Organic active layers for chemical sensors prepared by Matrix Assisted Pulse Laser Deposition (MAPLD)

V Myslík⁵, R Fryček⁵, M Vrňáta⁶, F Vysloužil⁶, P Fitl⁴, M Jelinek⁶
Institute of Chemical Technology, ⁵Department of Solid-State Engineering, ⁶Department of Physics and Measurements, Technická 5, 166 28, Prague 6, Czech Republic
⁴Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic

E-mail: vladimir.myslik@vscht.cz

Abstract. The article deals with MAPLD deposition of thin organic layers of acetylacetonates and polypyrrole. The chemical changes of acetylacetonates during deposition were characterized by their FTIR spectra and morphology by SEM portraits. All of the deposited layers were utilised for gas detection. The measurements of sensitivity of deposited systems to hydrogen, ozone, nitrogen dioxide and water vapour were done. The hydrogen sensitivity of sensors prepared from SnAcAc was found about S=20 (1000 ppm in clear air) at region 250-300°C (sensor temperature). Highest response S=35 to 100 ppb of ozone was achieved at low temperature (below 150°C). The maximum response S=10 to nitrogen dioxide (1 ppm) at 250°C was measured. Polypyrrolic sensors were exposed to ozone, their sensitivity was S=2 (100 ppb) achieved at very low temperature (25°C). It was found sensitivity to water present both as a vapour in atmosphere or contained in active layer.

1. Introduction

The Matrix Assisted Pulse Laser Deposition (MAPLD) [1] follows up the pulse laser deposition (PLD) [2-3], which is proved to be good at layers preparation of various organic materials. The MAPLD technology can be used for transport of large molecules (organic substances such as polymers or biomolecules) up to the molecule weight 10⁶ a.u. from target to substrate [4]. Contrary to the PLD method, it is assumed that at deposition of an organic material with the MAPLD technology, molecules of the material get released from the source target without being fragmentated at the same time. The target is made of a source organic material and a matrix (i.e. a volatile organic solvent) and is cooled down to temperature close to that of liquid nitrogen. The laser beam is of lower power density than in the case of PLD. The advantage of the MAPLD method includes relatively simple technological requirements, great flexibility of chemical composition of the source target and easy regulation of the technological process (energy of the laser beam, number of pulses, pressure and composition of the protective atmosphere).

This contribution deals with deposition and testing of acetylacetonates (Sn, In), and conducting polymer - polypyrrole for active layers of chemical gas sensors.

2. Experimental

The MAPLD deposition was carried out by KrF excimer laser (λ=248 nm, energy density of laser beam between Eₙ=0,05-0,6 J.cm⁻², repetition rate of laser pulses 10 Hz, spot 7.8 mm x 2.6 mm). The deposition chamber arrangement and the principle of the MAPLD technology shows figure 1. The used device (working chamber with optical elements) is shown on the figure 2. The deposition chamber was evacuated to a background pressure of 10⁻⁶ Pa while rotating target holder was still
cooled to the temperature of liquid nitrogen. The deposition proceeded in nitrogen working atmosphere at a pressure 3 Pa.

The layers were deposited on two kinds of substrates. The first one was the substrate of the chemical gas sensor (figure 3). It means small alumina plates equipped by interdigital electrodes for sensor response reading was used. On the back side of the plate Pt heating element was prepared. The second kind of the substrate (polished silicon and KBr - pellets) were applied for the layer characterization.

The source targets were prepared from an organic material and a matrix (suitable solvent). The selected substances for the layers creation are presented in the table 1. The final mixture was cooled to the temperature of liquid nitrogen and immediately transported to the working chamber. In case of materials SnAcAc and InAcAc, the organic material was dissolved in acetone, for polypyrrole in water matrix. The deposition conditions are summarized in the table 2.

| organic material | matrix   | content (wt. %) |
|-----------------|----------|-----------------|
| SnAcAc          | acetone  | ~ 3%            |
| InAcAc          | acetone  | ~ 3%            |
| polypyrrole     | water    | ~ 5%            |

Table 1. The list of the target compositions used

| material | no. of pulses | $E_L$ [J/cm²] |
|----------|---------------|---------------|
| SnAcAc   | 10000-20000   | 0.05-0.2      |
| InAcAc   | 10000-20000   | 0.05-0.2      |
| polypyrrole | 4000-20000   | 0.05-0.6      |

Table 2. Deposition condition of acetyl-acetonates and polypyrrols.

The deposited layers were characterized by FTIR, SEM, optical microscopy. As these layers are assigned for detection process, were investigated: sensors resistance, sensitivity to atmosphere containing small concentration of reducing or oxidizing gases and air humidity. The thickness of the layers was optimized with respect to the maximal sensitivity $S$ ($S = \frac{R_{\text{air}}}{R_{\text{gas}}}$, $R_{\text{air}}$ - sensor resistance in clear air, $R_{\text{gas}}$ - sensor resistance in air containing detected gas).

**3. Results**

There were found the ablation thresholds during the deposition conditions optimization. In case SnAcAc and InAcAc in acetone matrix the energy density of ablation threshold ($E_L^{\text{thr}}$) changed between 0.07-0.1 J.cm². The polypyrrole in water matrix means $E_L^{\text{thr}}$ on the level of 0.3 J.cm².
Another important parameter is energy density of laser radiation suitable for preparation of layers proper for sensing. The energy optimal for preparation of sensing layers based on acetylacetonates was $E_L \sim 0.15 \text{ J.cm}^{-2}$ while for layers based on polypyrroles was $E_L \sim 0.5 \text{ J.cm}^{-2}$. This result is given by the requirement of high ratio surface vs. volume on one side and sufficient rate of layer growth during the deposition on the other side.

The influence of working atmosphere (nitrogen) pressure was recently investigated in the range of $10^{-1}$ to $10^3 \text{ Pa}$. The optimal working pressure (3 Pa) was selected with regard to rate of layer growth and evaporation of matrix material.

In case of acetylacetonates the FTIR spectra were studied with the respect to energy density of the laser beam in the range of 0.1-0.4 J.cm$^{-2}$. The best similarity of the source substance spectrum with that of the substance transferred by MAPLD was observed at $\sim 0.2 \text{ J.cm}^{-2}$ for both SnAcAc (figure 4) and InAcAc (figure 5).

The morphology of the prepared layers was investigated by SEM. The sample of a SEM portrait ($E_L=0.1 \text{ J.cm}^{-2}$) is presented by the figure 6. It is known [4] the higher energy density of the laser beam, the smoother surface. Higher roughness (higher ratio surface vs. volume) is advantageous for active layers creation in the semiconductor gas sensors preparation.

**Figure 4.** IR spectrum SnAcAc, a) the source substance, b) the substance transferred by MAPLD

**Figure 5.** IR spectrum of InAcAc, a) the source substance, b) the substance transferred by MAPLD

**Figure 6.** SEM image of an InAcAc layer, deposited by MAPLD - $E_L=0.1 \text{ J.cm}^{-2}$, thickness $\sim 780 \text{ nm}$, (scale bar = 10 $\mu\text{m}$).
The MAPLD deposited layers were tested for gas sensing (air mixtures). With the respect to previous experiences the following combinations were selected. The SnAcAc layers are suitable for hydrogen detection, on the other hand the InAcAc is sensitive to oxidizing gases such as ozone and nitrogen dioxide. The polypyrrole based layers were sensitive to air humidity. The results examples are shown in the figures from 7 to 9.

4. Conclusions

The new modified laser technology MAPLD was used for deposition of thin layers based on metal acetylacetonates and polypyrrole. Under used conditions (matrix, power density of laser beam, pressure of ambient atmosphere, target-substrate distance), layers exhibited higher roughness then those prepared by conventional pulse laser deposition technique. The work yielded following results:

- The ablation threshold for water containing matrix was 3 times higher than for acetone containing one. This is in correspondence with volatility of both substances.
- It was determined optimal energy density for active layers deposition (~ 1.5 x $E_L^{\text{thr}}$).
The FTIR analysis confirmed good chemical composition similarity between the source and deposited substance in the case of acetylacetonates.

The SEM morphology observing demonstrated significant high ratio layer surface vs. its volume.

The hydrogen sensitivity of sensors prepared from SnAcAc was found about $S=20$ at region 250-300°C.

Highest response ($S=35$, 100ppb of $O_3$) was achieved at low temperature (below 150°C) on the InAcAc based sensors. The maximum response ($S\sim10$) to 1 ppm of nitrogen dioxide at 250°C was measured.

Polypyrrolic sensors are sensitive to ozone ($S\sim2$, 100ppb of $O_3$) and water vapour ($S\sim250$ to 60 % relative humidity) at extremely low values of temperature (25 °C).

Acknowledgements
This work was supported by the GA CR projects No. 104/03/0406 and No. 106/03/P061, CTU Research projects No. 6640770030 and No. 88/1, MSM 604 613 7302 and MSM 604 613 7306

References
[1] Piqué A, Wu P, Ringeisen B, Bubb D, Melinger J, McGill R and Chrisey D 2002 Appl. Surf. Sci. 186 408
[2] Vrňata M, Vysloužil F, Myslík V and Jelinek M 2000 J. Mat. Sci.: Materials in electronics 11 703
[3] Fryček R, Myslík V, Vrňata M, Vysloužil F, Jelinek M and Náhlík J 2004 Sens. and Act. B 98 233
[4] Cristescu R, Mihailescu D, Socol G, Stamatin I, Mihailescu I and Chrisey D 2004 Appl. Phys. A 79 1023