

MATRIX ASSISTED PULSE LASER EVAPORATION OF LARGE MOLECULES AND GAS SENSORS APPLICATION

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Abstract: It was shown that organic materials can be used as an active layer for conductivity gas sensors. It was found that Pulse Laser Deposition (PLD) is convenient technology for producing thin layers (from nanometers to micrometers). Metal Acetylacetonates (MAcAc) exhibit high sensitivity to oxidizing gases as well as reducing atmospheres. New technology - MAPLE – Matrix Assisted Pulse Laser Deposition has been developed for deposition of thin films from large organic molecules (up to several hundreds of amu). Starting material is embedded in frozen matrix, which plays important role during energy transfer while laser pulse hits the target.

First experiments have been done with Indium(III) acetylacetonate (InAcAc) and Tin(IV) bis(acetylacetonate) dichloride (SnAcAc). Thin layers of large molecules of dyes Nickel(II) phthalocyanine (PcNi) – and the Cu(II) para-tetramethylphenylporphyrin (CuTMPP) were prepared. To certify successful transfer of original material FTIR, Raman spectroscopy and SEM analysis of thin layers have been used. Chemical sensors with those layers were tested at different atmospheres and temperature dependent sensitivity was acquired. Results from DC measurements show, that MAPLE technology is very perspective for preparation of high demand chemical sensors.

Introduction

Laser technologies have been widely used for the structure micromachining of electronic elements as well as preparation of various thin films. For next generation of microelectronics and optoelectronics, surface coatings and intelligent multifunctional materials, technologies for thin organic film preparation will be needed. Thin organic films can be deposited by variety of techniques using solvents (aerosol, dip coating, spin coating, electrochemical) or depositions from solid states (vacuum evaporation, plasma polymerization).

The appropriate technique should be chosen with respect to material chemical and thermal stability, used substrate and film quality requirements. Recent works confirmed the suitability of pulse laser deposition (PLD) technology for the deposition of inorganic and organic active layers for gas sensor application [1,2,3]. Improved laser processing technology – Matrix Assisted Pulsed Laser Evaporation (MAPLE) for polymer deposition has been introduced [4]. The technology is unique for organic layer-by-layer control and possible deposition of heterostructures. This is unusual, comparable to other thin layers preparation from solution. Metallophthalocyanines and metalloporphyrines derivatives are very perspective materials for conductive and optical sensor application, solar cells and photographic copiers and printers. Like a specimen of those, Nickel(II) phthalocyanine - PcNi (486 amu) and the Cu(II)para-tetramethylphenylporphyrin – CuTMPP (731 amu) were selected.

Target preparation for MAPLE is different from PLD, that low concentration (1-5 wt. %) of organic material is dissolved and deep frozen by liquid nitrogen instead of pressing powder material into the tablet. The light-material interaction in MAPLE can be described as photothermal process where matrix molecules are preferentially evaporated [5]. The organic molecules obtain sufficient kinetic energy through collective collisions with the evaporating solvent molecules, to be transferred in to the gas phase. Solvent molecules in gas phase are evacuated. When substrate is placed in the flux of molecules, thin organic layer is grown.

Prepared sensors can be used as an element of safety gas detection systems as well as low-cost analytical tool for different gas concentration during industrial chemical production.

Materials and Methods

Commercially available (Fluka Chemicals, Sigma-Aldrich) SnAcAc and InAcAc were dissolved in

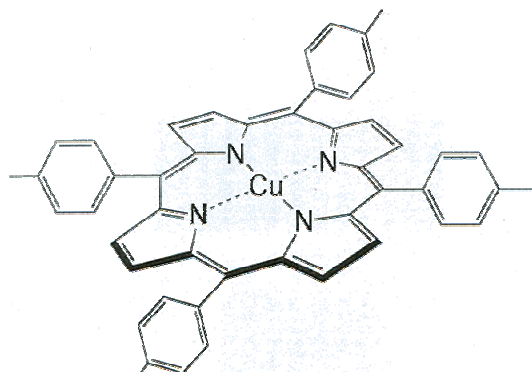


Figure 1. The structure of the Cu (II) para-tetramethylphenylporphyrin - CuTMPP

acetone and filtrated. Saturated solutions of PcNi in dimethylsulfoxide and CuTMPP in chloroform were prepared. Solution was frozen by liquid nitrogen and target was placed to pre-cooled rotating holder in the vacuum chamber. Deposition chamber was evacuated to a background pressure of 10^{-6} Pa, while rotating target holder was still cooled by flow of liquid nitrogen.

The deposition proceeded in nitrogen working atmosphere at a pressure 3 Pa and excimer KrF laser (wavelength 248nm), with repetition rate 10 Hz was used. The laser beam was focused on the target to create spot 7.8 mm x 2.6 mm. Energy density per pulse was applied regarding to precedent tests between 0,1 - 0,5 Jcm⁻².

For sensors fabrication small alumina plates (2x2,2 mm²) equipped by platinum interdigital electrodes for sensor response reading was used. On the reverse side of the plate was Pt heating element prepared. After thermal activation and stabilization layers exhibited semiconductor behaviour [1,2].

The sensitivity measurements were carried out in chamber (aprox. 1 cm³) with gas flow regime (0.04 dm³/min). The temperature of the sensor increases from 80°C to 350°C for 2 h and the atmosphere is periodically changed from synthetic air (mix of 80% N₂ and 20% O₂) to detected atmosphere. The sensitivity was evaluated for temperature of measurement as a ratio of layer resistance in the atmosphere containing ozone or nitrogen dioxide (R_{gas}) and the resistance in the air (R_{air}). For hydrogen sensitivity measurement the sensitivity is reciprocal value to above definition.

For ozone generation Hg-low pressure lamp was employed. The lamp was calibrated by quantitative oxidation and it produces 100 ppb of ozone.

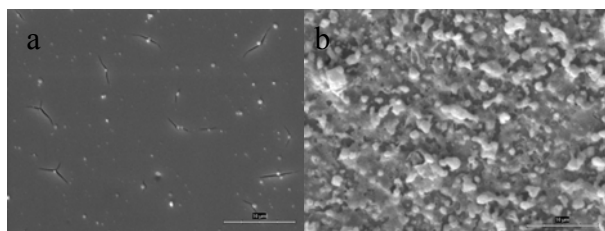


Figure 2. SEM image of the morphology of PLD (a), thickness 630 nm and MAPLE (b), thickness 780nm deposited InAcAc active layer (scale bar = 10 µm)

Calibration gases with 1 ppm of nitrogen dioxide, 1000 ppm of hydrogen and synthetic air (HC free) from company Linde Technogas were used. For SEM, FTIR and Raman spectroscopy double-polished silicon plates were added for each deposition as a substrate. The spectrum of the starting material was collected directly from pressed tablet of mixed KBr with powder material (FTIR) or directly from the powder (Raman). The FTIR spectra of starting material and deposited layers were recorded by Nicolet 740 apparatus, in transmission mode, with MIR range (4.000–400 cm⁻¹) and 4 cm⁻¹ resolution. The Raman spectra were recorded at the Jobin-Yvon LabRAM system, with Ar ion laser excitation at 514 nm.

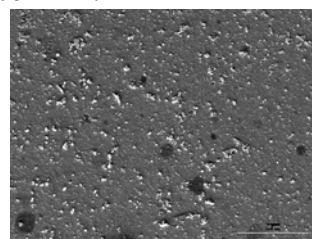


Figure 3. SEM image of the morphology of MAPLE deposited CuTMPP thin layer thickness 107 nm (scale bar = 10 µm)

Results

Morphology of prepared layers

At figure 1a) is SEM image of the InAcAc layers for gas sensors, deposited from pressed target by PLD with energy density, $E=0,6$ Jcm⁻² while 1b) is a layer prepared MAPLE, $E=0,1$ Jcm⁻¹. Both layers are prepared with similar thickness (630, 780nm respectively). When compared with conventional PLD, prepared layers are more uniform than MAPLE deposited layer. The higher roughness of deposited organic material was approved by Alfastep profilometer. While PLD layer roughness was measured about 50 nm, MAPLE layers exhibited about one order higher.

From computer simulation it is known [6], that during desorption from target the polymer is packed by molecules of solvent and this cluster avoids its fragmentation. Despite of relatively low energy density during the deposition of InAcAc, where one can expect desorption, the ablation already occurred with high flux of material and clusters were coupled to form droplets. Ablation threshold was possible shifted by intensive cooling of the target [7]. Lower layer of the deposited material is already neck-connected.

This high specific surface is desirable for deposition of layers for conductivity gas sensors, because of increased number of active sorption/desorption sites. Layer roughness could be advantageous when biocompatible material will be deposited.

The deposited layer of CuTTP, $E=0,1$ Jcm⁻² is formed by particles up to approximately micrometer in diameter. Over the surface there is randomly scattered several larger material islands, probably produced by a

few last laser shots, because they are not in the lower layer Fig.2. Roughness of CuTMPP layer is about 150 nm. Areas where solvent droplets reached the target are apparent in the deposited layer.

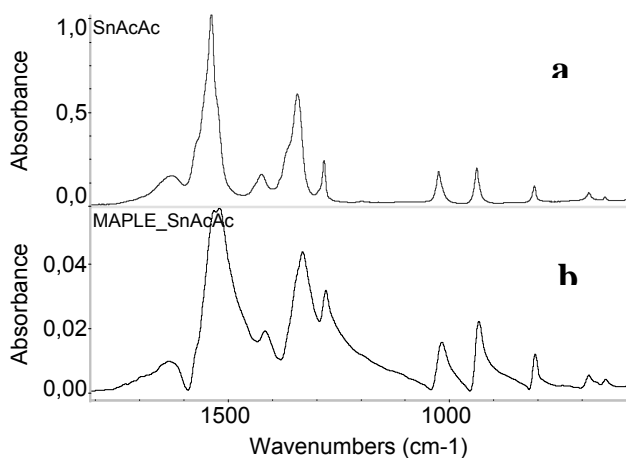


Figure 4. IR spectrum of a) pure SnAcAc pure b) MAPLE transferred material, $E=0,1 \text{ Jcm}^{-2}$

FTIR spectroscopy

The absorption FTIR spectrum of prepared SnAcAc films is shown (Fig.3). The strongest peak of characteristic absorption at 1538 cm^{-1} represents delocalized double bonds persists. Second intense band at 1343 cm^{-1} belongs to $\delta_d(\text{CH}_3)$ and $\delta_s(\text{CH}_3)$ vibration of acetates. In the “finger print region” double peak at 1120 and 933 cm^{-1} is also present. For both spectra maxima are at the same wavenumbers. Relative intensity of all peaks is also similar, which verify low fragmentation during MAPLE molecular transport.

In the spectrum of pure InAcAc is enhanced intensity of the enol-form of β -diketones at 1575 cm^{-1} (Fig. 4). All above described characteristic bands are at spectrum also present. In the prepared thin layer decreased level of enol-form is evident which is consistent with enhanced aliphatic hydrocarbons around 1400 cm^{-1} . During deposition some side reactions probably occurred because of wide band present at 1110 cm^{-1} which represent $\nu(\text{COC})$ peroxide group.

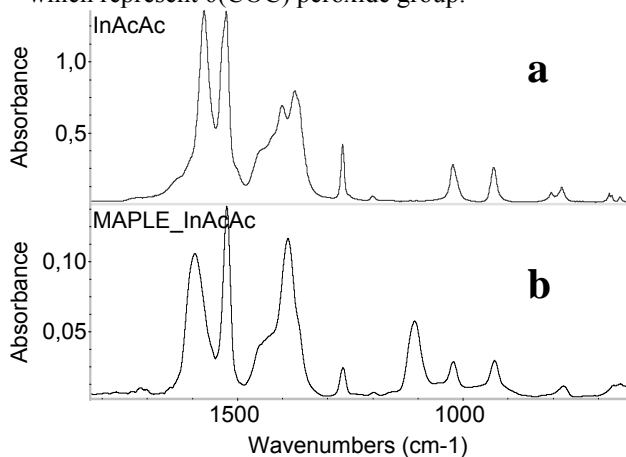


Figure 5. IR Spectrum of (a) pure InAcAc (b) MAPLE transferred material, $E=0,1 \text{ Jcm}^{-2}$

Raman spectroscopy

Thin layers of CuTMPP with different laser fluences ($0,1; 0,15$ and $0,2 \text{ Jcm}^{-2}$) Fig.6. In the starting material spectrum characteristic bands of the Cu porphyrin can be found. Stretching of C-C bond at $1238, 1477, 1564, 1595 \text{ cm}^{-1}$ and C-N stretching at 1367 cm^{-1} . Due to the position (shape and relative intensity) of bands, it can be concluded that CuTMPP remained unfragmented after deposition. The dependency on the laser fluence was not observed.

When very low deposition rates ($< 0,004 \text{ nm/pulse}$) of PcNi were observed by preliminary tests, we increased the fluence to $0,3; 0,4$ and $0,5 \text{ Jcm}^{-2}$ (Fig 6). The deposited layers in this case are presented by wide, not-separated belt which is caused by various products. The decomposition of dimethylsulfoxide matrix probably occurs when deposition was followed by distinctive odour of sulphide-like gases. The decomposed material would induce reaction with PcNi in the gas phase to form amorphous graphite-like structure, with unresolved bonds.

Sensitivity measurements

When synthetic air atmosphere is changed to ozone or nitrogen dioxide environment the resistance of heated InAcAc films rapidly increases, due to further chemisorption and bonding of free electrons. When detected gas is hydrogen, resistance decreases while the charged clusters are desorbed. This step is fully repeatable in a wide range of temperatures. The sensor is heated from back-side heating meander and temperature dependence of sensitivity is obtained. The set of two InAcAc sensors prepared by MAPLE technology was tested to ozone and nitrogen dioxide, because of their often co-existence during industrial UV processes or as an air pollution. The maximum of sensitivity to 100 ppb of ozone was reached until $165 \text{ }^\circ\text{C}$ ($S = 10-12$). On the other hand the maximum of sensitivity to nitrogen dioxide was found around 250°C ($S = 10$) (Fig. 5). This temperature dependent selectivity is caused probably due to different activation energy of chemisorption and can be easily used for construction of low cost analytical tool. The SnAcAc sensor response to

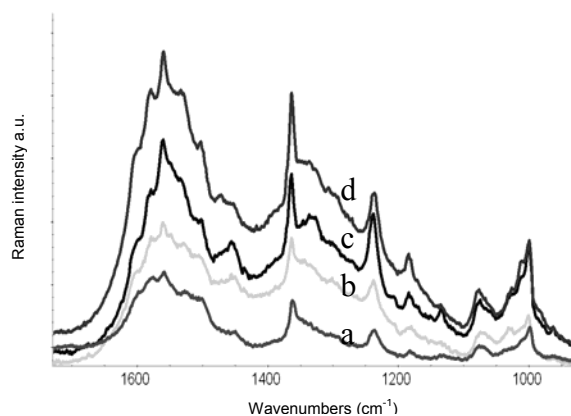


Figure 6. Raman spectra of CuTMPP, a) starting material b) MAPLE $E=0,1 \text{ Jcm}^{-2}$ c) MAPLE $E=0,15 \text{ Jcm}^{-2}$ d) MAPLE $E=0,2 \text{ Jcm}^{-2}$

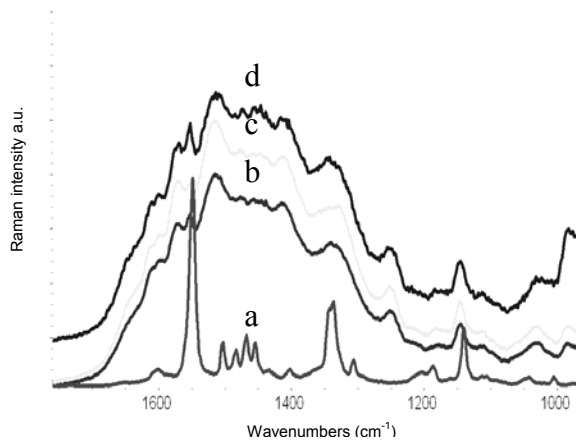


Figure 6. Raman spectra of PcNi, a) starting material, b) MAPLE $E=0,3 \text{ Jcm}^{-2}$, c) MAPLE $E=0,4 \text{ Jcm}^{-2}$, d) MAPLE $E=0,5 \text{ Jcm}^{-2}$

1000 ppm of hydrogen is shown at Fig. 6 with highest value $S = 16-19$ at $260-350^\circ\text{C}$ region. The repeatability of temperature dependent sensitivity of each sensor is evident (Fig. 7, 8).

Conclusions

The new modified laser technology MAPLE was used for deposition of thin organic layers of metal acetylacetonates. Under used conditions (matrix, power density of laser beam, pressure of ambient atmosphere, target-substrate distance), layers exhibited higher roughness than those prepared by conventional pulse laser deposition technique. The FTIR analysis approved very similar composition of thin layer to original material in case of SnAcAc. During deposition of InAcAc all function groups remained, but also new peak at 1110 cm^{-1} was found.

The Raman spectroscopy proved that CuTMPP remained unfragmented after deposition from chloroform matrix. The fragmentation of PcNi molecule during deposition from DMSO solution occurred.

The measurements of sensitivity to ozone, nitrogen

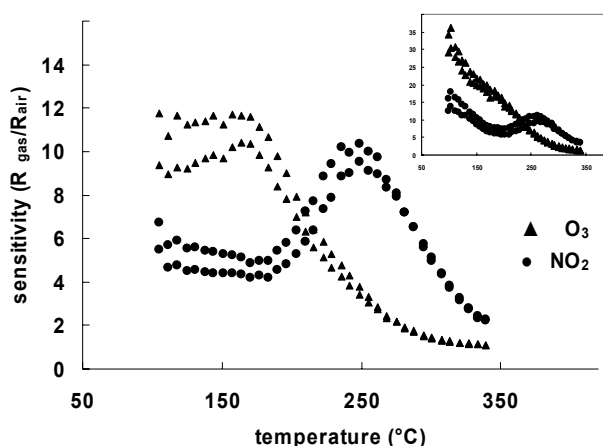


Figure 7. The temperature dependence of sensitivity to 100 ppb of ozone and 1 ppm of nitrogen dioxide of MAPLE prepared InAcAc sensor, sample I (inset: sample II)

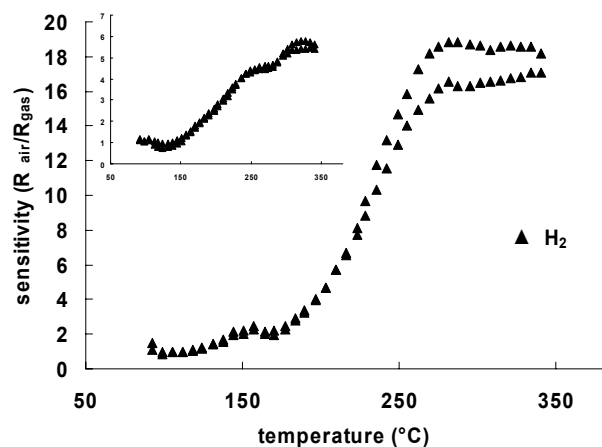


Figure 8. The temperature dependence of sensitivity

dioxide and hydrogen were done. 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 at 250°C was measured. This temperature dependent selectivity of InAcAc material could be crucial factor, when co-existing gases are measured and responses are overlapped. The hydrogen sensitivity of sensors prepared from SnAcAc was found about $S=20$ at region $250-300^\circ\text{C}$.

The presented data of each measurement shows sufficient repeatability. By preparation of second samples we approved the reproducibility of MAPLE process and its suitability for gas detection elements. The prepared and tested sensors are promising for construction of advanced electronic nose.

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