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Laser modification of electrical properties of conductive layers made on teflon substrates

Streszczenie. *W artykule przedstawiono wyniki badań właściwości elektrycznych warstw cienkich naniesionych na powierzchnię teflonu za pomocą technologii nanoszenia próżniowego. Dzięki poprawieniu właściwości adhezyjnych podłoża teflonowego poprzez modyfikację wiązką światłowodowego lasera impulsowego nanosekundowego uzyskano zmniejszenie rezystancji osadzanych ścieżek przewodzących.*

Abstract*. The paper presents results of examination of the electrical properties of conductive layers made in PVD process on the Polytetrafluoroethylene (PTFE, Teflon). Due to improvement of adhesive properties of PTFE substrate by laser modification with nanosecond pulses of fiber laser the decrease of resistance of deposited conductive paths was achieved. (****Laserowa modyfikacja właściwości elektrycznych warstw przewodzących wytworzonych na powierzchniach teflonowych****).*

Słowa kluczowe: osadzanie próżniowe, warstwy cienkie, modyfikacja teflonu, laserowa modyfikacja powierzchni
Keywords: vacuum deposition, thin layers, Teflon modification, laser modification of surface.

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Introduction

Today's need of new materials cause development of innovative technology. Physical vapour deposition (PVD) is one of the method of obtaining thin layers which is used for many years. This method does not guarantee proper and sufficient electrical properties of such layers for particular application. The rigorous requirements enforce using of specific substrates or pretreatment before PVD process [1]. When the kind of substrate is dictated by final usage, a pre-preparation of that substrate may be the way of improving its features. Particularly this concerns PTFE substrates [2].

Substrate

Teflon is known as a non-polar and non-stick polymer with a lot of advantageous properties especially thermal resistance and electrical insulation [3,4,5]. The combination of chemical and physical properties of PTFE (Polytetrafluoroethylene) Teflon ® is a consequence of its fluorocarbon structure. This unusual structure leads to a material which has an almost universal chemical inertness; complete insolubility in all known solvents below 300°C; excellent thermal stability and unsurpassed electrical properties, including low dielectric loss, low dielectric constant, high surface resistivity and high dielectric strength. Furthermore, PTFE does not embrittle at very high or at very low temperatures.

According to [6] the dielectric constant of Teflon® PTFE resins shows less change over a wide range of temperatures and frequencies than for any other solid material. This value remains essentially constant at 2.1 over the entire frequency spectrum. Volume resistivity (>10^{16} Ωm) and surface resistivity (>10^{16} Ω/□) for Teflon® PTFE resins are at the top of the measurable range. Neither resistivity is affected by heat-aging or temperatures up to recommended service limits [6].

Teflon can be used as the substrate for the Ag, Au and Cu layer deposition. It is also used for example as the buffer layer before SiO_2 deposition process to improve the electrical reliability of organic transistors [7]. The good adhesion is also needed in that case. The condensation coefficient of depositing metal varies depending on the kind of surface [8]. There is a strong correlation between surface roughness and hydrophobicity and properties of the deposited layer [9]. It is easier to receive the continuous metal layer with good electrical properties on the metal or glass surfaces then on the polymer ones. So making the combination of so extremely dissimilar materials is very attractive.

Method of laser modification

Various pre-treatment methods are known for the preparation of polymer surface for gluing, finishing or printing. The most obvious method for improving surface adhesion like sandblasting, polishing, wet cleaning, chemical etching or dry plasma etching are generally not applicable in the case of clean vacuum deposition processes [10]. Laser technologies are common in such micro technological applications. They are used to modify the surface and also to make non-standard connection between conductive elements [11,12].

There are generally two methods of laser treatment for modification of PTFE to increase the adhesion of surface. The first one leads to changes of surface profile and morphology in submicrometer scale and is also connected with generating of defects which can act as localized minimum of energy [13]. The goal of the second method is to change of surface chemical properties of the PTFE. The mechanism of laser beam influence in this case can rely on photoexcitation of PTFE molecules leading e.g to breaking of polymer chains. When another material were applied during laser treatment some chemical groups (CH_3, OH) can link to molecules of surface layer [14]. Lasers with pulses duration from nanoseconds to femtoseconds and wavelengths varying from 193 nm to 10,6 μm were also applied for surface micromachining of Teflon by ablation and evaporation [15]. Several complex methods using a laser beam were also developed [16,17].

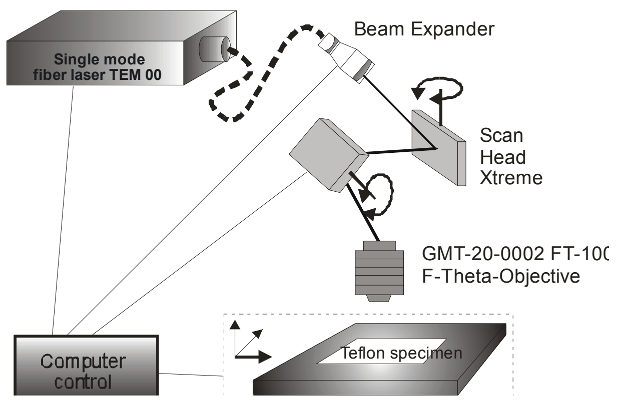


Fig.1. Scheme of the laser system: single mode fiber laser (SPI redENERGY G3 SM 20W)

In this paper the authors have proposed innovative method of using nanosecond laser beam with wavelength of 1070 nm for Teflon surface treatment. Research has been conducted by using single mode fiber laser (SPI redENERGY G3 SM 20W) with different scan velocity, duration of the pulse, energy and frequency. The laser system enables also changing the manner and resolution of scanning of the beam of laser radiation.

The authors lead the study with the laser energy from 6,8 μJ to 68 μJ. The possible way of scanning is presented in the figure 2.

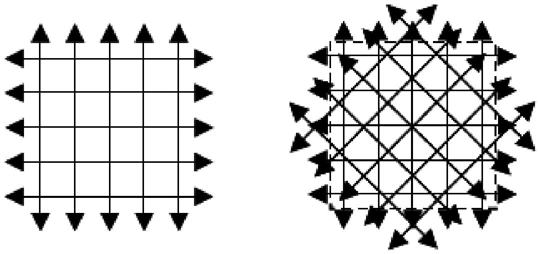


Fig.2 Manner of scanning a) bidirectional, b) different setting of a used jump and a speed of the pixelmarking [10]

Method of vacuum deposition

After laser modification of the PTFE surface authors put thin copper layer on a developed surface area of Teflon substrate. The electrical properties of the layers depend on technical parameters during process of applying conductive layers by thermal evaporation and the parameters of the surface.

Metal layers were applied on the surface using the Classic 250 Pfeiffer Vacuum system [18]. The tungsten boats were used as the resistance vapour source with evaporator current control during the research. The deposition process was carried out after obtaining the vacuum of 0.005 Pa (5×10^{-5} mbar). The pressure in the chamber changed to the value of 0.01 Pa (1×10^{-4} mbar) during the deposition. The application of the layer lasted 5 minutes. The cooper was used as the material for making a conductive layer on the Teflon surface during the process of layer manufacturing. During each process of a thin conductive layer deposition in a vacuum chamber there were some samples with modified surface and one which had not been modified. The last one is regarded as the benchmark in the process.

Evaluation methods

Applied research methods included optical microscopy investigation, study of contact angle and measurements of resistance of deposited layers.

Microscopic studies were carried out using the light microscope Neophot 21 with a magnification of 1000×. Examinations in the polarized light were applied. The effectiveness of the laser modification of PTFE surface and possibility of manufacturing durable metallic layers depends on properties of surface, which determine nucleation and coalescence processes. Surface energy is here essential parameter. Principally its value depends on the kind of a substrate material. Such a statement is based on the assumption that the substrate surface is energetically homogeneous. Disorders of the structure, defects and the growth rates in the surface profile of submicron scale cause local energy minima, which become sites of nucleation. Teflon has one of the lowest surface free energy (SFE) 20 mN/m. SFE is a measure of the interactions between a solid surface and a wetting liquid. It is expressed by the Young-Dupré equation:

$$\sigma_{SV} = \sigma_{LV}\cos\theta + \sigma_{LS} \quad (1)$$

where: σ_{SV} – surface free energy, σ_{LV} – liquid surface tension, σ_{LS} – liquid solid interfacial tension.

Estimation of surface free energy of polymers should take into account dispersive and polar components. For SFE of PTFE distilled water was applied in contact angle measurements, because of its low value of polar contribution of SFE (1.6 mN/m) compared to the dispersive contribution of SFE (18.4 mN/m).

Results

Microscopic study

Metallic layers were deposited onto modified PTFE surface, using mask of a shape specific for resistance measurement. The Cu thin structure created in the PVD process was presented in the figure 3.

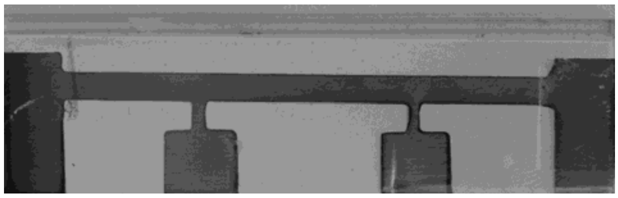
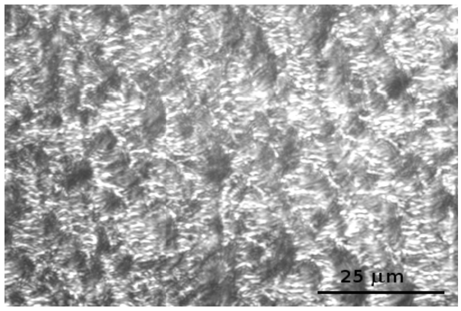
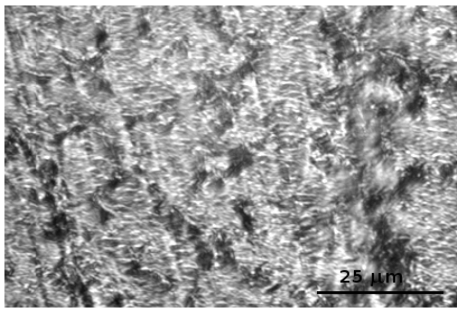


Fig.3. The image of created layer in the PVD process



a)



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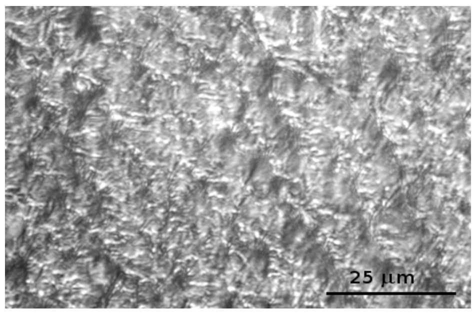

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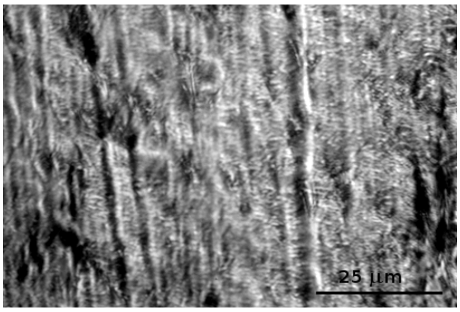


d)

Fig.4. Microscopic images showing thin Cu layer on the PTFE surface: a) without laser modification; b) after laser modification with energy 17 µJ; c) after laser modification with energy 20,4 µJ; d) after laser modification with energy 34 µJ

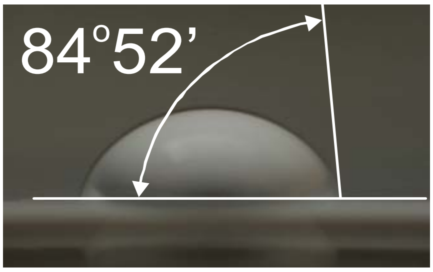
Selected results of the microscope investigations of the created samples are presented in the figure 4.

Surface of the PTFE after laser treatment shows weak interaction up to energy of laser pulse 17 µJ. Fiber laser with a greater energy (20,4µJ) causes weak but noticeable ordering on the surface. The laser beam with the biggest applied energy reveals arrangement on the surface of the structure consistent with the direction of the scanning of laser beam. The probable cause of increasing wettability can be not only laser cleaning process but also development of surface by laser treatment.

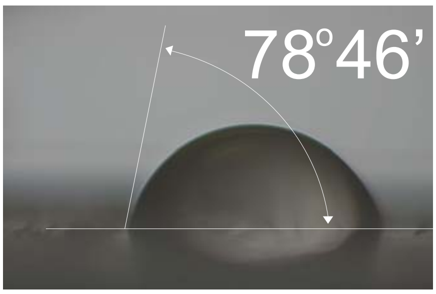
Contact angle (CA) measurements

Results of CA measurements [19] were presented in the figure 5. The biggest contact angle was observed for the surface which has not been modified by laser beam (fig. 5a). However simply correlation between the contact angle and the value of energy pulse does not exist. There is optimal value of energy pulse for which the better properties of wettability have been obtained (fig. 5d).

Variations in resistance were observed in the accomplished research. Thus better correlation between resistance of the Cu layers deposited on PTFE surface and the contact angle has been noticed than between energy of the pulse and CA.



a



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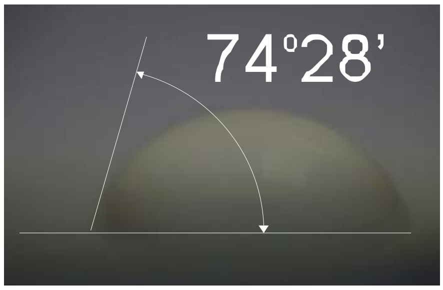

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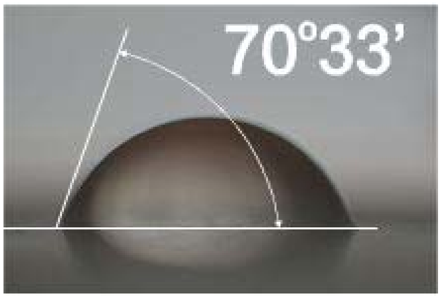

d)

Fig.5. Results of CA measurements: a) PTFE surface without laser treatment; b) PTFE surface after laser treatment, 34 µJ; c) PTFE surface after laser treatment, 13.6 µJ; d) PTFE surface after laser treatment, 20.4 µJ

Electrical resistance measurements

The resistance of produced test paths (fig.3), measured in the four-probe method, was in the range from 0,5Ω to 12Ω. All produced paths (of 5 cm length) manifested continuous conductivity. The differences in the resistance value depend on the energy of laser beam during the process of the surface modification. They also result from the parameters of the evaporation process.

The four-point method of resistance measurement is based on indirect measurement of the resistance of the samples using electrodes, which are placed on the sample, as it is presented in the figure 6.

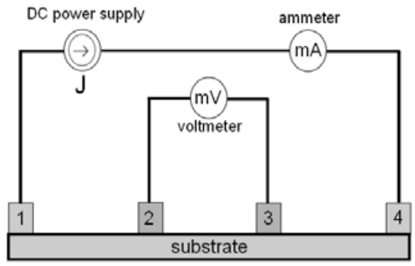

Fig.6. Scheme of the resistance measurement of applied layers.
1,4 – current probes; 2,3 – voltage probes

Next, the resistance was calculated using the rule:

$$R = \frac{1}{2}\left(\frac{U_{2-3}}{I_{1-4}} + \frac{U_{2-3}}{I_{4-1}}\right) \qquad (2)$$

where R – measured resistance, U - measured voltage drop between the pair of 2 and 3 electrodes, I - forced current between measuring electrodes i.e. 1 and 4 or 4 and 1.

The values of resistance of paths produced on the modificated PTFE substrates (R) in different process parameters in relation to the resistance of the reference path deposited on the substrate without laser modification

(R_o) are presented in figure 7. In the same figure 7 there is shown the dependence of contact angle of the PTFE surface after modification in relation to the contact angle value of PTFE without modification α/α_o versus laser pulse energy.

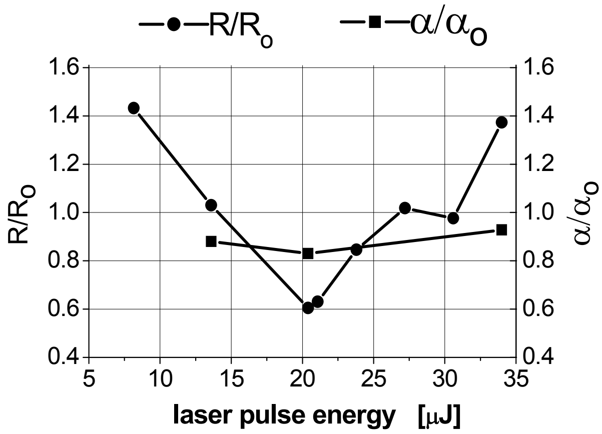

Fig.7. The dependence of produed layers resistance and contact angle on laser energy

The plot R/R_o allows conclude that there is an optimum value of the laser beam energy applied for surface modification. Another value of energy can result in the deterioration of the electrical properties of the layers. Changes in the resistance value are similar to α/α_o dependence.

Simulations of heating of the paths during current distribution with high density were also performed with using the approach described in [20,21]. The simulation results indicate a continuous metallic nature of the paths and good heat removal properties.

Summary

As the results of the investigation authors present the electrical properties of the metal layers made on PTFE with and without laser pre-preparation.

The structural and electrical properties of thin films deposited by PVD technique onto polytetrafluoroethylene (Teflon) substrates have been investigated in the work.

It is possible to modify the PTFE surface to achieve better electrical properties of thin layers. For particular power and depending on the value of wavelength of laser beam decreasing of resistivity of thin metallic layer deposited on PTFE substrate may be even 50%.

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