Polypyrrole active layers of gas sensors prepared by MAPLE technology

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Abstract. Thin layers of polypyrrole (PPY) were deposited by MAPLE (Matrix Assisted Pulse Laser Evaporation) technology. The deposition was carried out by KrF excimer laser from water and dimethylsulfoxide matrixes. Ablation thresholds \(F_{th}\) were determined to be \(F_{th} \sim 0.3\ J\cdot\text{cm}^{-2}\) for dimethylsulfoxide matrix and \(F_{th} \sim 0.45\ J\cdot\text{cm}^{-2}\) for water matrix. The roughness of deposited layers was measured by AFM and their chemical composition was characterized by FTIR spectroscopy. Finally, resistance of sensors with PPY active layer was measured in dependence on working temperature and relative humidity of surrounding atmosphere.

1. Introduction

Doped polypyrrole (PPY) is a material, whose applications in active layers of chemical gas sensors [1] and biosensors [2] are currently intensively investigated. It has both flexibility of chemical composition of organic substances and ability to change its physical properties by absorption of gas species on its surface.

In this contribution PPY active layers of gas sensors are prepared by advanced method - MAPLE technology. It was developed for deposition of thin layers of organic substances and biomaterials [3].

The principle of MAPLE technology is shown in figure 1. The material, which is to be deposited (basic material) together with low-molecular volatile substance (matrix) is embedded in frozen target. The matrix must fulfil following conditions: (i) it does not react chemically with basic material; (ii) it has high absorption coefficient on laser wavelength. Excimer laser pulse is incident on target surface and its energy is absorbed by matrix molecules. Hence small molecules of matrix are evaporated and consequently they transfer their kinetic energy to basic material. In this way the molecules of basic material are carried to substrate "mechanically", with neither photolytic nor pyrolytic damage.

MAPLE technology has some advantages in comparison with "conventional" depositing methods (such as dip-coating or spin-coating): a) retaining of chemical composition of basic material; b) simple controlling of deposited layer thickness by counting incident laser pulses; c) localization of laser spot to small dimensions and ability to create various patterns by direct writing; d) production of highly porous layers, suitable for sensor applications; e) possibility to prepare layered structures by changing source targets \textit{in situ} in deposition chamber.
2. Experimental

In our experiments 5 wt.% water solution of PPY doped by organic sulfonic acids (Sigma Aldrich) was used. In order to investigate influence of matrix, the targets for MAPLE deposition were prepared in two ways: a) freezing this water solution; b) evaporating water from original solution, conversion of solid phase to dimethylsulfoxide (DMSO) and subsequent freezing of resulting DMSO solution. Targets were placed to deposition chamber and their temperature was kept at -193°C by liquid nitrogen. The chamber was then evacuated to residual pressure 5 · 10⁻³ Pa.

The deposition was carried out under following conditions: KrF excimer laser (λ = 248 nm), laser fluence $F$ ranging from 0.1 to 0.6 J·cm⁻², repetition rate of laser pulses 10 Hz, distance between target and substrate 35 mm, rotating motion of target (to prevent "hole effect"), nitrogen working atmosphere.

The PPY layers (their thickness varied from 100 to 300 nm) were deposited to Alumina sensor substrates (figure 2) equipped with interdigital platinum electrodes on the front side and resistance heating on the back side.

For measuring AFM portraits and FTIR spectra PPY layers were also deposited to polished silicon wafers. AFM scans were taken from area of 5 × 5 μm as these dimensions are approximately by one order higher than roughness of deposited layers.

**Figure 1.** Mechanisms of energy and mass transport during MAPLE deposition.

**Figure 2.** Detail view on sensor substrate: (a) front side (b) back side
3. Results

Figure 3 depicts growing rate of PPY layers (calculated as a ratio of layer thickness and number of laser pulses) vs. laser fluence for both matrixes. The character of dependence corresponds to theoretical prediction and also includes information concerning ablation threshold. Ablation threshold \( F_{\text{th}} \) is the value of laser fluence for which derivation of the above mentioned dependence is maximal, i.e. it holds \( F_{\text{th}} \sim 0.3 \text{ J cm}^{-2} \) for DMSO matrix and \( F_{\text{th}} \sim 0.45 \text{ J cm}^{-2} \) for water matrix.

![Figure 3](image)

**Figure 3.** Growing rate of PPY layers deposited from \( \text{H}_2\text{O} \) (●) and \( \text{DMSO} \) (▲) matrixes in dependence on laser fluence.

Morphology of deposited layers was studied by AFM method. AFM portraits of three samples deposited from water matrix are shown in figure 4. Maximal value of \( z \)-coordinate represents surface roughness (i.e. difference between maximal and minimal thickness of deposited layer). It is apparent that layers deposited at lower laser fluences have in general lower surface roughness. Simultaneously, these layers are built from smaller particles - they have broken relief. We can suppose that such relief is advantageous for gas sensing applications.

![Figure 4](image)

**Figure 4.** AFM scans of PPY deposited from water matrix by various laser fluences:

a) \( F = 0.2 \text{ J cm}^{-2} \); b) \( F = 0.3 \text{ J cm}^{-2} \) and c) \( F = 0.5 \text{ J cm}^{-2} \).

FTIR spectra of pure PPY [4] have strong absorption bands at 1549 cm\(^{-1}\) and 1472 cm\(^{-1}\) (valence vibrations of \( \text{C=C} \) and \( \text{C-C} \) bonds in pyrrolic heterocycle), 1302 cm\(^{-1}\) (valence vibration of \( \text{C-N} \) bond), 1225 cm\(^{-1}\) (non-planar deformation vibration of pyrrolic heterocycle), 965 cm\(^{-1}\) and 678 cm\(^{-1}\) (non-planar deformation vibration of \( \text{C-C} \) bond).
Figure 5 compares FTIR spectrum of source PPY with that of PPY deposited from DMSO matrix. It is apparent that both spectra are similar, i.e. chemical composition of source material changes only slightly during the MAPLE deposition. Strong bands in the vicinity of 1560 cm\(^{-1}\), 1225 cm\(^{-1}\) and 678 cm\(^{-1}\) typical for PPY are retained also in deposited material. Intensity of the band at 1560 cm\(^{-1}\) corresponds to concentration of conjugated double bonds. Presence of conjugated double bonds is advantageous for sensor applications, as these systems are easily polarisable by molecules of absorbed gases. Simultaneously, higher concentration of these bonds causes decrease of material resistivity.
Figure 6. Resistance of sensor with PPY active layer for different temperatures. Measurement was carried out in "pure" synthetic air containing 100% relative humidity. The active layer was deposited from water matrix by laser fluence $F = 0.54 \text{ J} \cdot \text{cm}^{-2}$.

Figure 7. Resistance of the same sensor for different relative humidity (in "pure" synthetic air; isothermal measurement at $t = 25\degree \text{C}$).
For further experiments PPY layers were deposited to Alumina sensor substrates. Figures 6 - 7 present resistance vs. temperature and resistance vs. relative humidity dependence for sensor with 300 nm thick active layer. Sensors resistance \( R \) was measured for temperatures ranging from 24 to 40°C, so Fig. 6 represents only a part of this interval. Resistance \( R \) increases monotonously with increasing temperature and reaches values of \( R \sim 1.0 \cdot 10^8 \Omega \) at 40°C. Simultaneously, resistance \( R \) strongly decreases with increasing relative humidity of surrounding atmosphere (figure 7).

This behaviour can be explained by occurrence of residual humidity in active layer. Doped PPY contains anionic dopants acting as charge carriers. Mobility of these ionic charge carriers is strongly dependent on content of water in active layer. Thus increase of sensor temperature and/or decreasing relative humidity of surrounding atmosphere leads to decrease of residual humidity in active layer and hence decrease of charge carriers mobility.

4. Conclusions
Polypyrrole layers deposited by MAPLE technology are applicable for active layers of gas sensors. Our research showed that in order to achieve sufficient growing rate, laser fluences exceeding ablation threshold must be used. On the other hand, higher laser fluence suppresses formation of broken relief. From these contradictory requirements we may conclude that PPY layers for sensor applications should be deposited by \( F \approx 0.3 \) J·cm\(^{-2}\) from DMSO matrix and \( F \approx 0.45 \) J·cm\(^{-2}\) from water matrix. As for chemical composition, PPY deposited from DMSO matrix is more similar to source material than that from water matrix. With respect to resistance values sensors based on prepared layers should be operated at working temperature 20 - 30°C. Further research will be focused to PPY sensor layers with surface metallic catalysts such as Pd or Pt.

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