, NH_3, H_2S, CO or volatile organic compounds. Some of these pollutants are either explosive (like methane) or highly toxic (like carbon monoxide). The others cause disturbances in a human or animal body.

Living in the contemporary industrialized world requires the protection against the influence of these hazardous substances, what induces the need for continuous monitoring of the specified compounds. However the precise instrumental analyses are very expensive and time consuming. The achievements in microelectronics provided the development and massive production of low-cost semiconductive sensors, based on gas sensitive materials changing its resistance and/or impedance when hazardous substances appear in the air. First successful semiconductive sensors were made of metal oxides, i.e. ZnO, TiO_2, Fe_2O_3, Al_2O_3, Y_2O_3, SnO_2.

Eventually the tin dioxide became the dominating gas sensitive material. The most significant contribution into the development of this technology was provided by Japanese scientists and engineers including Naayoshi Taguchi [1], who developed a series of ceramic sensors called *Taguchi Gas Sensors (TGS)*. He started his own company — Figaro Gas Sensors, nowadays delivering millions of sensors annually.

Numerous research teams and companies all over the world undertook the challenge of Japan. Basing on technologies offered by microelectronic industry the new solutions were developed. Presently, the European companies have a significant share of market in the production of new SnO_2 sensors. SnO_2 based sensors are the best-understood type among the oxide-based gas sensors. Highly selective and sensitive SnO_2 sensors are not available yet. It is well known however that sensors selectivity can be fine-tuned over a wide range by applying the appropriate SnO_2 crystal structure and morphology, dopants, contact geometries, operation temperature or mode of operation, etc. [2].

The description of mechanisms of detection of various gases on the surface of semiconductive gas sensitive layer requires the application of electron theory of catalysis on semiconductors, originally formulated by F. F. Wolkenstein [3]. While the studies by R.S. Morrison [4], N. Yamazoe et al [5] and W. Göpel [6] especially contributed to the description of conditions of transport of electric charges through non-homogenous structure of SnO_2 layer in the presence of oxygen and reactive gases.

Our research studies were focused on the searches for dopants to SnO_2 and optimisation of the structure of thick film sensors, leading to increased sensitivity to chosen gases, selectivity, and the elimination or limitation of the influence of varying humidity in the surroundings [7–10].

2. Experimental procedure

Technology applied for the described sensors can be classified among standard methods including preparation of powder and inks, or printing and firing of layers.

The tin dioxide powders were prepared with Okazaky method, partially modified by authors research group. Hydrated fine-grained tin dioxide was mixed with e.g. platinum black in a planetary mill. After initial drying in 50°C, the powder mixture was annealed in 600°C for 1 h. Then, the powder was mixed together with organic carrier to provide the desired rheological properties. Sensors were printed on 250 μm alumina substrate (Hoechst) (Fig. 1). On the bottom side of the substrate, platinum heater (Pt–5545 ESL), simultaneously used as a temperature sensor, was placed (Fig. 2a). This heater enables very fast changes of temperature in the range from 20°C to 900°C. On the upper side, interdigital type electrodes were printed with golden ink (Au–8883ESL). Then the gas sensitive layers were screen-printed over the electrodes and fired at 850°C for various periods of time (Fig. 2b).

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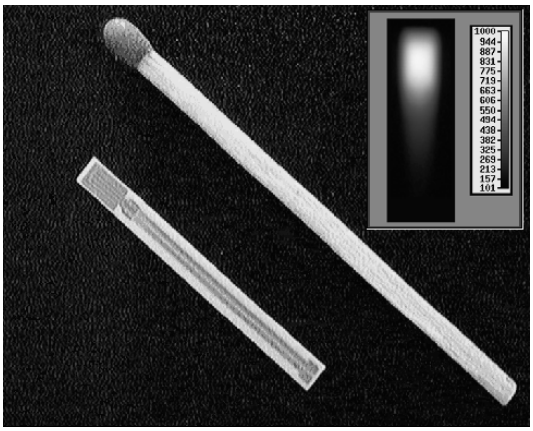


Fig. 1. Thick film gas sensor

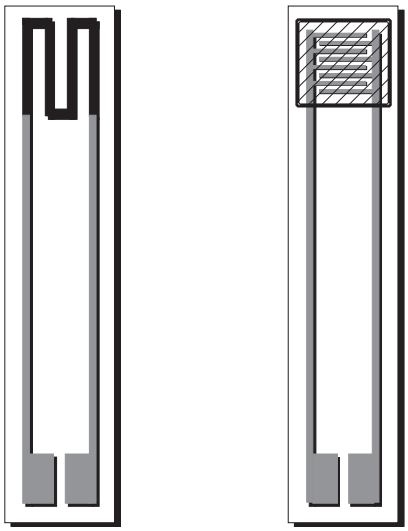


Fig. 2. Thick film gas sensor layout. Platinum heater (a) and gas sensitive layer deposited on interdigital type Au electrodes (b)

After several experiments concerning the selection of electrodes [11] and admixtures to SnO_2, several original compositions were developed. This enabled the fabrication of humidity insensitive thick film methane sensors based on cermet composition (SnO_2–Pt–black) [12], sensors revealing anomalous behaviour, obtained by adding rhodium to SnO_2 [13], sensors with active filter [14], and finally a cermet composition (SnO_2–RuO_2), sensitive to methane and insensitive to the presence of carbon monoxide.

Sensors with new compositions were investigated in various atmospheres, working with varying temperature of gas sensitive layer. In all cases, when new compositions were considered useful, the X-ray measurements of powders and layers were carried out with the use of Philips Materials Research Diffractometer. The average SnO_2 crystallite sizes and their distribution were determined, basing on the full width at half maximum (FWHM) of the peaks and diffractometric profile analysis. The microstructure of layers and distribution of Pt, RuO_2 grains and rhodium clusters in the SnO_2 layer were investigated with the use of ISM5800LV scanning microscope working together with X-ray microprobe Oxford ISIS 300.

The SnO_2 particles have porous structure and consist of crystallites of nanometric dimensions. The average size of crystallites determined with the use of X-ray analysis was about 30 nm. Electrical measurements made with the method of thermostimulated conductance allowed to describe the conductivity and sensitivity of tested gas sensitive thick films. During the conductivity measurements, sensors temperature was changed from 18°C to 700°C with the 2°C/min rate, set to avoid the hysteresis effect.

A.C. measurements were made with the use of Frequency Response Analyser FRA 1260 (Solartron) in frequency range from 0.1 Hz to 2 MHz. Sensors impedance spectra as a function of air composition were measured at different temperatures.

All these research studies enabled the explanation of the physical phenomena appearing in new compositions.

3. Results

Gas sensor characterisation usually requires two kinds of measurements:

- time response to a given gas concentration, measured for the sensor operating at the constant temperature,
- determination of the temperature at which the sensor reaches the maximum sensitivity to a given gas at the constant concentration.

The typical time responses to methane and carbon monoxide of our sensor with pure SnO_2 gas sensitive layer are shown in Fig. 3.

It is generally known that the sensors resistance R_{gas} decreases when the concentration of the reducing gas increases. Thus the conductance $G_{gas} = 1/R_{gas}$ of the sensor, increases at given temperature according to the following relation:

$$G_{gas} \sim P_{gas}^{n} \tag{1}$$

where P_{gas} is the partial pressure of the reducing gas in the air and n is the characteristic exponent, lower than 1, depending on the kind of gas and composition of gas sensitive layer.

On the other hand, the results of measurements with thermostimulated conductance provided the calculation of sensors sensitivity to selected gases. The sensitivity is defined as

$$S = \frac{G_{gas}}{G_{air}} \tag{2}$$

where G_{air} is the conductance of the sensor in pure and dry air, and G_{gas} is the conductance of the sensor in the air containing a given concentration of reducing gas. The characteristics of SnO_2 sensor sensitivity to CO, C_2H_5OH and CH_4 are sketched in Fig. 4.

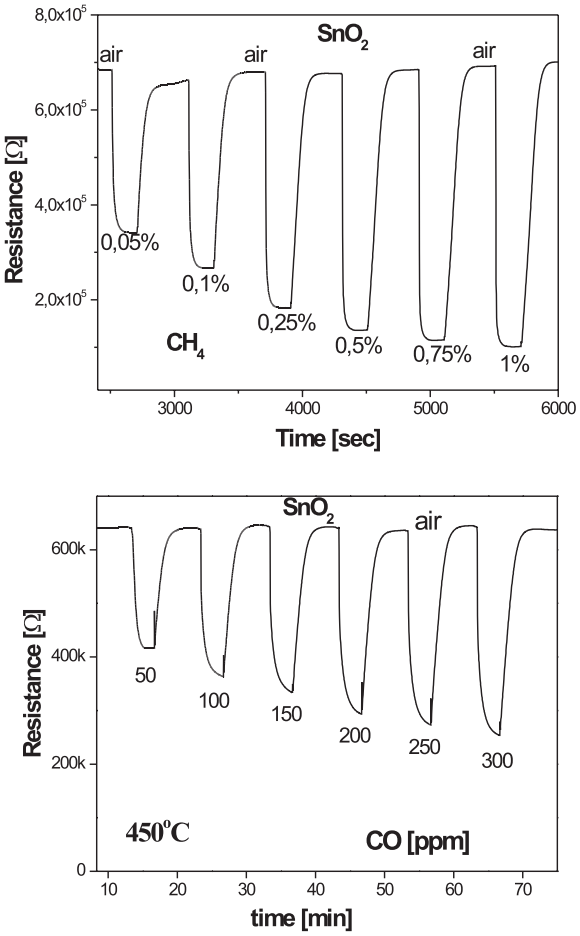


Fig. 3. Pure SnO_2 based sensor time responses to methane and carbon monoxide

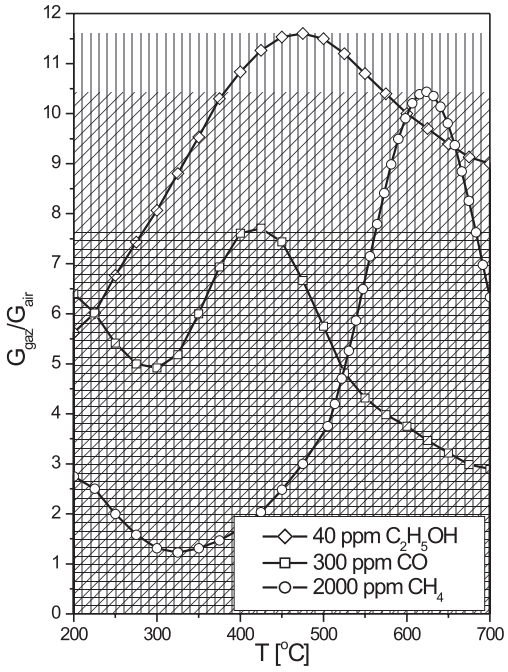


Fig. 4. The SnO_2 sensor sensitivity to carbon monoxide, ethanol and methane as a function of sensor operating temperature

Thus a major problem with the tin dioxide based sensors remains their lack of selectivity. Because of this phenomenon, called *cross-sensitivity*, if any reactive gas, other than the expected one, appears in the air, the sensor may give the false information. It is also known that e.g. variations of humidity level result in more or less drastic changes in conductivity of tin dioxide based sensors, thereby eventually masking the effect of toxic and hazardous gases on the sensors response.

Various attempts have been reported to minimise the influence of humidity on the sensor response in order to reduce the number of false or unrecognised alarms from hazardous gas warning devices.

For methane sensor, we have solved this problem using raw cermet composition based on tin dioxide and platinum black [10,12]. The SnO_2–Pt–black sensors do not change their electrical parameters in the environment with varying humidity (Fig. 5). Additionally very low influence of carbon monoxide presence on the response of described methane sensor was observed when the sensor operated at the temperature of 560°C.

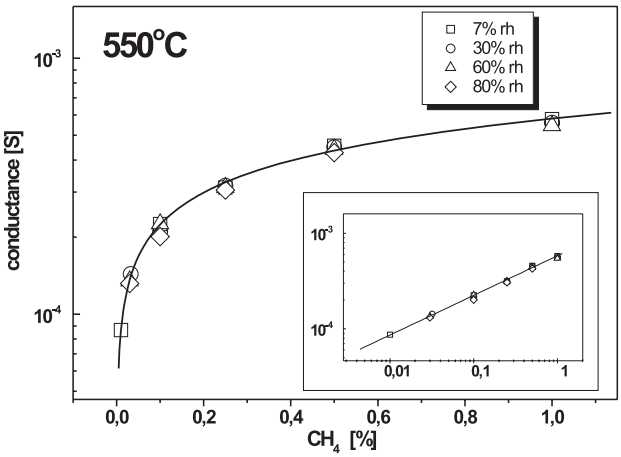
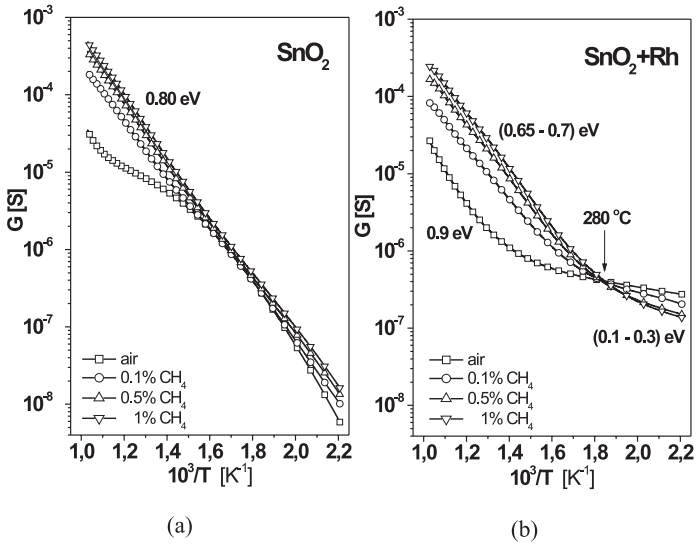


Fig. 5. Methane sensor response in different humidity levels [12]

Another interesting composition is the SnO_2 film doped on the surface with rhodium. The fired layer of tin dioxide was impregnated with the 0,01M of rhodium chloride, dried at room temperature and heated at the temperature of 600°C for 0,5 h. The measurements revealed the anomalous behaviour of these sensors. Below the characteristic temperature (280°C – Fig. 6), the sensors conductance decreases in the presence of reducing gases.

The mechanism associated with the presence of rhodium clusters can be connected with the increase of acceptor surface states concentration and causes the inversion of near-surface layers. It will be discussed in the next chapter.



(a) (b)

Fig. 6. Arrhenius plots for (a) SnO_2 and (b) Rh doped SnO_2, in pure air and in air containing 0.1%, 0.5% and 1% CH_4. Activation energies indicated were estimated from the slope

4. Discussion

Metal oxides used as sensing materials in semiconductor gas sensors have a wide band gap, typical for insulators. They possess conductivity in range of semiconductors due to point defects in the crystal structure. Thin dioxide is also a wide gap semiconductor with a band gap of 3.54 eV. Thin dioxide has a tetragonal rutile structure. Each crystallographic cell contains 2 tin atoms and 4 oxygen atoms. A lot of defects are present in SnO_2. The predominant donor in tin dioxide is a ionised oxygen vacancy. The presence of an oxygen vacancy causes two electrons of a tin atom to be free. The energy required to bring the first excess electron in the conduction band equals $\sim 0,04$ eV whilst for the second electron it equals $\sim 0,14$ eV [15]. If tin dioxide is exposed to ambient oxygen, the oxygen may adsorb on the sensor surface. The adsorbed oxygen traps one or two electrons from the bulk of tin dioxide.

The ionisation state of the adsorbed oxygen depends on the temperature of the sensor. This results in band bending and decrease of the sensor conductance. When the air contains also so called reactive gases, the reaction consists in the combustion of theses gases with adsorbed oxygen. For example, the reaction of methane with oxygen results in the desorption of water and carbon dioxide from the SnO_2 surface. A screen-printed gas sensitive layer consists of tin dioxide grains. The intergranular contacts in sintered samples are especially gas-sensitive and determine the sensor sensitivity. During the oxygen chemisorption on SnO_2 surface, the Schottky barriers appear, especially at intergranular contacts (Fig. 7).

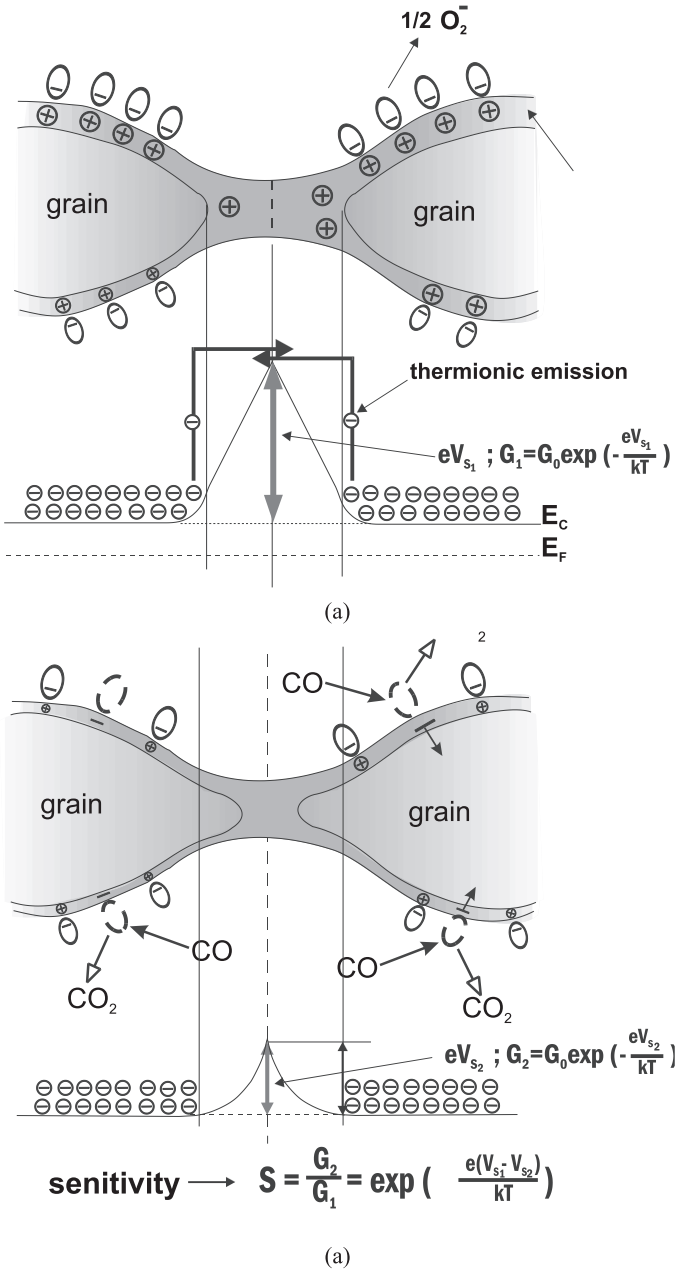


Fig. 7. Microstructure and energy band model of a gas sensitive SnO_2 thick-film (the potential barriers form as results of oxygen adsorption. (a) in air, (b) in the presence of reducing gas

The electrons may be assumed to cross the barriers by thermionic emission. As a first approximation, the conductance G_{air} and G_{gas} at a temperature T may be described by the following equations [16,17]:

$$G_{air} = G_0 \exp\left(-\frac{eV_{air}}{KT}\right) \tag{3}$$

$$G_{gas} = G_0 \exp\left(-\frac{eV_{gas}}{KT}\right) \tag{4}$$

and sensitivity

$$S = \frac{G_{gas}}{G_{air}} = \exp\left(\frac{eV_{air} - eV_{gas}}{KT}\right) \tag{5}$$

where G_0 may be considered as a factor that includes the bulk intergranular conductivity and geometrical effects whilst eV_{air} and eV_{gas} are the respective values of Schottky barrier between grains of SnO_2.

Using the described technology, the SnO_2 grains of the layer get the statistic dimensions (from micrometers to nanometres). Therefore the distribution of Schottky barriers height is broad-extend from about zero to the maximum value eV_s. In such circumstances it is better to use the percolation theory for carriers transport description [17]. Thus the conductance of the network could be described as

$$G \sim \exp\left(-\frac{eV_s}{KT}\right)^{\nu} \tag{6}$$

where ν is a specific exponent.

Much more complicated situation appears when the dopants are added to the SnO_2 layer. An interesting example may be a model, elaborated by authors group, describing the influence of ruthenium clusters on the inversion effect [13]. The observed phenomenon is caused by the specific features of rhodium (Rh 4d8.5 s1) as a transition metal. A weak form of chemisorption of oxygen with the surface of Rh clusters is the decisive factor here (Fig. 8a). The phenomenon appears at low temperatures. The process follows in two phases — first the dissociation of O_2 and then the capture of two electrons from rhodium d-band.

The phenomenon of oxygen adsorption of Rh cluster alone does not explain the influence of the air on the appearance of inversion layer. One should also take into account that the value of Fermi energy in Rh clusters is influenced by electrons from both s- and d-band. Electrons captured by oxygen from d-band decrease the value of Fermi energy in clusters. This leads to the growth of work function for electrons from Rh clusters by $\Delta\varphi_{Rh}$, what means the growth of barrier height and the appearance of inversion layer on SnO_2 surface (Fig. 8b). Additionally, the concentration of clusters on the surface of SnO_2 should be high enough for inversion areas to overlap (Fig. 8c).

Using mentioned arguments, the value of $\Delta\varphi_{Rh}$ [13] was estimated.

$$\Delta\varphi_{Rh} \cong \frac{9}{2}\eta_0 \frac{\Theta n_t}{r n_0} \tag{7}$$

where: η_0 — Fermi energy of cluster electrons, n_t — is the density of adsorption centres on the cluster surface, θ is the filling factor of the cluster surface, n_0 — is the density of conduction electrons in Rh, r — is the cluster radius.

These anomalous properties of SnO_2–Rh sensor disappear at higher temperature, where the intensive desorption of O^- and adsorption of O^{2-} starts.

Having a group of sensors revealing various sensitivity to different gases, we can think about the construction of so-called electronic noses. It is even possible to perform the quantitative analysis of gas mixtures using sensor array and e.g. neural networks [18, 19].

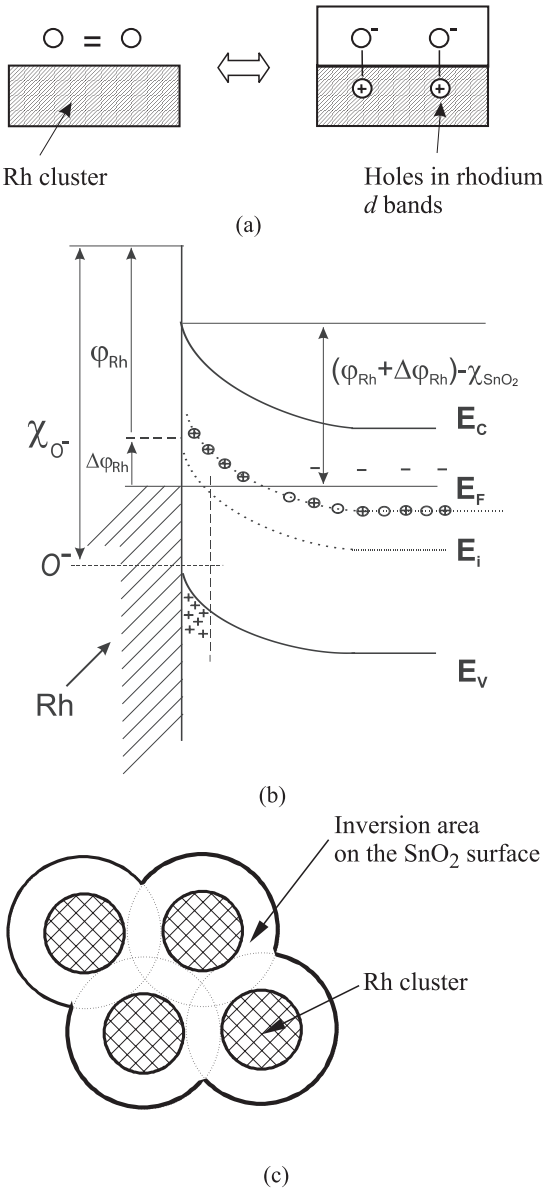


Fig. 8. Weak form of oxygen chemisorption on Rh surface (a). The influence of rhodium clusters on barrier height φ_{Rh} of SnO_2 + Rh surface when chemisorption of O^- dominates (b). Overlap of inversion areas on SnO_2 + Rh surface (c). E_c — conduction band
E_F — Fermi level of SnO_2 + Rh at low temperature
E_i — Fermi level of intrinsic SnO_2
E_v — valence band
X_0 — electron affinity of O^- to Rh clusters
φ_{Rh} — work function of Rhodium
X_{SnO_2} — electron affinity of SnO_2

5. Conclusions

It was observed that thick-film gas sensors based on semiconductive tin dioxide are suitable for detection of explosive and toxic gases and vapours. The improvement in their selectivity has been achieved due to microelectronic technology. The studies made by several research groups in various countries offer better and better understanding of physical and chemical processes that occur

during sensors operation. Basing on the already available solutions, it is possible to construct so-called electronic noses. The quality of new solutions in micro- or nanosensors tends to depend on possibilities to construct gas sensitive layers either from nanograins of identical dimensions, or programmed arrays of varying dimension grains, referring to the theoretical models developed before.

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