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Chemirezistory pro detekci plynů: materiály a struktury citlivých vrstev, detekční mechanismy

Chemiresistors for detection of gases: materials and structures of sensitive layers, detection mechanisms

Summary

This document deals with distinct branch of chemical sensors – chemiresistors for detection of gaseous analytes. The two introductory chapters delimit specific attributes of chemiresistors, describe their architecture and function of their constituents. The third chapter presents an overview of materials applied in sensitive layers of chemiresistors (metal oxides, organic non-polymeric complexes, organic polymers and polymerized ionic liquids). Each material is characterized by its charge-transport properties and a detailed analysis of transduction mechanisms taking part during the detection process. Following this, there are specified chemical features of the analyte molecule, which are essential to ensure its effective interaction with sensitive layer and hence detectability. The role of material morphology is also discussed. This "nano-scale" view of sensor operation is complementary with "macro-scale" parameters of chemiresistor device. So the last chapter presents certain synthesis: the proposal of a complex characterization of chemiresistor functionality in both scales. Such methodology is necessary for design of upcoming generation of chemiresistors.

The contribution of the author and his team to the topic of chemiresistors was reported in twelve references: [11], [13-15], [20-25] and [28-29], which are cited in the text.

Souhrn

Dokument se zabývá jedním význačným druhem chemických senzorů – totiž chemirezistory určenými pro detekci plynů. Ve dvou úvodních kapitolách jsou vymezeny specifické vlastnosti chemirezistorů, popsána jejich architektura a funkce jednotlivých komponent. Následuje přehled materiálů používaných pro citlivé vrstvy (oxidy kovů, organické komplexy nepolymerního charakteru, organické polymery a polymerizované iontové kapaliny). Každý z těchto typů materiálů je charakterizován mechanismy přenosu náboje a detailní analýzou převodních mechanismů probíhajících při detekci plynných molekul. Dále jsou uvedeny chemické vlastnosti, které musí mít molekula analytu, aby byla pomocí daného materiálu detekovatelná. Rovněž je diskutována role morfologie materiálu citlivé vrstvy. Tento pohled na fungování chemirezistoru v "nanoměřítku" je komplementární s "makroskopickými" charakteristikami chemirezistoru jakožto elektronické součástky. Poslední kapitola pak představuje jistou syntézu: navrhuje postup, jak komplexně charakterizovat funkci senzoru dle obou měřítek. To je nezbytné pro návrh příštích generací chemirezistorů.
Příspěvek autora a jeho týmu k prezentované problematice byl publikován ve dvanácti pracích: [11], [13-15], [20-25] a [28-29], které jsou citovány v textu.

Klíčová slova

chemirezistor pro detekci plynů, převodní mechanismy, materiály citlivých vrstev, detekovatelné vlastnosti analytů, souvislost parametrů chemirezistoru s převodními mechanismy

Keywords

chemiresistor for detection of gases, transduction mechanisms, materials of sensitive layers, detectable features of analytes, correlations between parameters of chemiresistor and transduction mechanisms

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1. Systematics of chemiresistors for gas detection

Although the first functional chemiresistors with oxidic sensitive layers were constructed in 1960's [1] and since 1990's they are commercially produced in large series, their research and development is far from being completed. Nowadays, while chemical composition of inorganic sensitive layers (metallic oxide, dopant, catalyst) has been usually optimized, the boom of nanotechnologies in recent years brings new challenges how to improve chemiresistors by tuning morphology of their sensitive layers. Further, application of organic materials for sensitive layers brought a new dimension to research of chemiresistors, as the organic materials offer a possibility to easily modify both chemical composition and morphology. There are recent reports in literature proving that this topic is still actual [2-5].

Chemiresistor is a passive sensing element which converts chemical input quantity (presence of detected gaseous analyte) into electrical output quantity (Fig.1).

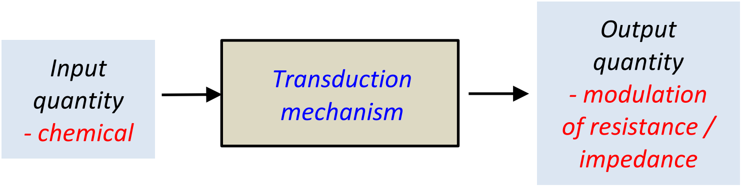


***Fig.1** – Functionality of chemiresistor.*

Chemiresistors have three specific features:

a) As for input quantity, there exist several millions of chemical substances and majority of them produces sufficient vapor pressure to be detectable by these gas sensors – so **there are millions various input quantities.** Moreover, each of detectable substances, i.e. *analytes*, can either be identified (determination of quality) or determined (determination of quantity), or can become a constituent of multicomponent mixture, which is distinguishable from another mixtures (the so-called classification).

b) To attain successful detection process, the chemiresistor has to fulfill two formal roles: receptor function and transduction mechanism [6,7]. Receptor function follows from the fact that these are contact sensors, i.e. direct chemical interaction of gaseous analyte species with surface of sensitive layer is essential. Transduction mechanism [7] can be interpreted as the ability of the chemical interaction that took place during the receptor process, to induce the measurable change of sensor resistance/impedance. As for transduction mechanism, the chemiresistors – unlike majority of the remaining chemical sensors – exploit **several mechanisms how the electrotransport properties of sensitive layer can be modified by the analyte:**

I) exchange of electrons,
II) entrapment of gaseous species with high permanent dipole into the sensitive layer,
III) formation of hydrogen bonds,
IV) formation of common molecular orbitals,
V) modulation of material internal free volume.

The wider consequences of the transduction mechanisms I) – V) are presented in Table 1. The details of each mechanism will be discussed in Chapter 3. All the above mentioned phenomena should be explained in the terms of interaction on phase boundary between gaseous analyte and surface of solid-state sensitive layer. In dependence on the nature of analyte and sensitive layer, more transduction mechanisms can occur simultaneously (e.g. molecules of alcohol which can provide electrons to sensitive layer thus acting as electron donors, are also able to form hydrogen bonds with organic sensitive layer thus decreasing mobility of free electrons/holes or can diffuse into porous sensitive layer thus increasing its permittivity). Individual transduction mechanisms can be favored or suppressed by setting sensor operating temperature. One should also take in mind that deeper understanding to transduction mechanism provides insight into response of the sensor in "nano-scale".

c) Although these sensors are called "chemiresitors", their output quantity can be either resistance or impedance, when performed in dc- or ac- mode of measurement. When measuring in dc-mode, we can monitor changes in concentration and mobility of charge carriers, when operating in ac-mode, also changes in material permittivity, dielectric polarization and capacity of depleted regions on grain boundaries are observable. The output signal represents complex, i.e. "macro-scale" response of chemiresistor device.

"Detectable feature" of analyte molecule	**Transduction mechanism (nano-scale)**	**Modulated physical quantity of sensitive layer (nano-scale)**	**Change of chemiresistor output quantity (macro-scale)**
redox behavior (oxidizing or reducing)	I) exchange of electrons	concentration of free electrons / holes	resistance, impedance
presence of permanent electrical dipole	II) dipole-dipole interactions	permittivity, mobility of counter-ions	impedance
presence of O-H or N-H bond	III) formation of hydrogen bonds	mobility of free electrons / holes	resistance, impedance
Lewis basicity / acidity	IV) formation of common molecular orbitals	mobility of free electrons / holes	resistance, impedance
solubility in the material of sensitive layer	V) modulation of internal free volume	mobility of ions	resistance, impedance

Table 1 *– Consequences amongst various aspects of chemiresistor functionality.*

The "macro-scale" response does not represent simply a sum of "nano-scale" responses; it depends also on morphology of sensitive layer, configuration of electrodes, the nature of sensitive layer-electrode contacts, etc. When sensor output signal is measured, current flows through its sensitive layer; for this reason the transducer mechanism is partially influenced by "volume" phenomena in morphological constituents of sensitive layer (larger grains, nanocrystallic grains, one-dimensional nanowires, nanotubes etc.) and partially by "surface phenomena" - i.e. nature of contacts between these nanoobjects (see also Fig.8).

2. Sensor architecture, function of individual constituents [8]

Sensor architecture – as the arrangement of chemiresistors (Fig.2) has been reported many times, we will restrict ourselves to basic facts. Three sensor components are necessary: insulating substrate (mechanical support), electrodes for measurement of electrical output and sensitive layer (it interacts with the analyte). One another component is optional – resistance heating for ensuring operating temperature. However, contemporary trend is focused on development of chemiresistors operating at ambient temperature.

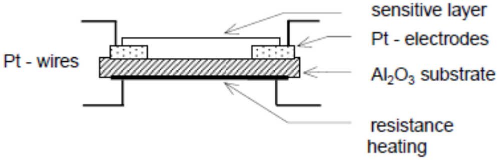


***Fig.2** – An example of chemiresistor architecture.*

The conventional chemiresistor **substrates** are chips made from Alumina – ceramics on basis of aluminium oxide, which is a good electrical insulator. The sensor has two interdigital measuring platinum electrodes on the front side (Fig.3a) and resistive heating on the back side (Fig.3b). Heating serves for adjustment of sensor working temperature. Alternatively, flexible textile substrates can be used. They are made of either woven or non-woven insulating textile (PES or PAD) and equipped with carbon screen-printed electrodes (Fig.3c).

The **electrodes** for signal reading are typically made of sputtered platinum which exhibits excellent chemical inertness. Nevertheless, for organic active layers screen-printed carbon electrodes are advantageous, because work functions of organic materials and carbon are so close to each other that the contact *organics – carbon* tends to Ohmic behavior [9]. Another positive aspect is that screen-printed carbon has enhanced adhesion to flexible substrates.

The material of the first choice for **resistive heating** is platinum for its inertness, thermal stability and possibility to directly evaluate its temperature by applying the Platinum-thermometer approximation.

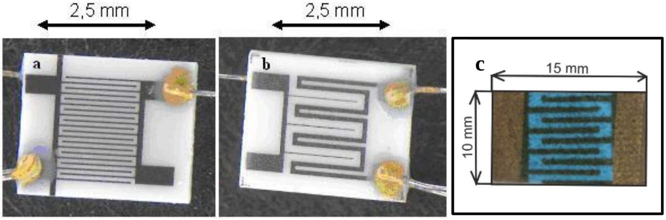


Fig.3a-c – *Real appearance of sensors used at UCT Prague: a) front view of ceramic substrate, b) back view of ceramic substrate, c) front view of textile sensor with phthalocyanine sensitive layer.*

Sensitive layer represents by far the most variable component of chemiresistor. Tuning its chemical composition and morphology is crucial for enhancement of "macro-scale" sensor parameters (sensitivity, selectivity, response and recovery time, detection limit, power consumption, service life etc.). This is the reason, why optimization of sensitive layer is a subject of intensive research and development.

Sensitive layer contains basic material and (optionally) catalyst. A detailed discussion regarding **basic material** is presented in Chapter 3. With respect to Chapter 3, we will categorize basic material into four classes: *3.1 - metal oxides*, *3.2 - organic non polymeric complexes*, *3.3 - organic polymers* and *3.4 - polymerized ionic liquids*. Such categorization reflects different chemical composition and charge-transport phenomena in materials. Thus *metal oxides* are considered to be conventional semiconductors forming covalent crystals with electron-hole conductivity. *Organic non-polymeric complexes* represent molecular electron-type or hole-type conductors with relatively small molecules bonded by weak non-covalent interactions. Hence there are obstacles in charge transport (hopping transfer of electrons and holes between the molecules). *Organic polymers* are mixed conductors of *hole - counter anion* or *electron – counter cation* type with large molecules and isotropic conductivity of backbone, *polymerized ionic liquids* are purely ionic conductors, whose molecules are bonded by Coulombic interactions and whose behavior resembles electrolytes, but not semiconductors.

Catalyst (when present in sensitive layer) have a form of small, non-aggregated particles of elemental noble metals, such as Pt, Pd or Au. The particles are usually located at the surface of semiconductor – basic material of sensitive layer. The catalyst speeds up detection process and shifts sensor operating temperature to lower values. Two mechanisms have been proposed to explain the catalyst role in chemiresistors [10]: (i) **"Spill over" effect** – the metal catalyst dissociates the molecule of oxygen, whose reactive anions can then "spill over" onto the surface of sensitive layer and react with detected analytes (Fig.4). "Spill over" effect is a chemical interaction. (ii) The second is called **"Fermi-level pinning"** – in this electronic interaction the adsorption of oxygen removes electrons from the catalyst and the catalyst, in turn, removes electrons from the supporting semiconductor (Fig.4). Both processes modulate sensor resistance or impedance.

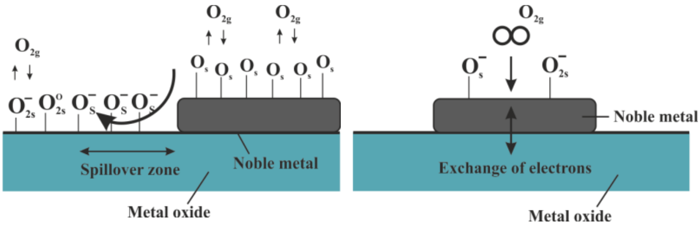


Fig.4 *– Schematic illustration of noble-metal catalyst on metal oxide: (i) spillover effect – left, (ii) Fermi level pinning – right* [10].

Just several results (based on our previous research published in [11]) illustrating the role of catalysts are summarized in Tab. 2 and Tab. 3. From the practical point of view, the presence of palladium catalyst in sensitive layer of chemiresistor increases its dc-sensitivity (S_{dc}) – see Eq. 5 - and decreases operating temperature (t_m). According to [10] palladium catalyst leads to "Fermi-level pinning". Of course, the nature of basic material of sensitive layer (tin acetyl-acetonate dichloride or SnO_2) also plays an important role.

layer / gas analyte	**H_2**	**MeOH**	**EtOH**	**n-PrOH**	**n-BuOH**
SnAcAc	11.0	13.7	22.0	6.0	3.6
SnAcAc + 2nm Pd	35.3	19.4	50.5	71.2	44.5
SnAcAc + 4nm Pd	67.6	20.6	19.8	13.5	17.6
SnO_2	5.2	3.8	3.9	3.1	2.8
SnO_2 + 2 nm Pd	5.3	3.4	2.0	3.3	4.5
SnO_2 + 4 nm Pd	20.0	7.3	3.8	-	-

***Table 2** – Maximum dc-sensitivity ($S_{dc\text{-max}}$) of chemiresistors with various sensitive layers to 1000 ppm of hydrogen or alcohol vapors. SnAcAc denotes tin acetyl-acetonate dichloride* [11].

layer / gas analyte	**H_2**	**MeOH**	**EtOH**	**n-PrOH**	**n-BuOH**
SnAcAc	456	526	538	538	559
SnAcAc + 2nm Pd	424	514	483	478	457
SnAcAc + 4nm Pd	424	477	466	478	478
SnO_2	577	572	574	550	596
SnO_2 + 2 nm Pd	351	478	558	393	383
SnO_2 + 4 nm Pd	422	451	570	-	-

***Table 3** – Temperatures (t_{max}, °C) of maximum dc-sensitivity of chemiresistors to 1000 ppm of hydrogen or alcohol vapours* [11].

3. Nano-scale view: Transduction mechanisms in distinct classes of basic materials for sensitive layers

3.1 Inorganic materials (metal oxides)

As mentioned in Chapter 1, **metal oxides** are conventional materials for sensitive layers of chemiresistors. The metal oxides are described as crystallic inorganic semiconductors, hence the charge transport is mediated by free electrons and holes. Due to occurrence of oxygen vacancies in crystal lattice, majority of oxides are natural n-type semiconductors (SnO_2, ZnO, TiO_2, WO_3) and only a few ones (CuO, NiO) represent p-type semiconductors (Fig 5) [12]. For both subgroups **the dominating transduction mechanism is *I) exchange of electrons between gaseous analyte and the semiconductor sensitive layer***. Considering grain structure of the sensitive layer, one obtains series (for n-type) or parallel model (for p-type) of current flow through individual grains – see (Figs 6-7).

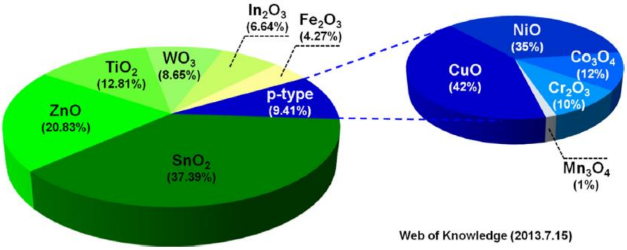


***Fig.5 –** Percentage of research papers dedicated to chemiresistors with sensitive layers based on distinct oxides* [12].

Owing to necessity of electron exchange, such interaction must has a character of chemisorption (ionosorption); in the event that the gas has a large electron affinity, such as O_2 or NO_2, it extracts electrons from the host semiconductor and is absorbed as anionic species such as O^-, O^{2-} or NO_2^-. Conversely, when the gas exhibits low ionization potential, like NO, it donates electrons to the sensitive layer and is absorbed as cationic species, such as NO^+. So the target gases, detectable on inorganic materials, fall into two groups - gases which undergo ionosorption (direct detection) and flammable gases (e.g. H_2, CO, CH_4) that do not ionosorb themselves, but can react with previously ionosorbed oxygen (indirect detection). Regardless the detailed mechanism, the energy band structure in the material of sensitive layer is modified accordingly.

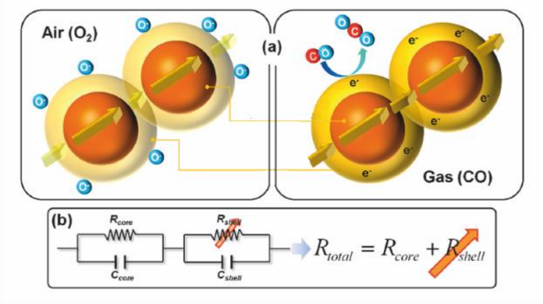


Fig.6 – *Gas sensing mechanism and equivalent circuit of n-type oxides. As the chemisorption of atmospheric oxygen generates surface layer with high resistance, the current flows preferably through a series combination of core and shell in each grain* [12].

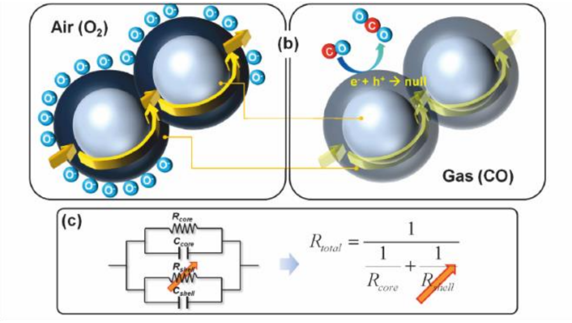


Fig.7 – *Gas sensing mechanism and equivalent circuit of p-type oxides. As the chemisorption of oxygen generates surface layer with low resistance, the current flows through a parallel combination of core and shell in each grain* [12].

The basic materials of oxidic sensitive layers behave like n-type or p-type semiconductors, so their response to gases can be stimulated by introducing dopant of the opposite type (the so-called compensation doping). This approach increases the relative contribution of the electrons donated to- / extracted from- sensitive layer by the molecule of gaseous analyte. We carried out a research [13-14] of sensitive layers based on SnO_2 (n-type material) with NiO or Fe_2O_3 (p-type dopants). The results are summarized in Table 4.

layer composition / basic material + dopant + catalyst		**content of dopant**			
		0.0 wt.%	**0.1 wt.%**	**1.0 wt.%**	**10.0 wt.%**
SnO_2 + NiO	$S_{dc\text{-m}}$	8.8	6.9	8.2	7.2
	t_{max}	485°C	440°C	430°C	440°C
SnO_2 + NiO + Pd	$S_{dc\text{-m}}$	1090	2820	250	520
	t_{max}	280°C	110°C	110°C	210°C
SnO_2 + Fe_2O_3	$S_{dc\text{-m}}$	8.8	11.2	13.7	1.8
	t_{max}	485°C	470°C	480°C	340°C
SnO_2 + Fe_2O_3 + Pd	$S_{dc\text{-m}}$	1090	600	130	1130
	t_{max}	280°C	190°C	100°C	105°C

Table 4 *– Maximum dc-sensitivity ($S_{\text{dc-m}}$) to 1000 ppm of hydrogen and the corresponding temperature (t_{max}, °C) as a function of different dopant concentration (in wt.%)* [13].

We also carried out a pioneering research of CuO, which is a representative of p-type semiconductors. The results are presented in [15].

Metal oxides, when compared with the other material classes which are referred to in this chapter, **are characterized by relatively easy formation and also high stability of nanostructures**. When given oxidic material is nanostructured, its electrophysical and chemical properties are significantly modified [2, 16-17].

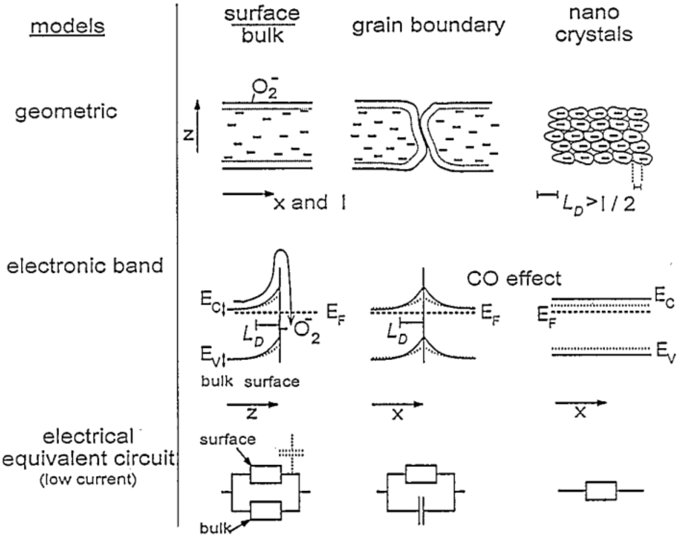


***Fig.8** – The influence of particle sizes on local conductivities and capacitances in chemiresistor active layers. The presented particle sizes are characterized by geometric structures, electronic band models and equivalent circuits describing the electrical behavior* [8].

In this context, it is usually mentioned the so-called "dimension effect" (see also Fig. 8), e.g. a comparison of the grain size d with the Debye length L_D:

$$L_D = \sqrt{\varepsilon kT / 2\pi e^2 N} \qquad (1)$$

where k is the Boltzmann constant, T is the thermodynamical temperature, ε the permittivity of the material and N is the concentration of free charge carriers. To control effectively properties of nanostructured material, the relation $d < 2\,L_D$ should be fulfilled. Then the position of Fermi level within band gap of the nanostructured oxide is varied and hence the surface processes during the detection can be controlled electronically. To say in other words, in such a case the grain is fully involved in the space-charge layer and the electron transport is affected by the charge of chemisorbed species. Further, nanostructures exhibit large surface-to-volume ratio with high concentration of active surface sites for chemisorption. One may notice that influencing of Fermi level position and creating surface active sites corresponds to "traditional" role of the metallic catalyst (described in Chapter 2), which is sometimes deposited to surface of sensitive layer. To conclude, **by nanostructuring sensitive layer, we can substitute the effect of metallic catalyst.**

For oxidic nanostructures the relationship of the surface-to-volume ratio with the dc-sensitivity to given gas S_{dc} is described by [18]:

$$S_{\mathrm{dc}} = \frac{\Gamma_{\mathrm{t}} k_{\mathrm{eth}} \sigma_0 \, C_{\mathrm{g}} \, \Phi}{n_0} \frac{V_{\mathrm{m}}}{V_{\mathrm{s}}} + 1 \qquad (2)$$

where Γ_t is a time constant, n_0 is the electron concentration in sensitive layer of sensor at operating temperature in the air atmosphere, k_{eth} is the reaction rate constant, C_g is the gaseous analyte concentration, σ_0 is a number of oxygen chemisorbed anions per unit area of surface, Φ is a ratio of surface area per volume of material (V_m) and V_s is the total system volume. Thus, S_{dc} has a linear relationship with $(V_m/V_s)\cdot k_{eth}$ and having a slope equal to $(\Gamma \, \sigma_0 \, C_g \, \Phi) / n_0$.

3.2 Organic non-polymeric complexes

Organic non-polymeric complexes can be specified (for our purpose) as those with relatively small molecules containing organic ligand with conjugated system of double bonds and central metallic cation (see Fig. 9). As for electrotransport properties they represent molecular conductors whose conductivity is ensured by occurrence of free electrons (e^-) or holes (h^+) in conjugated organic skeleton. As the molecules are small and (unlike metal oxides mentioned in 3.1) not covalently bonded to each other, the total conductivity of material is limited not only by concentration, but also by intermolecular hopping mobility of e^- or h^+. We will restrict ourselves to phthalocyanines and acetyl-acetonates, which are studied in our laboratory. Of the transduction mechanisms mentioned in Tab.1, **I) exchange of electrons**, and **IV) formation of common molecular orbitals** are the potentialities for this class of substances.

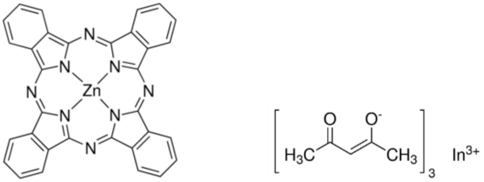


Fig.9 **–** *Structural formulae of zinc phthalocyanine (ZnPc) - left - and indium tris-(acetyl-acetonate) (InAcAc) - right. The organic ligands are phthalocyanine or acetyl-acetone,* Zn^{2+} *and* In^{3+} *are central ions.*

It is known that p-type Pc films exhibit high sensitivity to oxidizing gases such as NO_2 or Cl_2. Some authors interpret this sensitivity by means of transduction mechanism **I) exchange of electrons** i.e. gaseous analyte extracts π-electrons from conjugated organic skeleton; the positive charge produced is then delocalized and increases p-type conductivity [19]. The whole process follows subsequent scheme:

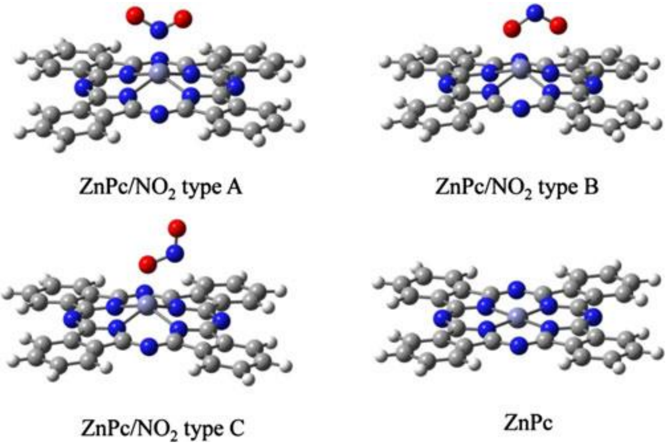
Gas + Pc ← *charge transfer* → Gas^- + Pc^+ ← *(de)localization of hole* → Gas^- + Pc + h^+

where the symbols Gas^- and Pc^+ denote ionized molecules and h^+ free hole. During the response period the process steps turn from left to right, during the recovery period from right to left. From this model, one obtains the relation:

$$R \sim {c_{\text{gas}}}^{-n/2} \qquad (3)$$

i.e. the sensor resistance *R* is indirectly proportional to concentration of gaseous analyte c_{gas} and *n* is a constant, $0 < n < 1$.

In [20] we offer a complementary view on detection of NO_2 on phthalocyanine based on transduction mechanism **IV) formation of common molecular orbitals**. The chemical interpretation of this detection process emphasizes formation of common molecular orbitals between a free electron pair of NO_2 (Lewis base) and central zinc cation (Lewis acid). Possible configurations of $ZnPc/NO_2$ complex are depicted in Fig. 10.



ZnPc/NO_2 type A

ZnPc/NO_2 type B

ZnPc/NO_2 type C

ZnPc

***Fig.10 –** The calculated structures of the complexes formed between ZnPc and NO_2* [20].

For each of these three configurations, energy of common orbitals was calculated (Fig.11). The conclusion is that for ZnPc/NO_2 complexes the highest occupied orbitals are sufficiently close to each other (the "gap" between them varies from 0.04 to 0.28 eV) to create a conducting orbital with a locally increased density of states. Moreover, this conducting orbital is associated with the highest molecular orbitals of the ZnPc molecule. So the charge-transport obstruction (connected with hopping between molecules) is significantly reduced.

The "prominent" character of detection NO_2 gas on ZnPc chemiresistors was verified by testing dc-responses of these sensors to hydrogen; it holds the relation $S_{\text{dc-NO2}} >> S_{\text{dc-H2}}$ [20]. Hydrogen has not the ability to form common molecular orbitals with ZnPc.

This large affinity of NO_2 Lewis base to central Me^+ cations contained in MePc can also become a powerful tool for **indirect detection of organic nitrates** R-NO_2. For example in [21] we successfully detected 2-nitrotoluene (most common taggant in explosives) on AgPc active layers. The response of AgPc to 2-nitrotoluene was negligible but when the molecules of 2-nitrotoluene were exposed to UV radiation, they released NO_2 gas which was subsequently detected.

We can suppose the same transduction mechanism, i.e. **IV) formation of common molecular orbitals** also in our previous works devoted to acetyl-acetonates [22-24]. Here, when testing InAcAc chemiresistors, the detection limits for ozone (O_3) and NO_2 were achieved to be 20 and 200 ppb respectively. Like NO_2, the molecule of ozone is also able to act as Lewis base, which provides electrons to In^{3+} central cation (Lewis acid) present in InAcAc.

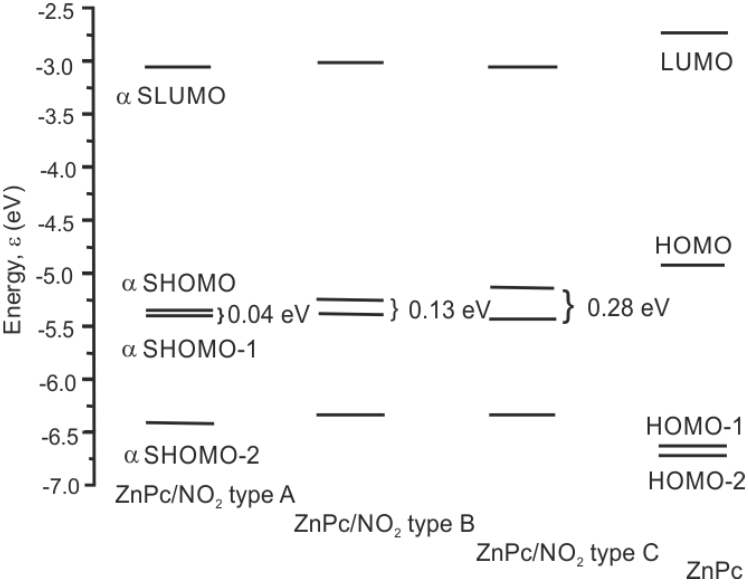


***Fig. 11** – The energy of the frontier orbitals for various systems: ZnPc/NO_2 type A, ZnPc/NO_2 type B, ZnPc/NO_2 type C and with ZnPc without interaction with gas. The electronic levels were calculated by B3LYP/6-31G(d) method* [20].

3.3 Organic polymeric materials

In this section we will discuss the results achieved on **polypyrrole** (PPy), which is a typical representative of conductive polymers and its application in chemiresistors is studied in our laboratory for many years.

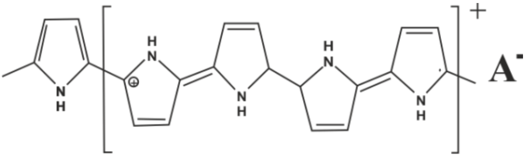


***Fig. 12 –** Structural formula of polypyrrole.*

From the point of electrotransport properties, we can classify polypyrrole as a mixed conductor. In one-dimensional polymer backbone (Fig. 12) with conjugated system of double bonds and delocalized π-electrons the charge is transported by positively charged polarons or bipolarons (in fact holes h^+). This transport is highly isotropic – in the direction of backbone. The positive charge of backbone is compensated by counter-anions A^-; these can be present as small inorganic species such as Cl^- or SO_4^{2-} but also large organic ones, e.g. $R\text{-}SO_3^-$, where R- represents alkyl or aryl group. The charge transport ensured by counter-anions is anisotropic, because they are not bonded to one particular site.

In such situation, two transduction mechanisms (see Tab.1) occur in sensitive layers based on PPy: **II) dipole-dipole interactions** – when analytes with high permanent dipole (typically water molecules) enter the polymer, they increase its electrical permittivity by dipole-dipole interactions and simultaneously strongly stimulate mobility of counter-anions A^-. It holds the relation:

$$\mu_{\mathrm{ion}} \sim \exp\left(-\frac{\Delta w_{\mathrm{i}}}{2\varepsilon_{\mathrm{r}}\mathrm{k}T}\right) \qquad (4)$$

where μ_{ion} is the mobility of counter-anion, Δw_i the activation energy of ionic movement, ε_r relative permittivity of polymer, k Boltzmann constant and T thermodynamical temperature. The influence of transduction mechanism II) dipole-dipole interactions is by far the most pronounced when detecting water (humidity), because its relative permittivity (ε_{rH2O} = 81) is by one order of magnitude higher when compared with that of other polar analytes (alcohols, aldehydes, ketones etc.).

III) formation of hydrogen bonds (Fig.13) – when the molecule of analyte forms hydrogen bond with PPy, the degree of conjugation in polymer backbone is decreased and hence the mobility of h^+ decreases.

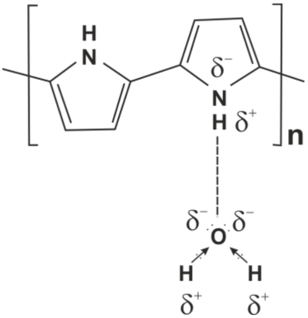


***Fig. 13** – Hydrogen bond between water molecule and PPy.*

There is also a possibility to distinguish the contribution of both transduction mechanisms in PPy, i.e. II) dipole-dipole interactions from III) formation of hydrogen bonds. We carried out such research in [25]. This alternative method is based on investigation of log–log plot of *real part of complex admittance* versus *frequency* (i.e. Re Y versus f). While at small f the Re Y values are frequency-independent, after reaching certain critical value, the so called cross-over frequency fc, sublinear increase of Re Y with increasing f takes place. It was found that Re Y grows proportional to fn for frequencies exceeding fc. The exponent of this growth (n) is called fractional exponent. It holds $n \leq 1$ for conducting polymers. The values of fc and n are important material parameters characterizing disordered polymers.

Fig. 14 depicts the log–log plot of *real part of complex admittance* versus *frequency* for PPY-based sensor. It can be estimated that in our case *f*c ≈ 5x10^4 Hz and *n* ≈ 0.18. The *f*c values decrease from 3x10^5 Hz for "fresh" polypyrrole to 1x10^5 Hz for "aged" material. The smaller *f*c values indicate that there is partial fragmentation of PPY backbone as a result of material "ageing". The value of fractional exponent *n* of our samples is significantly smaller than unity, it means that the charge transfer properties are not predominantly determined by mobility of polarons in the polymer backbone, but they are strongly affected by presence of dopants (counter-anions) and in PPY. **To conclude, in our case the transduction mechanism II) dipole-dipole interactions dominates.**

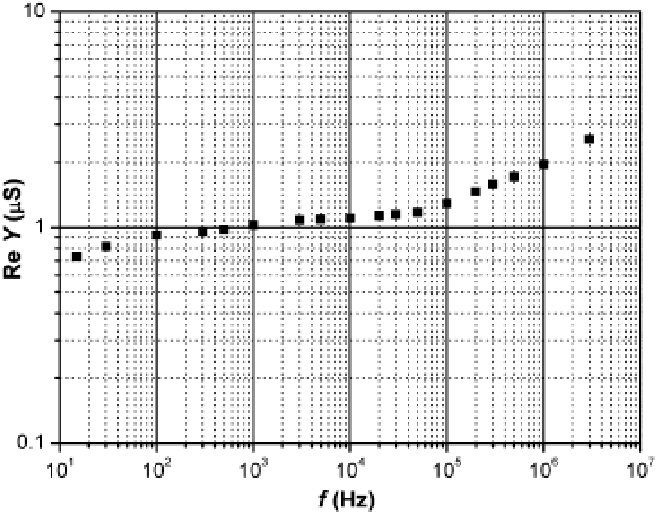


***Fig. 14** – The log-log plot of real part of complex admittance vs. frequency of signal for PPy-based sensor in synthetic air containing 90% relative humidity at isothermal conditions (*t_m *= 22°C)* [25].

3.4 Polymerized ionic liquids

Polymerized ionic liquids (PILs) have been first time reported in 1998 and a brief overview of their properties can be found e.g. in [26]. Their electrotransport properties are unique (when compared with other organic substances), as they are purely ionic conductors. At present we make first experiments with $[P_{4,4,4,n}]^+$ poly $[AC3S]^-$, whose structure is depicted in Fig. 15.

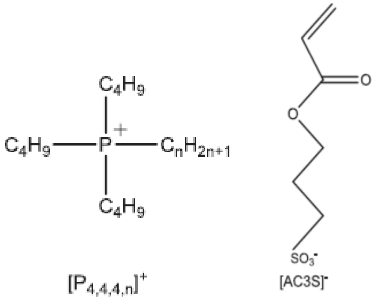


Fig. 15 *– Structural formula of* $[P_{4,4,4,n}]^+$ *poly* $[AC3S]^-$ *ionic liquid, which is used in our chemiresistors..*

It is apparent that $[P_{4,4,4,n}]^+$ poly $[AC3S]^-$ is composed of the polymeric anion with strictly localized negative charge (i.e. zero charge mobility) and non-polymeric cation, which responsible for charge transport. The mobility of relatively large cation is strongly influenced by internal free volume in the polymer.

There exist also "inverse" PILs with fixed cations and mobile anions, but this is not our case. PILs have promising applications as the materials for selective membranes, in chemical catalysis, for gas storage etc. What is surprising, their applications in chemiresistors has not been reported yet.

PILs are characterized by high capacity to absorb gases (analytes) with small molecules – especially CO_2 and water. On such absorption, the internal volume of polymer is modified and mobility of ions changes [27]. As a result, the transduction mechanism **V) modulation of material internal free volume** occurs. This property of

PILs is very valuable, because namely CO_2 (its molecule has neither redox properties, nor dipole moment) cannot be detected on chemiresistors by any other mechanism.

The results of our pioneering measurement of chemiresistors with $[P_{4,4,4,n}]^+$ poly $[AC3S]^-$ were presented in [28]. They were successfully tested in detection of simulants of chemical warfare agents.

4. Macro-scale view: Parameters of chemiresistor device

Response of chemiresistor measured by dc-signal, evaluation of dc-sensitivity (S_{dc}) [11] **-** The dc-sensitivity of sensor (S_{dc}) is evaluated for temperature of measurement t_m and concentration of detected gas component c_i as a ratio of sensor resistance in the air (R_{air}) and the resistance in the atmosphere containing detected gas at this temperature (R_{gas}):

$$S_{\mathrm{dc}}(t_{\mathrm{m}}, c_{\mathrm{i}}) = \frac{R_{\mathrm{air}}(t_{\mathrm{m}})}{R_{\mathrm{gas}}\,(t_{\mathrm{m}}, c_{\mathrm{i}})} \qquad (5)$$

Such defined quantity has values higher than 1 when detecting reducing gases on n-type layers and is dependent on temperature, nature and concentration of detected gas. The *sensitivity* versus *temperature* dependence can be measured by `temperature scan method' based on continual increasing of sensor temperature at the constant rate (approx. 2 °C/min), with simultaneous atmosphere change from the status without detected gas (`clean' synthetic air) to that containing given concentration of analyte in synthetic air and vice-versa. The temperature of maximum sensitivity t_{max} can also be evaluated by this method.

Additionally, the output of `temperature scan method' contains certain information about the detection mechanisms, which are dominant at given temperature of measurement t_m. This can be revealed by deconvolution of $S_{dc} = S_{dc}(t)$ plot (i.e. central line in Fig. 16) to distinct Gaussian peaks – the procedure is described in details in [2].

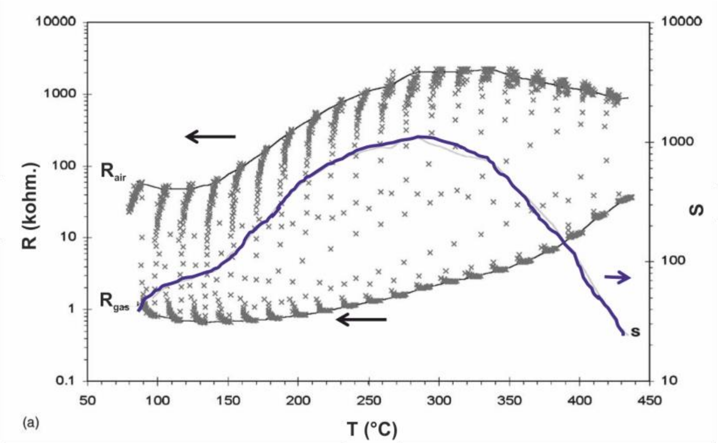


***Fig. 16 –** A typical output of `temperature scan method'. Horizontal axis represents temperature of chemiresistor and also time (both in linear scale), left vertical axis sensor resistance R and right vertical axis its dc-sensitivity* [29] S_{dc}.

Impedance of sensors, Nyquist plots [29]- During the impedance measurements real part Re (*z*) and imaginary part Im (*z*) of complex impedance (*z*) has been obtained as a function of measuring signal frequency. One of the possibilities of obtained data representation is to construct Nyquist diagram, i.e. to plot Im (*z*) vs. Re (*z*) dependence in Gaussian plane for different frequencies. The whole diagram is situated in IV. quadrant of Gaussian plane (positive real part and negative imaginary part of (*z*)), which corresponds to occurrence of resistances and capacities in equivalent circuit. The diagram consists of several arcs, partially overlapped. Increasing frequency of measuring signal corresponds to shift from the right to the left in the diagram.

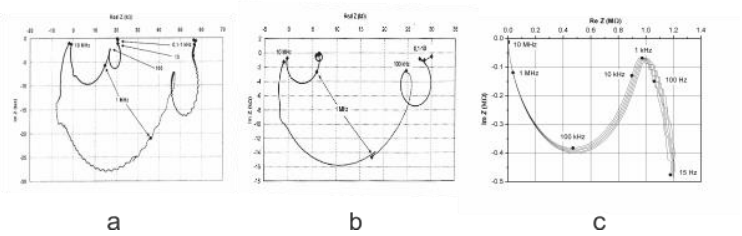


***Fig. 17** – Schematic view: Nyquist plots of chemiresistors with sensitive layers based on: a) metal oxide – SnO_2; b) organic non-polymeric complex – SnAcAc; c) organic polymer – PPy. Number of arcs in Nyquist plot and occurrence of low-frequency tail correspond to distinct charge transport mechanisms* [25] [29].

Phase-angle sensitivity (S_{pa}) [29] of chemiresistors is evaluated for given operating temperature of sensor and concentration of detected gas as follows:

- determine an argument of sensor complex impedance in air at given frequency of measuring signal according to equation $\theta_{air} = \arccos [(\mathrm{Re}\,(z_{air})) / |z_{air}|]$
- at the same frequency after atmosphere change determine an argument of sensor complex impedance in detected gas $\theta_{gas} = \arccos [(\mathrm{Re}\,(z_{gas})) / |z_{gas}|]$
- phase-angle sensitivity S_{pa} is a difference of these arguments:

$$S_{\mathrm{pa}}\left(t_{\mathrm{m}}, f, c_{\mathrm{gas}}\right) = \theta_{\mathrm{air}}(t_{\mathrm{m}}, f) - \theta_{\mathrm{gas}}\left(t_{\mathrm{m}}, f, c_{\mathrm{gas}}\right) \qquad (5)$$

Phase-angle sensitivity (in angle degrees or radians) is hence not only a function of sensor temperature t_m and concentration of detected gas c_{gas}, but also frequency of measuring signal *f*.

5. Future prospects: Comprehensive study of correlation between transduction mechanisms and macro-scale parameters

In order to better understand all the above mentioned transduction mechanisms (listed in Tab. 1), i.e. to explain physicochemical processes taking place in nano-scale during detection, and to better correlate them with macro-scale parameters of chemiresistor device, which are referred to in Chapter 4, a complex set of diagnostic methods and theoretical approaches is necessary. Nowadays, the monitoring of processes in "living" gas sensors is no longer an unsolvable problem [2, 3, 6].

Owing to dimensionality of the problem (Fig.18), the co-operation of surface-science specialists (they bring diagnostic tools for in-situ studying of gas-solid interfaces) with experts in nanotechnologies (technological background) and experts in measurement and interpretation of "macroscopic scale" chemiresistor response (area of measuring technique) is necessary.

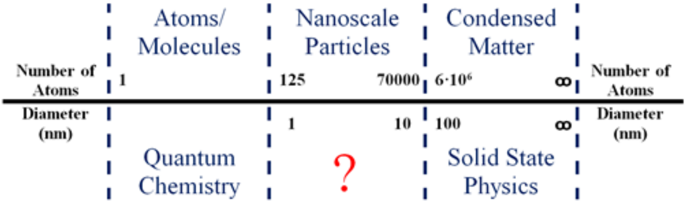


Fig. 18 – Size of nanostructured sensitive layers of chemiresistors compared with individual atoms and with bulk solids (up); approaches for their study (down) [2].

Nano-scale diagnostics - **To determine the total surface area of nanostructured sensitive layers** we can use **BET** (Brunnauer Emmet Teller) analysis. **TDS** (Thermal Desorption Spectroscopy) - with possibility of gradual thermal desorption of chemisorbed oxygen - serves for determination of total number of active sites for chemisorption; **SEM, AFM and STEM** (Scanning Transmission Electron Microscopy) techniques enable a detailed study of

morphology of sensitive layers; combination of **FIB** (Focused Ion Beam) and **EDX** (Energy-Dispersive X-ray analysis) is suitable for three-dimensional mapping of chemical composition; **EBIC** (Electron Beam Induced Current) - provides three-dimensional mapping of electric conductivity of nanostructured objects.
As for the **diagnostic methods characterizing chemisorption of gas analytes on surface of sensitive layer**, these are mainly spectroscopies performed not at high vacuum conditions, but at "elevated" pressure in residual atmosphere containing studied analyte. These methods have been developed to follow the physicochemistry of gas detection in real time and under operating conditions. A typical example of such spectroscopy is **NAP-XPS** (Near-Ambient Pressure X-ray Photoelectron Spectroscopy) – it enables in-situ studies of chemisorption of gaseous analytes. The total pressure of given analyte in measuring cell corresponds to its partial pressure at common atmosphere, when it is contained at concentrations of units of ppm. Other possibilities in this area are provided by in-situ performed **FTIR spectroscopy** and **Raman spectroscopy**, or **HREEL** (High Resolution Electron Energy Loss spectroscopy).

Macroscale diagnostics - For detailed analysis of detection properties in macroscale, it is necessary to measure following characteristics of chemiresistors: DC (i.e. amplitude) - sensitivity (S_{dc}) and its dependence on temperature t - from deconvolution of $S_{dc} = S_{dc}(t)$ plot to distinct peaks one can obtain information about detection mechanisms; **impedance spectra and phase sensitivity of chemiresistors** - in Nyquist plots, there are indices about both morphology of sensitive layers and the interaction between sensitive layer and gaseous analyte; **dynamics of sensor response - response and recovery time as a function of operation temperature** - from these data, kinetics of detection reactions and their activation energy will be obtained; **long-term stability of sensor parameters**.

Finally, all the obtained results should be analyzed and correlated, general consequences according to Fig. 19 can be formulated.

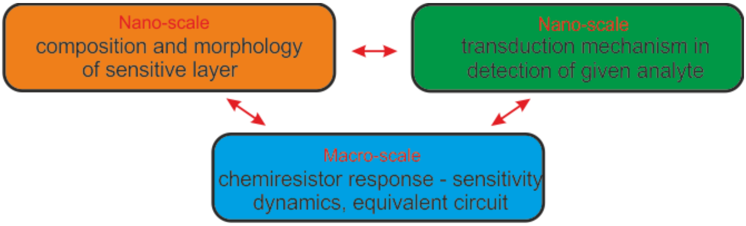


***Fig. 19** – General consequences amongst the parameters of chemiresistor.*

Eqs. (2) or (3) or determination of fractional exponent *n* according to Fig.14 provide possible theoretical approaches. These studies (accompanied by optimization of the deposition technology) will enable to suggest appropriate generalized principles (or findings), which should be followed when designing the next generations of chemiresistors with nanostructured sensitive layers.

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- research of both organic and inorganic materials for sensitive layers of gas sensors
- detection of toxic and combustible gases, chemical warfare agents and detection of taggants in explosives by chemiresistors

Research projects

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Graduate students during last 10 years (ING-3, PHD-4)

Jitka Kopecká (Ph.D. 2015) *1-D structures of conductive polymers for chemical sensors*, Pavel Horák (Ph.D. 2015) *Preparation and characterization of metal oxide-based nanostructures for gas sensing application*, Jan Vlček (Ph.D. 2014) *Study of nanostructured diamond layers*, Lukáš Rusyniak (Ing. 2010) *Impedance measurement of chemical gas sensors*, Dušan Kopecký (Ph.D. 2009) *Chemical gas sensors with active layers based on organic substances*, Jan Vlček (Ing. 2009) *Preparation of thin films by pulsed laser deposition method*, Dušan Kopecký (Ing. 2006) *Chemical gas sensors with polymeric active layer deposited by MAPLE technology*

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