Laser-deposited tin dioxide and tin acetylacetonate layers for gas sensors

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Thin active layers were deposited by the pulsed laser deposition (PLD) method from tin dioxide and tin acetylacetonate targets. The deposition was carried out employing an excimer KrF laser. The structure and parameters of the deposited layers were studied in connection with gas sensor applications. The influence of Ni dopant and Pd catalyst was investigated, employing PLD technology in order to introduce dopants as a multilayered structure. The properties of these layers were studied by Fourier transform infrared (FTIR), and X-ray photoelectron (XPS) spectroscopies and by measurement of their d.c. resistance. Under reducing gases the resistance of Ni-doped tin dioxide with a Pd catalyst layer decreases by ~ 3 orders and the resistance of tin acetylacetonate with a Pd catalyst by ~ 2 orders (synthetic air versus 1000 ppm H2. Due to this, such layers are suitable as the active layers of gas sensors.


1. Introduction
Pulsed laser deposition (PLD) technology can be used for the deposition of both organic and inorganic substances [1]. It has several advantages in comparison with conventional depositing methods (thick layer technology, r.f.-sputtering, spray pyrolysis, thermal oxidation or the sol-gel method). The PLD technology enables easy control of chemical composition, thickness of the deposited layer, dopant concentration and morphology. The precise control of chemical composition during the deposition of multilayer structures may be carried out in situ in one technological step.

Chemical sensors utilizing the change of the surface conductivity [2] are based on the ability of thin semiconductive layers of metal oxides such as SnO2, In2O3, ZnO and TiO2 to absorb oxygen and, at higher temperatures, ionize oxygen on their surfaces. The absorption leads to bonding of free electrons and the formation of a depleted layer under the semiconductor surface. The oxygen anions above the depleted region react with the reducing gas molecules when exposed to the effect of the reducing atmosphere. The depth of the depleted area decreases and the conductivity increases. Tin dioxide (SnO2) 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 the addition of dopants (e.g., chlorides or oxides of Fe3+, Ni2+) and surface catalysts (e.g., Pd, Pt).

The surfaces of some organic substances [3–5] also exhibit the ability to enter into reversible chemical reactions with gases or vapors. The principle of a conductivity change is in a high polarization of delocalized pi-electrons in the system of conjugated double bonds. It has been found that metal complexes of acetyl-acetone (MACAc), for example, can be used to prepare thin laser-deposited layers rich in the semiconductive metal oxide and a polymeric carbon chain containing conjugated double bonds. A combination of these two phases is apparently active in contact with a reducing atmosphere, accompanied by an increase of both sensitivity and selectivity for various kinds of gases.

The aims of this work can be summarized as follows: (1) to verify the suitability of the PLD method for the deposition of gas sensitive inorganic and organic substances; (2) to investigate the influence of dopants in the active layer; (3) to investigate the catalytic metal influence; (4) to prepare multilayer structures in one technological step.

2. Technology
Gas sensitive semiconductive films were fabricated using the PLD method. The optimization of this method was studied in recent studies [6, 7], which observed influences of energy density, working atmosphere pressure and composition, the target-substrate distance and other arrangements of the deposition chamber. The highest sensitivities to reducing atmosphere were obtained for an energy density of about 0.6 J cm2, deposition time of 5 min, and repetition rate of 5 Hz, in the following arrangement: Krf-excimer laser wavelength 248 nm, laser spot: 2.5 × 1.5 mm2, energy of up to...
The deposition was carried out from SnAcAc and SnO₂. We used SnAcAc, SnO₂ and SnO₂ with 10% (mass) content of NiO targets. Powder material (Fluka Chemicals) was submitted to a pressure of 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 a Pt-heating circuit [8, 9]. In order to optimize the content of NiO, we investigated 0.1, 1 and 10% mass concentration in the active SnO₂ layer. In the case of 0.1 and 1% concentration the dopants were present in the form of multilayered structures.

Because of the analysis of the deposited layers by FTIR spectroscopy, KBr substrates were employed for the deposition. For the measurement of sensor properties, layers were 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 the sputtered catalytic layer was optimized from the standpoint of the sensor sensitivity. There were two methods. The first utilized a gradual equivalent thickness increase with a step of 0.5 nm Pd. This method yielded the optimal thickness to be about 3.5 nm. This result was verified by the second sequence; one step sputtering of 2.5, 3, 3.5, 4 nm, respectively.

3.1. FTIR spectroscopy

The deposition was carried out from SnAcAc and SnO₂ targets at energy densities in the range from 0.15 to 1.5 J cm⁻². The FTIR spectra of all the prepared layers were measured. Fig. 1 compares the following spectra: bulk SnO₂ layer (a), the initial SnAcAc (b), the layer deposited at \( E_T = 0.3 \) J cm⁻² from an SnAcAc target (c) and the deposited layers after heat treatment (d). Spectra (b) and (c) exhibit good agreement, indicating that the composition of the deposited layer agrees well with that of the initial substance. It is significant that the absorption band at 658 cm⁻¹ cannot be identified here; this band corresponds to SnO₂, indicating that the SnAcAc complex is stable under these conditions, and does not decompose to SnO₂ and an organic residue. Chemical changes that occurred during the activation were also evaluated using FTIR spectroscopy.

The best correspondence between the spectra of the target material and those of the deposited layer was observed at an energy density of about 0.3 J cm⁻² for SnAcAc. The minimal threshold energy density required for the deposition of SnO₂ was 0.3 J cm⁻², and for SnAcAc less than 0.15 J cm⁻².

3.2. XPS spectroscopy

Fig. 2(1) presents \( O_1s \) spectra of distinct materials and layers (starting from the bottom): bulk tin dioxide, bulk tin acetylacetonate, the as-deposited SnAcAc layer \( E_T = 0.6 \) J cm⁻² and the same layer after thermal activation. The binding energy of 531.0 eV corresponds to oxygen bonded in SnO₂ while the binding energy of 532.6 eV represents oxygen atoms bonded in carbonyl groups of acetylacetonic 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 content is estimated to be only about 10%. Finally, after thermal activation, the \( O_1s \) line is rather weak. In contrast to the previous case, the “carbonyl” oxygen prevails after the activation process. This is probably due to the presence of hydrogen in the atmosphere during activation. Hydrogen reduces the tin dioxide almost completely, but not the carbonyl groups. So the content of carbonyl groups is practically the same as in the state before activation while the content of tin dioxide decreases significantly. This spectrum also shows the presence of hydroxyl groups as a result of water vapor adsorption, because the porosity (observed by transmission electron microscopy (TEM)) of the layer after thermal activation is high.

Fig. 2(2) depicts \( C_1s \) spectra of the samples in the same order as Fig. 2(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 persists partially after the deposition, but disappears completely after the thermal activation. The thermal activation also leads to a widening of the main maximum, which is connected to graphitization.

The basic conclusions following from the Sn₃p spectrum in Fig. 2(3) are similar to these from the O₁s spectrum, i.e., there is a significant maximum at 486.5 eV representing tin dioxide. It is dominant in the spectra of