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**IMPEDANCE A FÁZOVÁ CITLIVOST CHEMICKÝCH VODIVOSTNÍCH  
SENZORŮ**

**IMPEDANCE AND PHASE-ANGLE SENSITIVITY OF CHEMICAL GAS  
SENSORS**

## Summary

Chemical gas sensor developed for detection of reactive gases, which is working on the principle of electron exchange between analysed gas and semiconductive active layer, is an object of intensive research for several decades. At present there are commercially available devices containing chemical gas sensors. Nevertheless, plenty of problems concerning sensors has not been solved yet: new, above all organic materials and biomaterials for active layer are intensively examined; the technologies of their deposition are optimised and the possibilities of improving selectivity are investigated.

The measurement of impedance has been selected as a tool for study of chemical gas sensors, because of its broad applicability and also capability to give us information concerning both sensor (type of material in active layer, material morphology – grain size, mechanisms of charge transport in active layer and electrical behaviour of contacts to active layer) and detected gas (various phase-angle sensitivity to different gases, possibility to distinguish amongst gases according to dipole moment of their molecules).

The presented contribution deals with measurement of impedance of sensors with both inorganic and organic active layers, representation of obtained data by Nyquist diagrams and introduction of the so called phase-angle sensitivity. Further, we have studied dependence of phase-angle sensitivity on frequency and amplitude of measuring signal, chemical composition of active layer, parameters of activation process and composition of reference atmosphere to which sensitivity is related. The relation between chemical and physico-chemical properties of substances taking part in the detection process on one side and electrical behaviour of sensor on the other side are also discussed in general terms.

## Souhrn

Chemický vodivostní senzor určený pro detekci reaktivních plynů, který pracuje na principu výměny elektronů mezi analyzovaným plynem a polovodičovou aktivní vrstvou, je předmětem výzkumu již po několik desetiletí. V současné době jsou běžně komerčně dostupné přístroje obsahující chemické senzory plynů. Přesto zůstává řada problémů v této oblasti nedořešená: intenzivně se studují nové, především organické materiály a biomateriály pro aktivní vrstvu, optimalizují se technologie jejich deposice, hledají se způsoby zvýšení selektivity senzorů.

Měření impedance bylo zvoleno jako metoda studia chemických vodivostních senzorů, neboť je to nástroj se širokým využitím, schopný poskytnout údaje jak o senzoru (typ materiálu aktivní vrstvy, jeho morfologie – velikost zrn, informace o mechanismech přenosu náboje v aktivní vrstvě a chování kontaktů na aktivní vrstvu), tak i o detekovaném plynu (různá fázová citlivost na jednotlivé plyny, možnost rozlišení mezi plyny podle velikosti dipólového momentu jejich molekul).

Předkládaná práce se věnuje měření impedance senzorů s anorganickými i organickými aktivními vrstvami, reprezentaci získaných dat pomocí Nyquistových diagramů a zavedení tzv. fázové citlivosti. Dále se zkoumá závislost fázové citlivosti na frekvenci a amplitudě měřicího signálu, chemickém složení aktivní vrstvy, technologii aktivace a druhu referenční atmosféry. V obecné rovině jsou diskutovány souvislosti mezi chemickými a fyzikálně chemickými vlastnostmi látek zúčastněných v procesu detekce a elektrickým chováním senzoru.

**Klíčová slova:**

chemický vodivostní senzor, oxidické a acetylacetonátové aktivní vrstvy, impedance, Nyquistovy diagramy, fázová citlivost, vliv složení aktivní vrstvy a detekovaného plynu na fázovou citlivost

**Key words:**

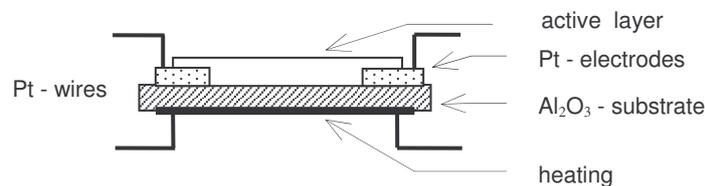
chemical gas sensor, oxidic and acetylacetic active layers, impedance, Nyquist diagrams, phase-angle sensitivity, influence of both active layer and detected gas composition on phase-angle sensitivity

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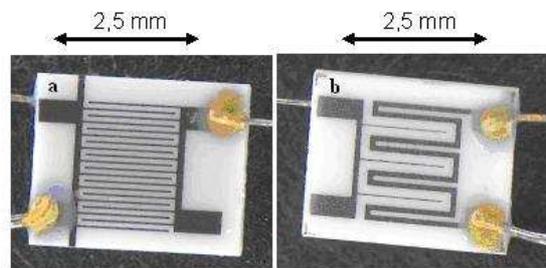
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## 1. Chemical gas sensors

Chemical gas sensors (CGS) are sensors that have an ability to transform chemical input quantity – concentration of detected gas - into electrical output quantity – change of electrical resistance or impedance. CGS are based on interaction of solid-state active layer with surrounding gaseous atmosphere. The active layer does not change its chemical composition during detection process, it only interchanges either directly or intermediately electrons with molecules of detected gases. Thus only reducing (their molecules act as donors of electrons) or oxidizing (acceptors of electrons) gases are detectable. Electric properties of active layer can be described by theory of semiconductors. The schematic arrangement of planar CGS is depicted in Fig. 1, its real appearance in Fig. 2.



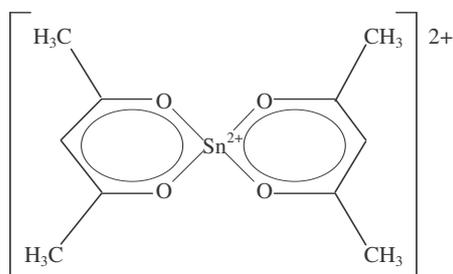
**Fig. 1** - Schematic arrangement of chemical gas sensor.



**Fig. 2** - Real appearance of the sensor chip: a) platinum measuring electrodes on the front side; b) resistive heating on the back side.

The sensor substrates are chips having dimensions approx. 2.5 x 2.5 mm 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 and resistive heating on the back side. Heating serves for adjustment of sensor working temperature. Each interdigital electrode has 10 “combs” and their distance is 40  $\mu$ m. The basic material of sensor active layer was deposited on the chips by Pulsed Laser Deposition (PLD) method employing KrF excimer laser. The deposition was carried out from targets of source materials, which can be divided in two categories: a) inorganic materials - namely oxides of some transition metals (such as SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, NiO,

TiO<sub>2</sub>); b) organic metal complexes – acetylacetonates of tin, indium, iron (SnAcAc, InAcAc, FeAcAc). Structural formula of tin acetylacetonate is in Fig. 3. Chemical composition of basic material is modified in some extent during PLD. Major modification is typical for organic substances in category b) of course.



**Fig. 3** - Structural formula of tin acetylacetonate – SnAcAc (bis(penta-2,4-dionato stannic cation)).

Besides the basic material, active layer may also contain dopants added to its “volume” and catalyst – elemental noble metal sputtered to its surface. The as-deposited active layer is not able to detect gases at all, or it exhibits some sensitivity, but the values of its physical and physico-chemical parameters are very unstable in time. The next step hence must be the so-called “activation” of sensor; it means further technological treatment (temperature cycles, cyclic changing of surrounding atmosphere composition, long-term heating to working temperature etc.). The aim of all these procedures is to shift material of active layer nearer to thermodynamical equilibrium and to terminate significant chemical, thermodynamical and crystallographical changes in it even before practical sensor operation.

## 2. Electrical properties of chemical gas sensors

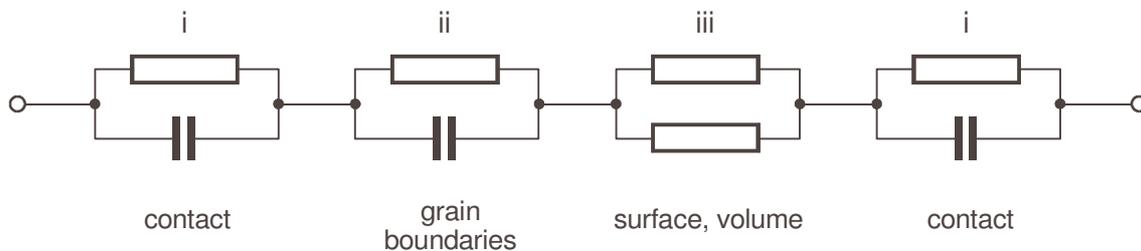
### 2.1 Impedance measurements as a tool of characterization of CGS

The above mentioned sensor system or more precisely its active layer can be characterized by studying its: a) morphology (SEM, AFM methods); b) chemical composition (FTIR, XPS methods); c) electrical properties (measuring of electrical resistance or impedance). It is important, however, that impedance measurement is capable to provide information concerning all these three areas. As it will be explained later, on basis of impedance measurements we can presume the dimensions of grains in active layer material and we are also

able to find differences in charge transfer mechanisms between inorganic and organic layers. Last, but not least, the phase-angle sensitivity, which has not been applied in chemical gas sensors yet, is also defined from impedance. The themes of presented paper are just impedance measurements and phase-angle sensitivity of CGS.

## 2.2 Equivalent circuit of sensors

The electrical properties of chemical gas sensors can be represented by simple equivalent circuit [1] depicted in Fig. 4. In this circuit there are series of parallel RC-elements corresponding to: (i) Schottky contacts between electrode and active layer, (ii) grain boundaries in active layer (when the typical grain dimension is higher than Debye length ( $\lambda_D$ )) and (iii) parallel combination of resistances of active layer “surface” and “volume” (Fig. 4).



**Fig. 4** - Equivalent circuit of CGS with active layer based on inorganic material and Schottky contacts between electrode and active layer.

The interaction of sensor system with detected gas can be formally described as a change of equivalent circuit parameters. But on the other side the values of equivalent circuit parameters are strongly affected by technology of active layer preparation and its consequent structure. Now we can briefly discuss (i), (ii) and (iii) contributions to equivalent circuit in dependence on technology and concrete arrangement of sensor. The findings in this chapter are also illustrated by Fig. 5.

- (i) contribution of contacts between measuring electrodes and active layer – Each sensor has to have at least two contacts to active layer enabling to measure its resistance or impedance. The behaviour of these contacts can be theoretically expressed by two extremes: a) Schottky contact contributes to equivalent circuit by parallel combination of resistance and capacity; b) ohmic contact is represented only by resistance. Reference [2] studies behaviour of Pt-TiO<sub>2</sub> contact. For as-deposited platinum and temperature lower than 450 °C the contact exhibits Schottky character. However, when the contact is submitted to annealing at 800 °C in oxygen (or in the air), it becomes ohmic by irreversible process. At low temperatures in as-

deposited state platinum atoms on surface act as acceptors in n-type intrinsic TiO<sub>2</sub>. The original Pt<sup>0</sup> atoms on substrate surface are oxidized to Pt<sup>2+</sup> ions during annealing. The cations have significantly lower radius in comparison with original atoms and hence they easily diffuse into volume of TiO<sub>2</sub>. Here Pt<sup>2+</sup> cations are trapped as isoelectronic Pt<sup>4+</sup> cation (isoelectronic with Ti<sup>4+</sup> contained in TiO<sub>2</sub>) releasing simultaneously two electrons, so they behave as donors (in contrary to Pt<sup>0</sup>). Pt<sup>4+</sup> ion is presented mostly in interstitial positions. This is the reason for irreversible change from Schottky to ohmic character of contact during thermal activation of sensors.

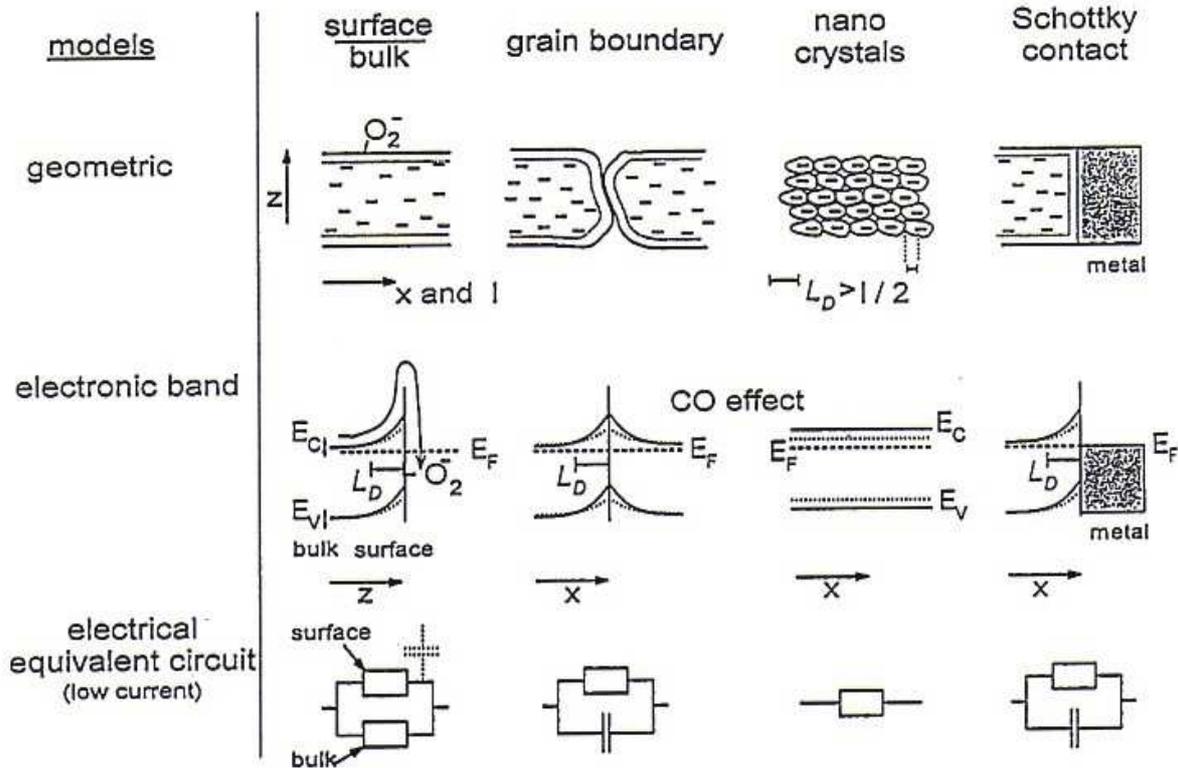
In our case we have a very similar Pt-SnO<sub>2</sub> contact system. Tin dioxide has narrower band-gap than titanium dioxide, so the transformation to ohmic behaviour is even easier. It is supposed that the Pt-SnO<sub>2</sub> contacts become ohmic at temperature 600 °C used for activation of our oxide-based sensors.

- (ii) grain boundaries contribution – It is well known, that active layer of CGS has always polycrystalline character. Typical dimension of individual grains and its relation to Debye length ( $\lambda_D$ ) is the crucial parameter in polycrystalline material. Debye length is a width of depleted region, which is formed as a result of bonding free electrons after chemisorption of electronegative oxygen atoms to grain surface. If the grain dimensions are larger than Debye length, then in “common” detection atmosphere containing excessive oxygen potential barriers on grain boundaries are formed and the behaviour of these boundaries corresponds to a parallel combination of resistance and capacity. If the grain dimensions are smaller than  $\lambda_D$  (which means that active layer contains the so called nanocrystals), potential barriers on grain boundaries are not present, boundary capacity disappears and active layer behaves as a pure resistor. That is unambiguously convenient for measurement by dc-signal.

For a given material the value of Debye length for electrons is a decreasing function of temperature (e.g. for SnO<sub>2</sub> at  $T = 600$  K is corresponding  $\lambda_D = 25$  nm). The critical grain dimension also depends on concentration of dopants because material doped by acceptors has lower electron concentration and material doped by donors has higher electron concentration. For example in the aforementioned SnO<sub>2</sub> Debye length can be enlarged by dotation of acceptor Al up to 100 nm at  $T = 600$  K. On the contrary, dotation by donor e.g. Sb would be inconvenient in this case. The theory of grain boundaries behaviour is detailed in [3].

- (iii) resistance of active layer “surface” and “volume” – The mutual relation between the influence of surface and volume of active layer on resulting properties is dependent on its thickness. There are differences between thick-layer (influence of volume is dominating) and thin-layer (influence of

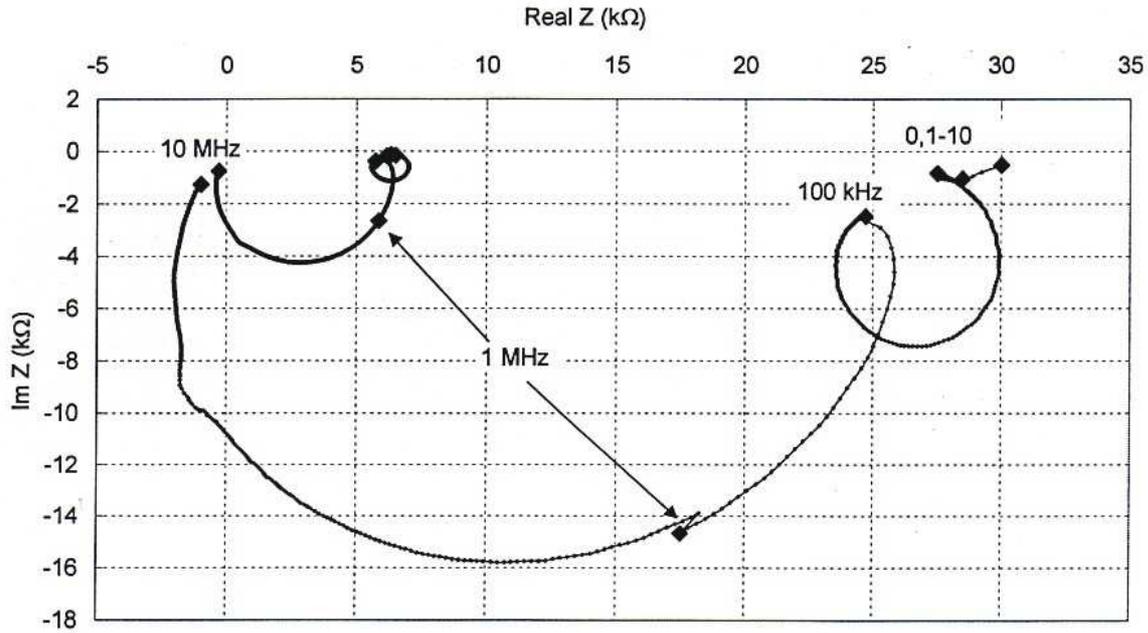
surface) sensors. It is difficult to distinguish them strictly, but our sensors with active layer thickness 100-500 nm are considered as thin-layer ones.



**Fig. 5** - Influence of active layer morphology (upper part) on band structure (middle part) and contribution to equivalent circuit (downer part) [1]. The contribution to equivalent circuit is valid for measurement with low voltage.

### 2.3 Nyquist diagrams, determination of equivalent circuit parameters

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. A typical appearance of Nyquist diagram of chemical gas sensor is in Fig. 6. 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 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.



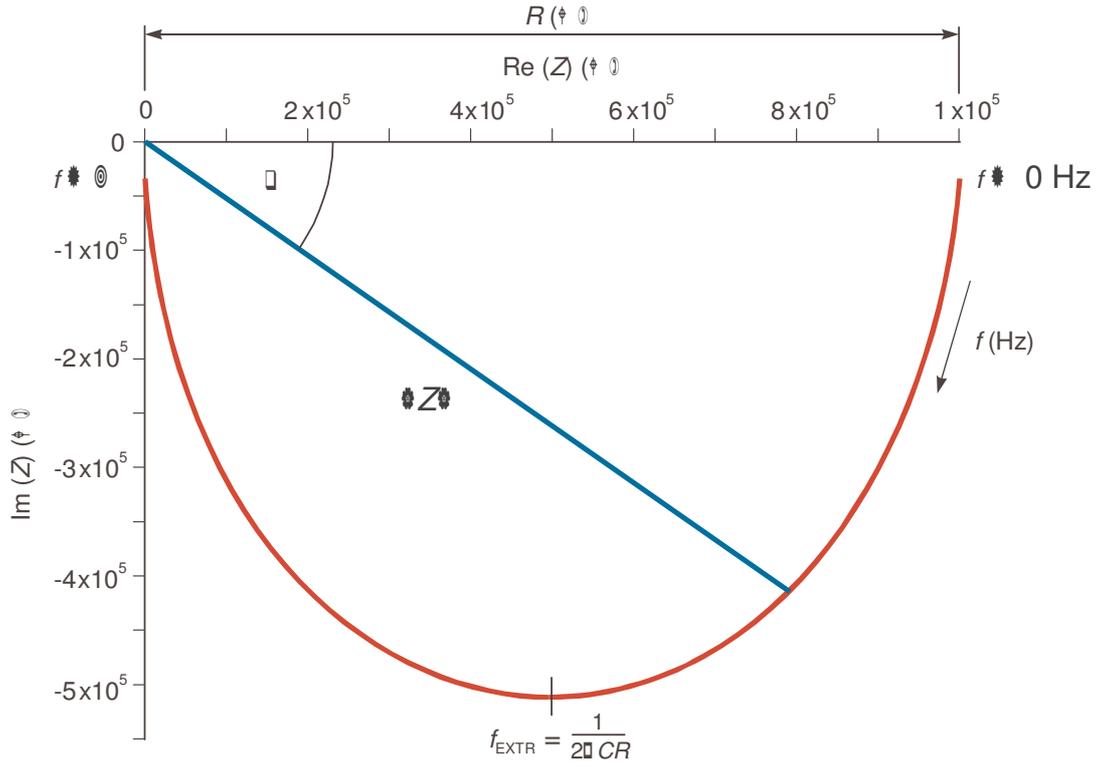
**Fig. 6** - Nyquist diagram of sensor based on SnAcAc in synthetic air (outer arcs) and 1000 ppm of hydrogen (inner arcs). Variable frequency is a parameter of points in this diagram.

Using symbolic calculus for ac-circuits one can deduce that each parallel RC-element is represented by one semicircle (arc). It stands that the diameter of semicircle equals value of resistance ( $R$ ) and simultaneously frequency corresponding to  $\text{Im}(z)$  extreme, i.e. the lowest point of semicircle fulfils condition (1):

$$f_{EXTR} = \frac{1}{2\pi CR} \quad (1)$$

From this condition the procedure of determining of equivalent circuit parameters from Nyquist diagram is derived (see also Fig. 7):

- in given coordinates the diameter of semicircle equals resistance  $R$
- then the frequency of testing signal  $f_{extr}$  corresponding to the lowest point of semicircle is determined
- according to equation (1) capacity  $C$  is calculated.



**Fig. 7-** Determining of parameters  $R, C$  of equivalent circuit from Nyquist diagram.

## 2.4 Definition of phase-angle sensitivity of CGS

In Nyquist diagram there are values of sensor complex impedance ( $z$ ) plotted in dependence on frequency in Gaussian plane. It stands for each point that absolute value of complex impedance  $|z|$  is the distance of this point from zero, i.e.:

$$|z| = \sqrt{(\text{Re}(z))^2 + (\text{Im}(z))^2} \quad (2)$$

The argument of complex impedance  $z$  is an angle  $\theta$  which is given by connecting line between zero of Gaussian plane and representation of  $z$  and positive half-axis of real axis. Hence it stands:

$$\theta = \arccos\left(\frac{\text{Re}(z)}{|z|}\right) \quad (3)$$

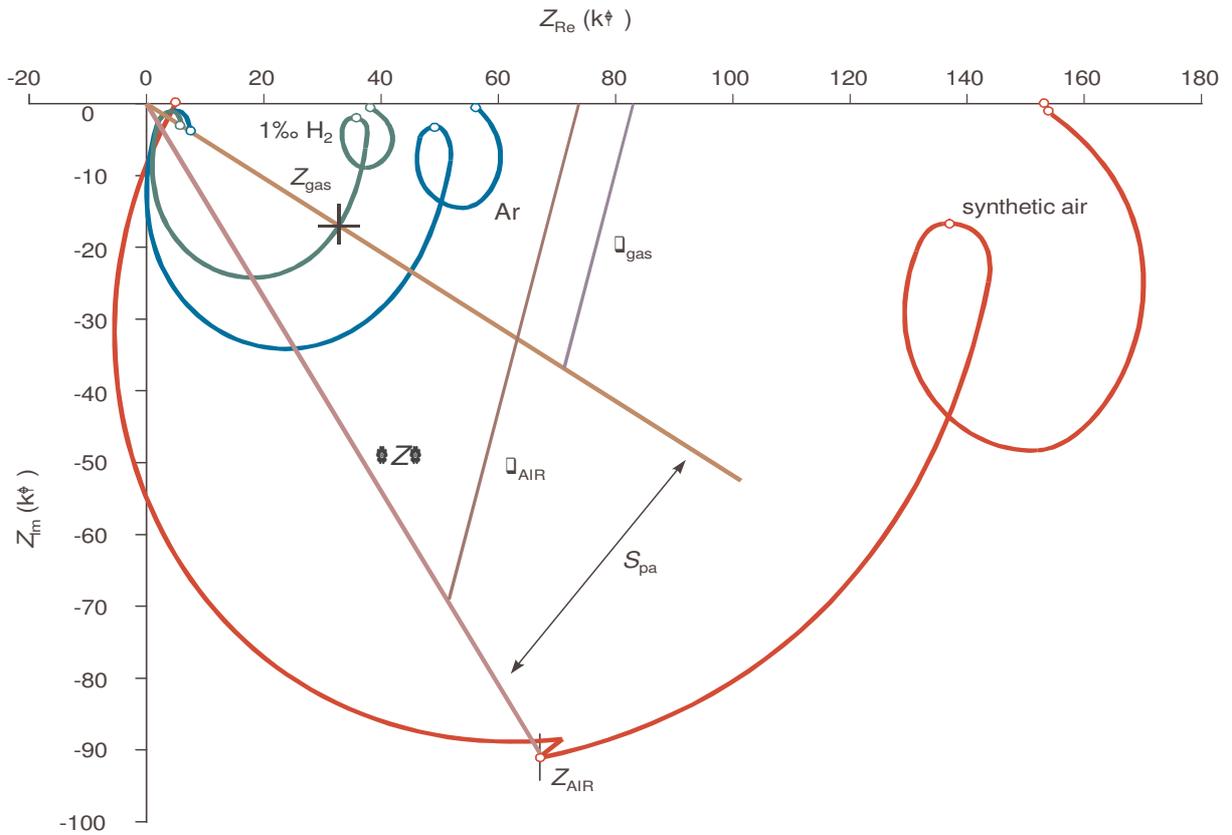
The argument of complex impedance simultaneously corresponds to current-voltage phase shift (for CGS current always leads voltage, because of occurrence of capacities and not inductances in equivalent circuit).

The phase-angle sensitivity of CGS is defined for given temperature and concentration of detected gas as follows:

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

$$S_{pa} = \theta_{air} - \theta_{gas} \quad (t, c_{gas}, f) \quad (4)$$

Phase-angle sensitivity (stated in degrees or radians) is hence not only a function of temperature and concentration of detected gas, but also of measuring signal frequency. All procedure of  $S_{pa}$  determining is illustrated in Fig. 8.



**Fig. 8** - Determination of phase-angle sensitivity  $S_{pa}$ . The figure depicts Nyquist diagrams of  $\text{SnO}_2 / \text{Pd}$  sensor at working temperature  $350^\circ\text{C}$ . There are three diagrams: a) response to 1000 ppm of hydrogen (the smallest arcs); b) pure argon (middle arcs) and c) synthetic air (the largest arcs). Argument of sensor complex impedance in 1000 ppm of hydrogen is marked as  $\theta_{gas}$ , argument of complex impedance in synthetic air as  $\theta_{air}$ . Phase-angle sensitivity  $S_{pa}$  is than a difference of these two angles. The determination was carried out at frequency of 1 MHz.

The main reason for introduction of a new quantity – phase-angle sensitivity - is in ability to measure current-voltage phase shift with high accuracy. Thus the measurement by ac-signal gives us chance to consider processes proceeding in active layer, structure of active layer and finally to increase sensor sensitivity.

### 3. Experimental

The measurement of impedance has been carried out in a workstation, which is placed in Department of Solid-State Engineering ICT Prague. The fundament of workstation is an impedance analyser HP4192A LF (Hewlett Packard).

Impedance analyser HP4192A LF is fully automatized, highly accurate apparatus for measurement of the following impedance parameters: absolute value of complex impedance ( $|z|$ ), absolute value of admittance ( $|Y|$ ), phase angle ( $\theta$ ), resistance ( $R$ ), reactance ( $X$ ), conductance ( $G$ ), susceptance ( $B$ ), inductance ( $L$ ), capacity ( $C$ ), dissipation factor ( $D$ ) and quality factor ( $Q$ ).

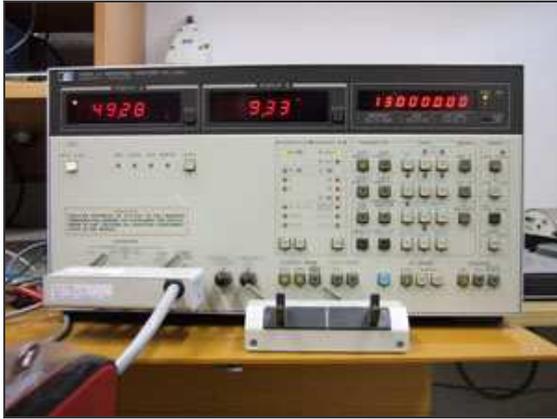
The apparatus can measure absolute value of impedance in the range from 0.1 m $\Omega$  to 1.2999 M $\Omega$  with maximal resolution 100  $\mu\Omega$ , phase angle varying from  $-180$  to  $+180$  degrees with resolution of 0.01 degree. Frequency range is from 5 Hz to 13 MHz with resolution of 1 mHz.

For measurement of CGS the amplitude of testing signal was set from 10 to 500 mV and its frequency changed in 10 Hz – 10 MHz range. Two separate measurements were carried out: Re ( $z$ ) vs. frequency and Im ( $z$ ) vs. frequency.

The apparatus was connected with PC through HP-IB interface that enables to display results of measurement in real time by program in LabVIEW version 7.1. The analyser is also equipped with professional 1 m long shielded cables with BNC connectors (HP 16048A). They serve for connecting between analyser and measuring device.

During the measurement, sensor is placed in measuring device, i.e. shielded box with measuring chamber inside (Fig. 10). The wire outlets from measuring chamber are symmetric without parasitic capacities. The chamber also has cables for sensor heating power supply and cables for reading the sensor signal. There is also gas distribution – teflon tubing for gas inlet and outlet.

The workstation also has multimeter METEX M-4640A for measurement of voltage drop on sensor heating, laboratory power source for heating and membrane pump.



**Fig. 9** - HP4192A imp. analyser.



**Fig. 10** - Detail view of measuring device.

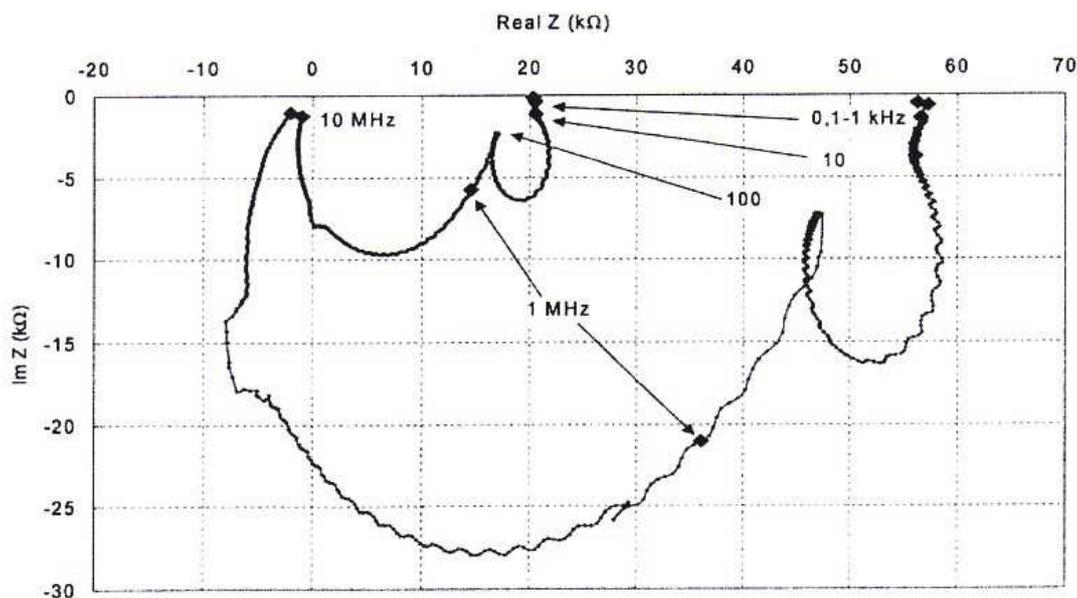
## 4. Results

### 4.1 Nyquist diagrams of sensors with a single-component active layer

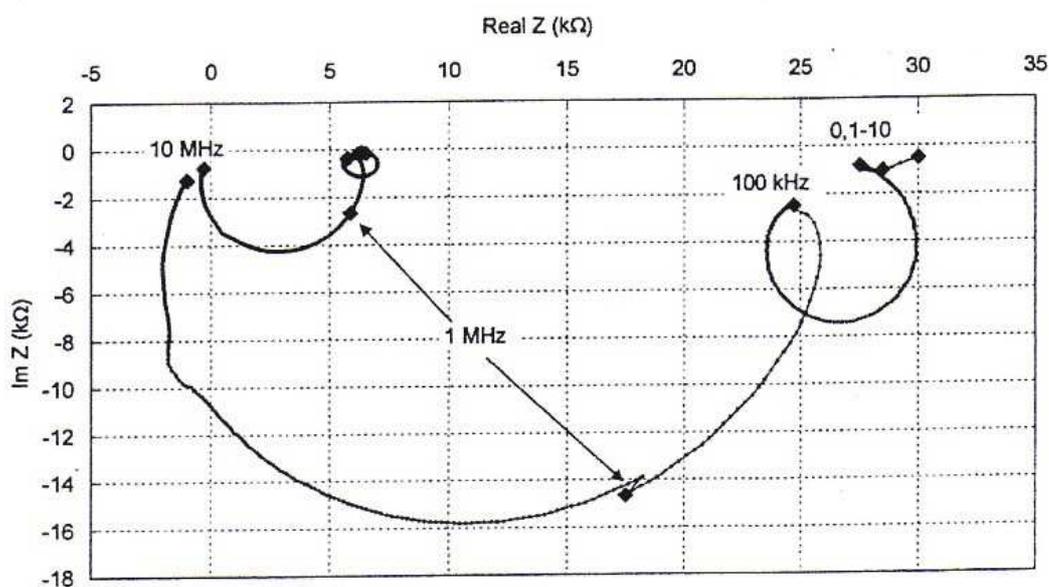
An extensive set of experiments was carried out on the above-described workstation and the impedance of approximately 50 sensors with variable composition of active layers was measured. At the beginning of experiments only sensors with single-component active layer (i.e. oxide or acetylacetonate) were investigated, but later also sensors with active layers containing various dopants and catalysts. In all cases sensor impedance as a function of measuring signal frequency was measured and Nyquist diagrams were constructed.

As the extent of this contribution is limited, we will discuss in detail only Nyquist diagrams of sensors containing single-component active layer, i.e. basic material. Also general trends will be illustrated here. Figs. 11 and 12 compare Nyquist diagrams of sensors with active layer based on pure  $\text{SnO}_2$  and  $\text{SnAcAc}$ . The measurements were carried out in two-wire arrangement in frequency range 100 Hz – 10 MHz for both “pure” synthetic air and 1000 ppm of hydrogen in synthetic air. The testing confirmed that the character of diagrams is practically independent on amplitude of testing signal. In the amplitude range 10-500 mV the absolute value of complex impedance varied less than 5 % relatively.

The absolute value of sensor impedance in 1000 ppm of hydrogen is always lower than in “pure” synthetic air (in limitary case for frequency of testing signal  $f \rightarrow 0$  Hz only real part of complex impedance i.e. resistance is measured and because of detection of reducing gas on n-type semiconductor, the following relation  $R_{air} > R_{gas}$  must be valid).



**Fig. 11-** Nyquist diagram of sensor with active layer based on pure  $\text{SnO}_2$  at working temperature of  $570\text{ }^\circ\text{C}$ . Outer arcs correspond to “pure” synthetic air and inner arcs to 1000 ppm of hydrogen in synthetic air.



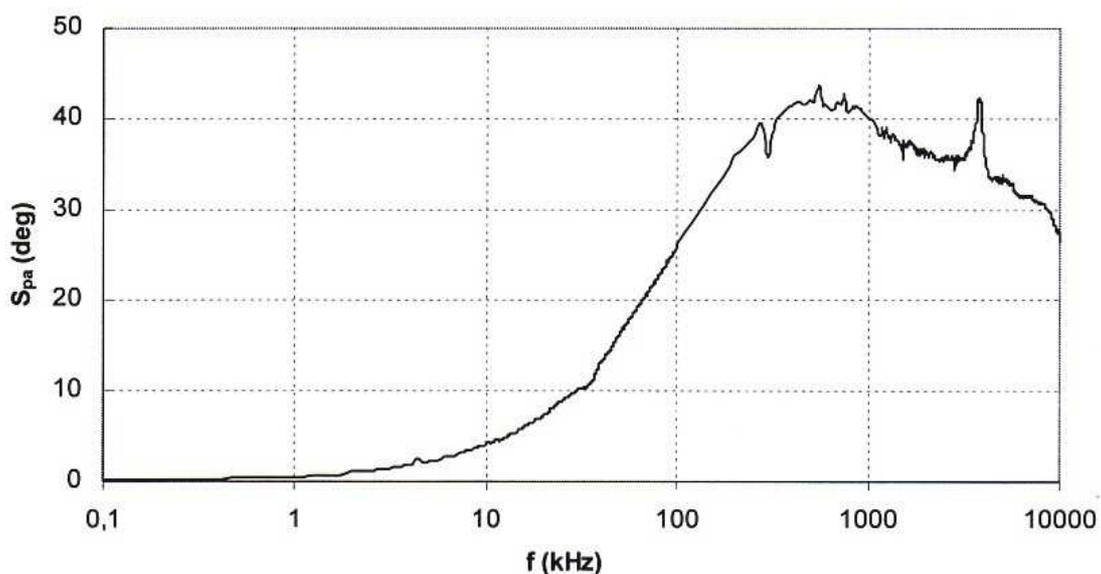
**Fig. 12-** Nyquist diagram of sensor with active layer based on  $\text{SnAcAc}$  at working temperature of  $430\text{ }^\circ\text{C}$ . Outer arcs correspond to “pure” synthetic air and inner arcs to 1000 ppm of hydrogen in synthetic air.

As mentioned above, according to the theory each arc corresponds to one parallel RC-element in equivalent circuit. It was proved that in the selected scale all Nyquist diagrams of  $\text{SnO}_2$  (inorganic material) based sensors have two arcs (Fig. 11), while the diagrams of  $\text{SnAcAc}$  (organic metal complex) based sensors have the third arc at low frequencies (from 100 Hz to 10 kHz) –see Fig. 12.

Explanation of this behaviour is presented in [5]. The contacts between platinum electrodes on chip and active layer are ohmic at least in case of SnO<sub>2</sub> layers submitted to previous thermal activation and hence can be represented by resistor in equivalent circuit. Under these circumstances, there are still two remaining “candidates” for creation of RC-elements in equivalent circuit: (a) depleted regions in grain boundaries – the grain dimensions are larger than Debye length in our case; that was also proved by SEM; (b) existence of another, slow charge transport mechanism, namely ionic conductivity of active layer (commercially produced acetylacetonates were used; they contain compensative Cl<sup>-</sup> and Br<sup>-</sup> anions in concentrations of several weight percent. The occurrence of the third arc can be explained according to our hypothesis by existence of movable dipoles in polar molecules of acetylacetonates. These dipoles are able to synchronize their movement with external measuring signal up to frequencies of approx. 10 kHz.

#### 4.2 Phase-angle sensitivity in dependence on active layer composition

Phase-angle sensitivity  $S_{pa}$  was subsequently evaluated from Nyquist diagrams. This quantity also depends on measuring signal frequency (Fig. 13) and working temperature of sensor. Both organic and inorganic layers achieve maxima of  $S_{pa}$  values at 700 kHz frequency (22 °C), at 1 MHz frequency (300 °C) and 3 MHz frequency (570 °C). All of the further presented  $S_{pa}$  values were evaluated at frequency of 1 MHz because of unambiguous graph interpretation in its neighbourhood (1 MHz is out of region of arcs overlap).



**Fig. 13** - Phase-angle sensitivity  $S_{pa}$  vs. measuring signal frequency dependence for sensor with active layer based on pure SnO<sub>2</sub> (working temperature 280 °C, 1000 ppm of hydrogen, reference gas synthetic air).

The values of phase-angle sensitivity for various composition of active layer are summarized in Table 1 (previously published in [5]). The following conclusions can be made from these data: (i) low-temperature phase-angle sensitivity of single-component active layers containing only basic material is negligible; (ii) the addition of dopants and catalysts leads to significant increase of low-temperature  $S_{pa}$  and namely SnO<sub>2</sub>/Pd, SnO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>/Pd and SnAcAc/FeAcAc/Pd systems exhibit  $S_{pa} = 11.4 - 36.0$  deg.; (iii) at sufficiently high working temperatures (for pure SnO<sub>2</sub> it means even 570 °C) all sensor systems in Table 1 achieve  $S_{pa} > 10$  deg., (iv) there is no correlation between dc-sensitivity and phase-angle sensitivity values, but for some applications, such as increasing sensor selectivity or processing of signal from sensor array, it may be paradoxically advantageous.

Material	$S_{pa}$ (deg) at 22 °C	$S_{pa}$ (deg) at $T_{max}$ (°C)	$S_{dc}$ at $T_{max}$ (°C)
SnO <sub>2</sub>	≈ 0	10.3 (571)	5 (571)
SnO <sub>2</sub> / Pd	36.2	40.1 (284)	1100 (284)
SnO <sub>2</sub> / Fe <sub>2</sub> O <sub>3</sub> / Pd	11.4	24.3 (105)	1130 (105)
SnAcAc	≈ 0	16.7 (430)	28 (430)
SnAcAc / Pd	5.6	10.2 (383)	174 (383)
SnAcAc/ FeAcAc/ Pd	12.0	36.7 (413)	111 (413)

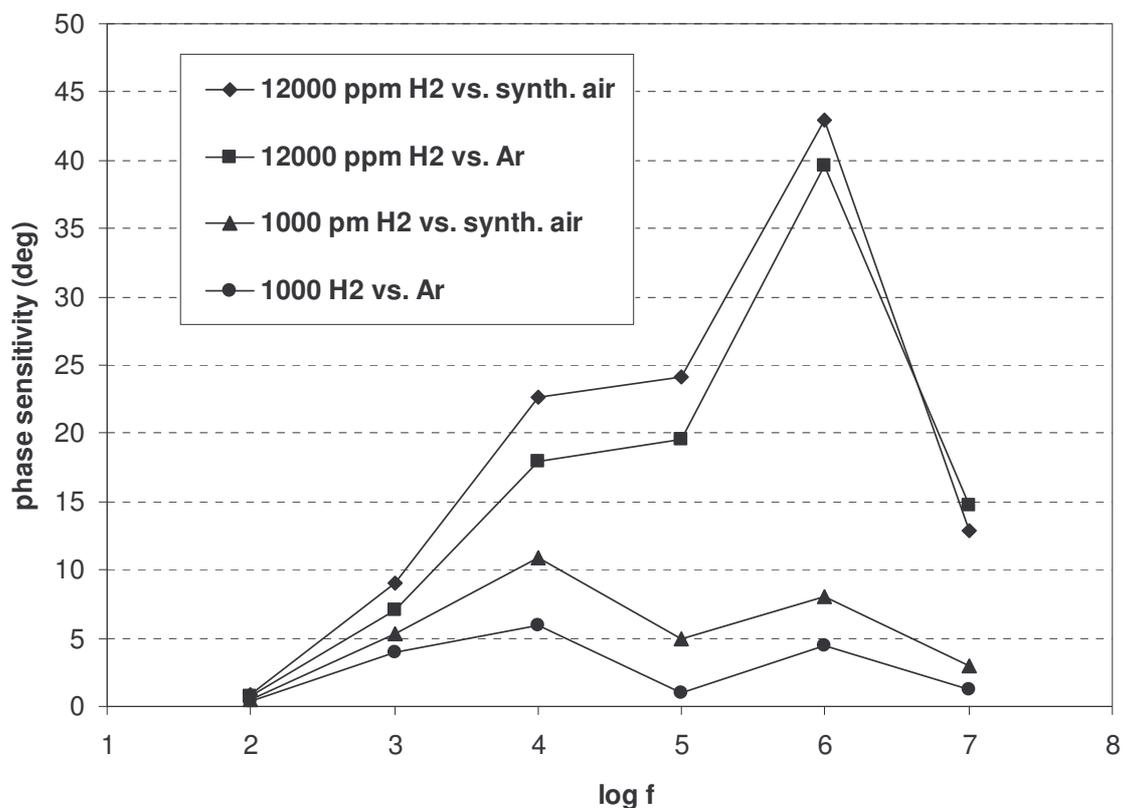
**Table 1** - Overview of phase-angle sensitivity  $S_{pa}$  (measured at 1 MHz) and dc-sensitivity  $S_{dc}$  to 1000 ppm of hydrogen (reference gas synthetic air in both cases). DC-sensitivity  $S_{dc}$  is defined as a ratio of sensor resistance in synthetic air and in hydrogen,  $T_{max}$  is temperature of maximal dc-sensitivity for given sensor.

### 4.3 Phase-angle sensitivity in dependence on reference atmosphere

In the next stage of research [6] we investigated wider spectrum of reference atmospheres to which  $S_{pa}$  can be related. Besides synthetic air and synthetic air with 1000 ppm of hydrogen also pure argon and 12 % of hydrogen in argon was utilized. It is important from the methodical point of view that these newly utilized atmospheres do not contain oxygen. Pure argon – inert gas sorbs to active layer without electron exchange and hence it serves as absolute etalon, to which reducing (gas acts as electron donor) or oxidizing (gas acts as electron acceptor) behaviour can be related. Hydrogen in argon is an example of strongly reducing atmosphere. The above-presented Fig. 8 (in chapter 2.4)

depicts Nyquist diagram of SnAcAc for synthetic air, argon and 1000 ppm of hydrogen in synthetic air. The absolute value of complex impedance decreases in sequence: synthetic air > argon > 1000 ppm of hydrogen in synthetic air. This is also a sequence of increasing reducing properties. That is the reason why phase-angle sensitivity is always higher when related to synthetic air than related to argon.

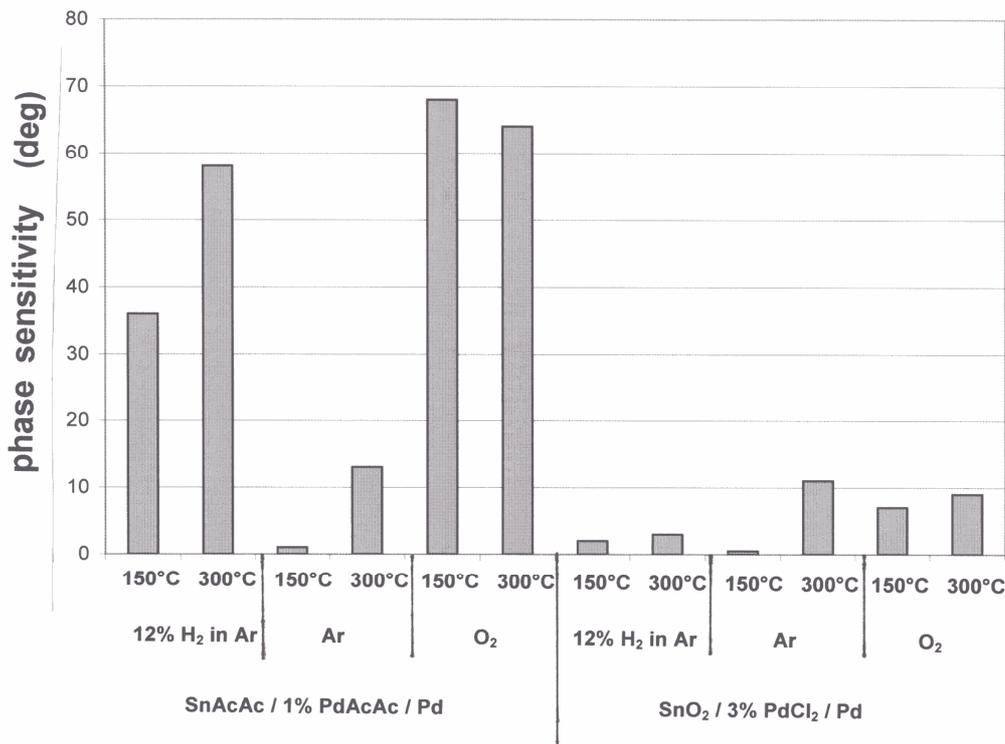
Fig. 14 presents comparison of phase-angle sensitivity  $S_{pa}$  achieved during the detection of 12 000 ppm or 1 000 ppm of hydrogen in relation to argon or to synthetic air. These measurements were carried out for sensors based on both SnAcAc and SnO<sub>2</sub> (not presented here). It is apparent that there exists either absolute or at least local maximum of  $S_{pa}$  on frequency 1 MHz (verification of previous frequency selection for  $S_{pa}$  measurement).



**Fig. 14** - Phase-angle sensitivity  $S_{pa}$  of SnAcAc based sensor vs. frequency (detection of 12 000 ppm or 1 000 ppm of hydrogen, working temperature 430 °C). Phase-angle sensitivity is calculated in relation to both synthetic air and argon.

#### 4.4 Phase-angle sensitivity in dependence on parameters of sensor technology

Finally also the influence of parameters of sensor activation process on phase-angle sensitivity was investigated. The activation was carried out in three atmospheres: (a) 12% of H<sub>2</sub> in Ar; (b) pure Ar and (c) pure O<sub>2</sub>. The results are summarized in Fig. 15 [6-7]. It is apparent that: (i) in general, higher  $S_{pa}$  values were achieved by SnAcAc based systems; (ii) the best activation atmosphere (with respect to  $S_{pa}$ ) was pure oxygen.



**Fig. 15-** Phase-angle sensitivity of SnAcAc based systems (left) and SnO<sub>2</sub> based systems (right) in dependence on composition of activation atmosphere (12 % of H<sub>2</sub> in Ar or pure Ar or pure O<sub>2</sub>) and activation temperature (150 °C or 300 °C).

#### 5. Conclusions

The presented contribution is a result of systematic research in the field of impedance properties of chemical gas sensors. The topic taken from references [1-4] dealing with possibility of sensor impedance measurement and interpretation of obtained results was firstly applied to our samples (sensors with active layers based on oxides and acetylacetonates of metals prepared by pulsed laser deposition method).

The main results can be summarized (according to the chronology of research) into the following points:

- (i) investigation of impedance properties of sensors with organic active layers (acetylacetonates of tin, iron and palladium [5] and [8])
- (ii) finding and description of differences in Nyquist diagrams between oxidic and acetylacetic systems (organic active layers have contribution to impedance apparent at low frequencies 100 Hz – 1 kHz in the air, which is connected with the existence of movable dipoles in their molecules)
- (iii) introduction of phase-angle sensitivity  $S_{pa}$ , which is defined on basis of change of current-voltage phase shift on sensor in dependence on surrounding atmosphere composition
- (iv) investigation of  $S_{pa}$  vs. measuring signal frequency dependence (it was shown that optimal frequency for evaluation of  $S_{pa}$  is 1 MHz) and  $S_{pa}$  vs. measuring signal amplitude (change of amplitude in the range of 10 mV - 500 mV has no considerable effect on  $S_{pa}$  value)
- (v) studying of  $S_{pa}$  for various chemical composition of active layer (single-component or multicomponent layer; influence of dopants and catalysts; the highest phase-angle sensitivity was found in SnAcAc / 1% PdAcAc / Pd layer; investigation of dependence of  $S_{pa}$  on activation technology (namely composition of activating atmosphere and temperature of activation – optimal results yielded oxygen activation atmosphere; measuring of  $S_{pa}$  for various reference atmospheres (synthetic air or argon)
- (vi) finding of systems with low-temperature sensitivity (e.g. SnO<sub>2</sub> / Pd or SnAcAc / PdAcAc / Pd – see Table 1); they have  $S_{pa} > 10$  deg. even at 22 °C.

Phase-angle sensitivity of sensors is a quantity measurable with high accuracy; it can be also utilized for signal processing by methods of statistical analysis or by neural networks.

## 6. Application of research results in education

Major part of the above-presented knowledge has already been included in the subject “Chemical gas sensors”, which is being lectured in Department of Physics and Measurements at ICT Prague for students of specialization in 9<sup>th</sup> semester. In last three years two diploma students and one PhD student have learnt this topic under my supervision.

An independent laboratory is currently being build on Department of Physics and Measurements that will enable deposition of active layers CGS based on conducting polymers or biological substances by modern MAPLD

(matrix assisted pulsed laser deposition) method without reliance on Physical institute Na Slovance. Impedance analyser, which enables to measure properties of prepared sensors, will be also part of this laboratory. In addition, impedance analyser is a universal apparatus applicable also for gas sensors based on another principles (e.g. change of resonance frequency of crystal cut, surface acoustic wave sensors etc.). Thus a complete workplace will be created for common laboratory education of specialists (co-operation of Department of physics and measurement and Computing and Control Engineering and at education of diploma and PhD students from these departments.

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## **Curriculum vitae**

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### **Professional Positions:**

- 1993-1996 postgraduate research student, Department of Solid-State Engineering, Institute of Chemical Technology, Prague; Thesis: Laser Annealed Contacts to A<sup>III</sup>B<sup>V</sup> Semiconductors
- Since 1998 assistant professor, Department of Physics and Measurement, Institute of Chemical Technology, Prague

### **Technical interests:**

- chemical gas sensors, research of active layers based on conducting polymers and metallic organic complexes, laser deposition of both organic and inorganic substances (PLD and MAPLD technology)

### **Teaching activities:**

- Chemical gas sensors – for specialization students, also in English
- Physics – seminars and laboratories
- Measurement and Control – laboratories

### **Publications:**

- about 40 papers in technical journals and proceedings of conferences

### **Professional Experience:**

- basic research in sensors (technology, new materials, processing of data from sensor arrays)
- introduction of a new subject for specialization students
- head of research team