

## Gas sensitive thin inorganic and organic layers prepared by pulsed laser deposition

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Thin active layers of chemical sensors were deposited from tin dioxide and tin acetylacetonate (SnAcAc) targets by the pulsed laser deposition (PLD) method. The deposition was made by employing excimer KrF laser (wavelength 248nm, energy density 0.3- 2.5 J.cm<sup>-2</sup>, pulse duration 16 ns). The Pt-electrodes in the interdigital configuration serve for reading of the sensor response - DC resistance of active layer. Under reducing gases the resistance of the active layer decreases (1000 ppm H<sub>2</sub> ~ 2-3 orders). For the stabilisation of sensor properties it is necessary to use dopants (compounds of Ni). In this case the PLD technology enables an original solution- introduction of dopants as a multilayered structure. In order to improve the sensor parameters, catalytic Pt or Pd is vaporised to the surface of active layer in the form of non-aggregated particles.

**Keywords:** laser deposition, chemical sensors, tin dioxide, tin acetyl-acetonate

### 1. Introduction

Chemical sensors utilising the change of the surface conductivity are based on the ability of thin semiconductive layers of metal oxides such as SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, ZnO and TiO<sub>2</sub> to absorb and, at higher temperatures, ionise oxygen on their surfaces. The absorption leads to bonding of free electrons and the formation of a depleted layer under the surface of the semiconductor. The oxygen anions above the depleted region come into a reaction with the reducing gas molecules when being exposed to the effect of the reducing atmosphere. The depth of depleted area decreases and the conductivity increases.

Tin dioxide (SnO<sub>2</sub>) gas sensors are widely used for detecting reducing gases. In many cases the planar set-up is employed. The physical parameters of this material are enhanced by addition of dopants (e.g. chlorides or oxides Fe<sup>3+</sup>, Ni<sup>2+</sup>) and surface catalysts (e.g. Pd, Pt).

The surface of some organic substances also exhibits the ability to enter into reversible chemical reactions with gases or vapours [1,2,3]. The principle of a conductivity change is in a high polarisation of delocalised  $\pi$ -electrons in the system of conjugated double bonds. It has been found that e.g. metal complexes of acetyl-acetone (MAcAc) can be used to prepare thin laser deposited layer, rich in the semiconductive metal oxide and a polymeric carbon chain containing conjugated carbonyl group. A combination of these two phases is apparently active in the contact with a reducing atmosphere, accompanied by an

increase of both sensitivity and selectivity for various kinds of gases.

The PLD technology can be used for the deposition of both organic and inorganic substances [4]. It has several advantages in comparison with conventional depositing methods (thick layer technology, RF-sputtering, spray pyrolysis, thermal oxidation or the sol-gel method). There is not need to use solvents (typical for thick layer technology). The precise control of chemical composition during the deposition of multilayer structures may be carried out *in situ* in one technological step.

The goals of this contribution can be summarised as follows: 1) to verify the suitability of PLD method for the deposition of special organic and inorganic substances, 2) to investigate the influence of dopants in the active layer, 3) to investigate the catalytic metal influence.

### 2. Technology

Gas sensitive semiconductive films were fabricated using PLD - method. The optimisation method was studied in recent works [5,6,7]. There were observed influences of energy density, working atmosphere pressure and composition, the target-substrate distance and other arrangements of deposition chamber to the layers sensitivity. The highest sensitivities to reducing atmospheres were obtained for energy density of about 0,6 J.cm<sup>-2</sup> and deposition time of 5 min, repetition rate of 5 Hz in the following arrangement: KrF -excimer laser  $\lambda = 248$  nm, laser spot : 2,5x1,5 mm<sup>2</sup>, energy of up to 700 mJ/pulse, pulse duration 15 ns. O<sub>2</sub> -working atmosphere at

pressure of 5 Pa (oxides), N<sub>2</sub> - working atmosphere at pressure of 5 Pa (SnAcAc). The technological set-up is described in a previous work [5].

The Pd catalytic layer was prepared by cathode sputtering. The as-deposited layers were subjected to special heat treatment because of their structure formation, activation, stabilization and electrode-layer junction formation (ohmic). SnO<sub>2</sub> was submitted to thermal shocks of about 600 °C, while SnAcAc to 430 °C for 9 h.

The chemical properties of these films were investigated by XPS, their morphology was studied by SEM and their electrical properties by sensitivity measurements.

### 3. Experimental

We used SnAcAc, SnO<sub>2</sub> and SnO<sub>2</sub> with 10% (mass) content of NiO targets. Powder material (Fluka Chemicals) was subjected to a pressure about 85 MPa without heat treatment.

The sensitive layers were deposited on ceramic alumina substrates fitted on the first side with a set of Pt - interdigital electrodes and on the other side with Pt - heating circuit [6,7]. In order to optimize the content of NiO, it was investigated 0.1; 1 and 10 % mass concentration in active SnO<sub>2</sub>-layer.

For measurement of sensor properties, layers have been simultaneously deposited on ceramic substrates fitted on one side with a set of interdigital contacts and on the other side with a heating circuit.

The thickness of sputtered catalytic layer was optimised from the point view of sensor sensitivity. There were two methods. The first utilized gradual equivalent thickness increase with a step of 0.5 nm Pd. This method yielded optimal thickness to be about 3.5 nm. This result was verified by the second sequence - one step sputtering 2.5, 3, 3.5; 4 nm respectively.

#### 3.1 XPS spectroscopy

Fig.1-1 presents O<sub>1s</sub> XPS spectra of distinct materials and layers (starting from the bottom): bulk tin dioxide, bulk tin acetyl-acetonate, the as-deposited SnAcAc layer (E<sub>i</sub>= 0.6 J.cm<sup>-2</sup>) and the same layer after thermal activation. The binding energy of 531.0 eV corresponds to oxygen bonded in SnO<sub>2</sub>, while the binding energy of 532.6 eV represents oxygen atoms bonded in carbonyl groups of acetyl-acetonic ligand cycles. The line corresponding to as-deposited SnAcAc layer is strongly asymmetric, but it is apparent that "oxidic" oxygen clearly dominates in this case. The asymmetry is caused by the presence of "carbonyl" oxygen, but its contents is estimated to be only about 10 percent. Finally, after thermal activation the O<sub>1s</sub> line is rather weak. The wide peak in the case (d) represents probably number of oxygen bonding states. This spectrum also shows the presence of hydroxyle groups as a result of water vapor adsorption, because the porosity (observed by TEM) of the layer after thermal activation is high.

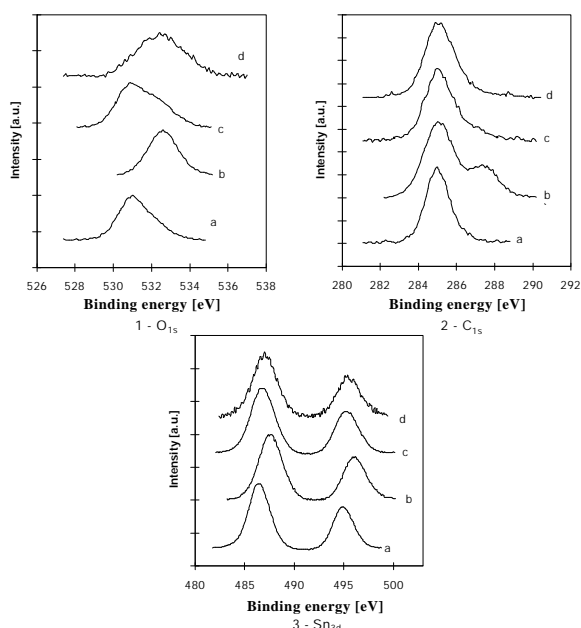


Fig. 1: The XPS (1 - O<sub>1s</sub>, 2 - C<sub>1s</sub>, 3 - Sn<sub>3d</sub>) line of a) bulk SnO<sub>2</sub>, b) the initial SnAcAc, c) The layer deposited at E<sub>L</sub> = 0.3 J.cm<sup>-2</sup> from an SnAcAc target, d) The deposited layers following heat treatment

Fig.1-2 depicts C<sub>1s</sub> XPS spectra of the samples in the same order as Fig.1-1. The main maximum of binding energy at 285.0 eV represents carbon atoms bonded with aliphatic single bonds.

The adjacent maximum at 287.4 eV in the spectrum of bulk SnAcAc reveals the presence of a carbonyl group in the acetylacetonate. This maximum persist partially after the deposition, but it disappears completely after thermal activation. The thermal activation also leads to a widening of the main maximum, which is connected to graphitization. The basic conclusions following from Sn<sub>3d</sub> spectrum - Fig.1 - 3 are similar to these from O<sub>1s</sub> and C<sub>1s</sub> spectra, i.e. there is a significant maximum at 486.5 eV representing tin dioxide. It is dominant in the spectra of both pure tin dioxide and the as-deposited layer. The maximum for tin bonded in acetyl-acetonate is shifted to higher energies (about 488.0 eV). The signal is weak after thermal activation. Tin dioxide is partially reduced by hydrogen atmosphere and liquid (430°C) metallic tin diffuses to "bulk" material or evaporates.

#### 3.2 Sensitivity of active layer

The sensitivity of active layer in chemical sensors was evaluated by employing the temperature of measurement t<sub>m</sub> and the concentration of detected gas component C<sub>i</sub> as a ratio of layer resistance in the air R<sub>air</sub> and the resistance in the atmosphere containing detected gas at this temperature R<sub>gas</sub>:

$$S_i(t_m, C_i) = \frac{R_{air}(t_m)}{R_{gas}(t_m, C_i)} \quad (1)$$

Such defined quantity has values higher than 1 during the detection of reducing gases and is dependent on temperature, nature and concentration of detected gas.

The sensitivity vs. temperature dependence has been measured by - "temperature scan method" (Fig. 4)- based on continual increasing of sensor temperature from 80 to 500 °C at a rate in the range from 2 to 5 °C/min, the atmosphere changes every 3 minutes from the state without detected gas (0 ppm - clear air) to this one containing 1000 ppm of hydrogen and vice-versa.

**4. Results**

Figures 2 and 3 depict the dependence of maximal sensor sensitivity and sensitivity maximum temperature versus equivalent thickness of Pd – catalytic layer (equivalent thickness corresponds to homogenous planar distribution of metal). In fact palladium is present in the form of separated aggregated particles. Pd was deposited by sequential sputtering with 1 nm steps on SnAcAc active layer. The maximal sensitivity was found to be about 1nm for Pd – equivalent thickness. It is apparent (Fig.2-4) that increasing catalyst thickness leads to an increase of sensor sensitivity and decrease of optimal sensing temperature. The best sensitivity was achieved for equivalent thickness between 3.5 – 4.0 nm of Pd.

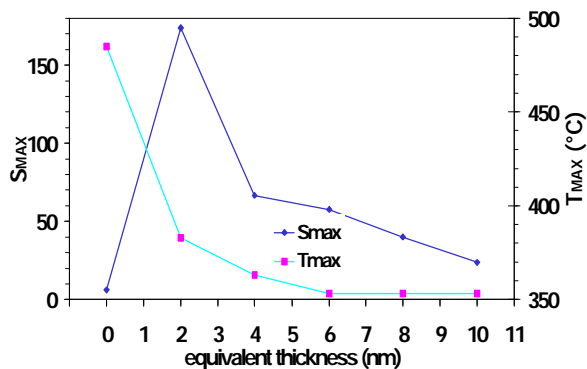


Fig. 2 : The maximal SnAcAc-sensor sensitivity and sensitivity maximum temperature dependence versus equivalent thickness of Pd - catalytic layer - sequential sputtering

**5. Conclusions**

This contribution deals with the properties of acetyl-acetate and oxidic layers prepared by the pulse laser ablation deposition method, (PLD). Moreover the palladium catalyst used in the process are together NiO dopant mentioned. The properties of the deposited layers were studied on basis of their XPS spectra and by electrical conductivity measuring.

It must be taken into account that XPS spectroscopy is a method of surface analysis. It is clear that on the surface of as deposited layers the ratio of amounts of tin acetyl-acetate vs. tin oxides SnO<sub>x</sub> is approximately 1:9.

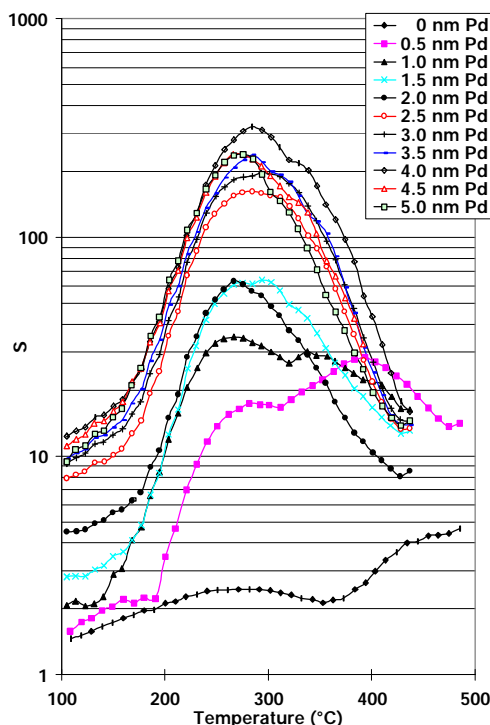


Fig. 3: The SnO<sub>2</sub>-sensor sensitivity dependence versus sensor temperature and equivalent thickness of Pd - catalytic layer - sequential sputtering

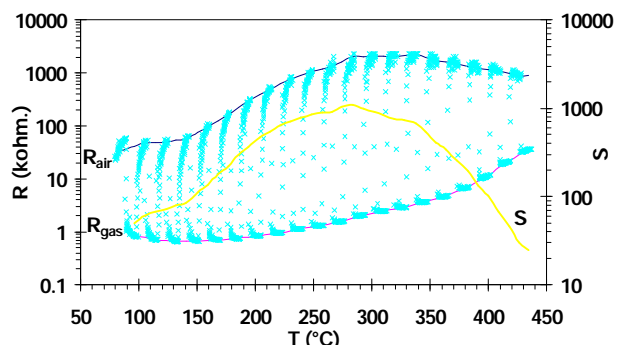


Fig. 4 : The resistance and sensor sensitivity dependence versus temperature - SnO<sub>2</sub> - sensor with equivalent thickness of 3,5 nm Pd, the maximal sensitivity - 1093 is achieved at 284 °C.

During the thermal activation of deposited layers the following processes take place: 1) tin oxides are reduced by hydrogen contained in activation atmosphere, 2) tin acetyl-acetate is predominantly transformed to tin carboxylate, 3) carbonic chains with conjugated double bonds tend to graphitization.

Changes in the electrical conductivity were evaluated in connection with detection of a reducing atmosphere. The SnAcAc sensors yielded the best sensitivity of 174 at 383 °C. Figure 4 depict highest sensitivity of SnO<sub>2</sub> layer. All of these sensor layers were equipped with catalytic Pd- layer. These are better values than the conventional thick-layer technology enables. It

can be concluded that laser technology is suitable for preparation of active layers of chemical sensors.

For further study we will try to improve sensor parameters by using new materials (acetylacetonates of Sn, In, TiO, Fe) multilayers, dopants (donors and acceptors), catalysts (Pt, Pd, V<sub>2</sub>O<sub>5</sub>) and selective surface membranes. We will investigate response of PLD prepared sensors to hydrogen, carbon monoxide, lightest alkanes and alcohols and ozone. It can be expected that the PLD method will permit modification of the basic material by addition of doping agents or the formation of doped areas. The PLD technology thus extends the capabilities of deposition of exactly defined structures, which can improve sensitivity and especially selectivity of sensors. The presence of an organic phase may also lead to a decrease in the working temperature and an increase in the lifetime.

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