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Pulsed laser deposition of polytetrafluoroethylene-gold composite layers

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Abstract. PTFE-metal composites are promising candidates for use as sensor materials. In present study PTFE-Au composite layers were deposited by alternated ablation of pressed Teflon pellets and gold plates with focused beam of an ArF excimer laser at 6 J/cm^2 fluence, while keeping the substrate at 150 °C temperature. The morphology and chemical composition of the $\sim$3–4 μm average thickness layers was studied by electron microscopy and energy dispersive X-ray spectroscopy. The layers were mainly formed of PTFE gains and clusters which are covered by a conductive Au film. For testing the applicability of such layers as sensing electrodes, composite layers were prepared on one of the two neighbouring electrode of a printed circuit board. Cholesterol and glucose solutions were prepared using 0.1M NaOH solvent containing 10% Triton X-100 surfactant. The electrodes were immersed in the solutions and voltage between the electrodes was measured while a constant current was drawn through the sample. The influence of the analyte concentration on the power spectral density of the voltage fluctuation was studied.

1 Introduction

Due to the good mechanical, thermal and chemical stability polytetrafluoroethylene (PTFE) is a promising candidate for sensor preparation where its role can be either the immobilization of the component responsible for the sensing or even the participation in the sensing mechanisms when detecting humidity [1], SO$_2$ [2,3], O$_2$, CO$_2$ [4] or other gases [5,6]. The pulsed laser deposition (PLD) of PTFE thin layers is a thoroughly studied research field, the method allows the deposition of stoichiometric thin films with morphology ranging from compact to sponge-like structure [7–9]. The electrical and wetting properties can be tuned by addition of metals. Recent studies showed that PTFE/silver composite structures deposited by PLD using PTFE/Ag targets have a rough morphology with increased specific surface attributed to the deposition of PTFE grains and show improved conductive and wetting properties due to the Ag content [10].

In the last few years several attempts have been made for fabrication of non-enzymatic sensors for the detection clinically important analytes, as glucose [11,12], cholesterol [13,14] or urea [15]. These researches are motivated by the fact that, although the amperometric and potentiometric detectors based on incorporation of enzymes into the active electrodes [16–19] show good selectivity, the enzyme immobilization process is the most difficult step of the production process. The non-enzymatic sensors are based on conductive electrodes with high specific surface and charges involved in electrocatalytic process are detected by amperometric measurement methods. While classical detection techniques are based on the measurement of the time-averaged value of the sensor signal, in some cases the existence of "fingerprints" of the analytes [20–22] in the low amplitude time-varying components of the signal were also demonstrated. This detection method is called fluctuation-enhanced sensing (FES). In a recent work the PTFE/Ag composite layer covered electrodes were immersed in cholesterol solution and the voltage fluctuation was measured while driving a constant current through the electrodes. It was found that power spectral density of the "noise" depended on the cholesterol concentration; however a quick aging of the electrodes due to the silver oxidation was observed [23].

In this work we present our results on the pulsed laser deposition of PTFE/gold composite layers onto electrodes of printed circuit boards and their behavior in fluctuation enhanced sensing measurements is monitored when immersed in solutions of cholesterol and glucose and their mixture.

2 Experimental

2.1 Thin film deposition

Composite layers formed of PTFE and gold were prepared by pulsed laser deposition onto one electrode of a printed
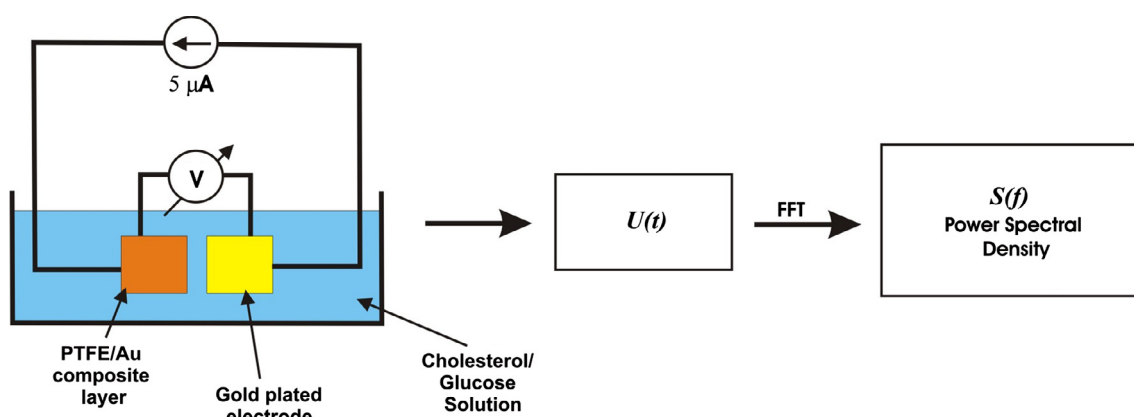
a e-mail: kega@physx.u-szeged.hu

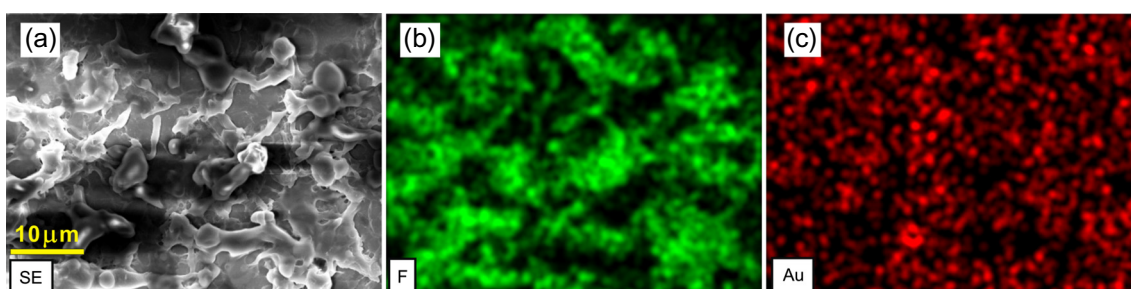**Fig. 1.** Measurement procedure for the fluctuation-enhanced sensing.

Fig. 2. Electron microscopic image of the rough composite layer covered electrode (a) and elemental distribution on the same area for F (b) and Au (c).

circuit sample board containing a pair of 2×2 mm^2 gold plated electrodes with 1 mm separation distance as presented in detail earlier in reference [23]. The disk-shaped target was composed of two halves of disks: one of bulk Au and one of pressed PTFE powder. The experimental conditions were chosen based on the results of our earlier studies [9,10] as to assure degradation-free transfer of PTFE and appropriate mixing of Teflon and metal in order to obtain a rough surface conductive composite layer. The continuously rotated target was ablated with 5000 pulses of an ArF excimer laser ($\lambda = 193$ nm, FWHM $= 20$ ns) focused onto a 0.8 mm^2 area while the applied fluence was 6 J/cm^2. During the deposition the sample board facing the target at 4 cm distance was kept at 150 °C temperature. The morphology and the elemental distribution of the prepared layers were studied with a Hitachi S4700 scanning electron microscope (SEM) equipped with a Röntec QuanTax energy-dispersive X-ray spectrometer (EDX).

2.2 PTFE/Au composite layers as sensor electrodes

A 0.1M NaOH solvent containing 10% Triton X-100 surfactant was used to prepare solutions of 2 and 5 mM cholesterol, 5 and 15 mM glucose and their mixtures. The fluctuation based sensing measurements were performed as follows: the sample board was immersed vertically into the solutions until the two electrodes became fully covered (Fig. 1). A constant current of 5 μA was drawn through the circuit and the $U(t)$ voltage between the two electrodes was measured with 38 nV resolution at a sampling rate of 4000 Hz for a period of 15 s. The $S(f)$ power spectral density of the voltage fluctuation was obtained by fast Fourier transform (FFT) in LabView software environment. The signal was divided in 30 pcs. of 0.5 s segments and their FFT spectra were averaged. Reference measurements on untreated electrodes were also carried out.

3 Results

3.1 Thin film characterization

As the electron microscopic image in Figure 2a shows, the layers have a rough surface, since the PFFE (-[C$_2$F$_4$]$_n$-) is mainly transferred in form of grains and larger clusters, only a minor part can be originated from repolymerization from larger polymer chain fragments. Elemental microanalysis was realized by EDX and the results proved that the gold is more uniformly distributed over the deposited area. More detailed previous studies showed that the darker areas on the image showing the elemental map of the gold (Fig. 2c) can be attributed to the shielding effect of the PTFE grains, since their size is larger than the $\sim$1 μm detection depth of the EDX. As the alternate ablation of the two components results in the
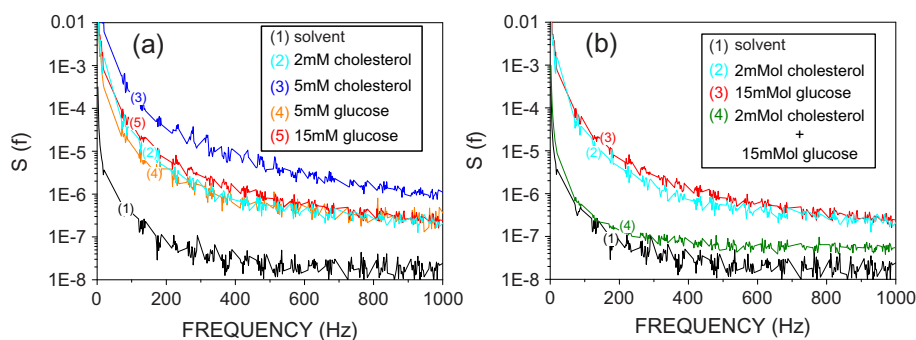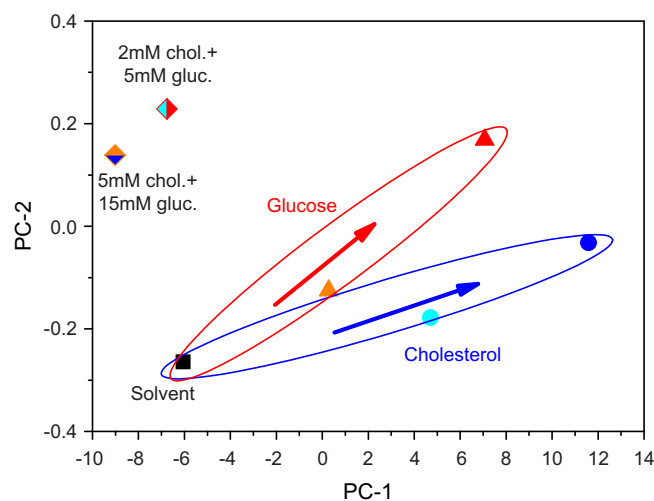
Fig. 3. Spectra of the voltage fluctuation for different solution types when using composite layer covered electrode (a) and comparison of the spectra recorded with a two component solution to the corresponding single component spectra (b).

covering/mixing of the Teflon structures with the metal, the layers became conductive; moreover the wettability is also increased as compared to pure PTFE. These properties of the layers assure an increased contact area when the electrode is immersed in the solution, as compared to the original, uncovered electrodes.

3.2 Fluctuation-enhanced sensing

For voltage fluctuation measurements each solution was tested with a new sample board. $S(f)$ power spectral density function was obtained in 0–2 kHz frequency range with 2 Hz resolution according to the sampling rate and the length of the $U(t)$ signal used for FFT. In most cases the harmonics of the 50 Hz grid frequency appeared in the spectra, which were cut off. In case of untreated electrodes the analyte and its concentration did not show observable influence on the obtained $S(f)$ spectra. In contrast to this, there was a noticeable difference between the spectra obtained in presence of cholesterol and glucose solutions with different concentrations (Fig. 3a). In case of the conducting pure solvent the noise spectrum originates from its characteristic resistance fluctuation, which is a general property of conductive elements in electronics. In case of cholesterol and glucose solution the charge transfer related to their electrocatalytic reaction at the surface of the rough electrode also contributes to the detected noise. This indicates that due to their rough surface such composite layers may serve as active electrodes in non-enzymatic electrocatalytic sensors. In case of real measurements the interference between the different analytes being present in monitored solution has to be taken into account. The Figure 3b shows an example spectrum for a solution containing both cholesterol and glucose as compared to appropriate single component solutions. Although we expected the spectra of the mixtures to be situated somewhere between those corresponding to the single component solutions, there is no straightforward relationship between the corresponding spectra.

A quantitative comparison of the spectra was realized by principal component analysis (PCA). Since value

Fig. 4. Result of PCA analysis of the voltage fluctuation spectra recorded for different solutions represented in PC-1 - PC-2 plane. The arrows indicate the tendency for increasing concentrations of single component solutions.

ranges of the $S(f)$ functions cover several orders of magnitudes, their logarithm was calculated and then fitted with a third order exponential decay function. Thus smooth curves following the tendencies of the spectral functions were obtained and their 2–100 Hz frequency range was submitted to PCA analysis. Figure 4 shows the plotted values of the first two components of the resulting scores matrix (PC-1 vs. PC-2). The data points indicate that even if there is a tendency when varying the concentrations of cholesterol and glucose solutions, one cannot find a connection between the position of the data points for the mixtures and the concentration of the components. PCA can be used also for evaluation of infrared absorption spectra of multicomponent samples. Supposing no interaction between the components, the total absorbance is the summarized absorbance of the individual constituents. In case of a three component sample, performing a PCA analysis on IR spectra recorded for different mixtures and plotting the results in plane a ternary graph-like triangular point distribution can be obtained with
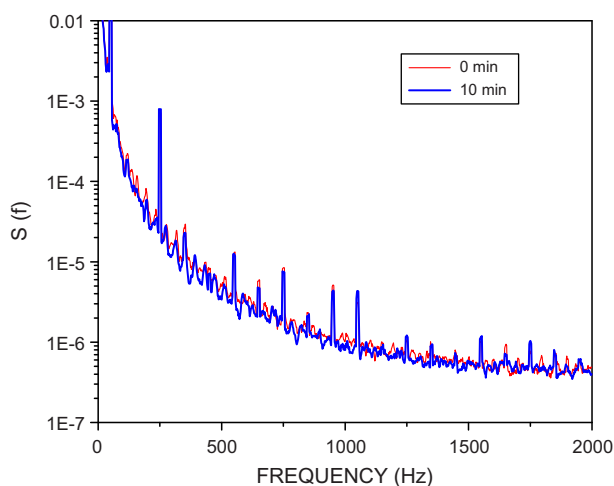
Fig. 5. Averaged spectra recorded at the beginning and at the end of 10 min aging test.

points corresponding to the three pure samples on the corners of the triangle, as demonstrated in by Bacci et al. (calcareous samples [24]) and Norgaart et al. (sucrose and its components [25]). Obviously, in case of four constituents the first three PC components of the score matrix have to be plotted in a 3D coordinate system, etc. In our case the solution can be considered as a three component sample formed of solvent, glucose and cholesterol. When either the cholesterol or glucose was dissolved, the linear shift in PC-1 - PC-2 plane of the data points as the function of concentration was visible in our case, too. The behavior of the cholesterol-glucose mixtures was different from the above mentioned case of IR spectral analysis, which can be partly attributed to the lack of component-specific peaks in the recorded noise spectra and partly to the fact that the presence of one solved component influences the interaction of the electric charges with the other solved component resulting in a non-additive aspect of the noise spectra. This suggests that in presented experimental parameters the fluctuation enhanced sensing accompanied with principal component analysis is not a practicable way for multicomponent analysis in liquid phase. A possible solution could be the monitoring of the noise when altering the driving current (and consequently the constant component of the measured voltage), since the electrocatalytic process of glucose and cholesterol is voltage dependent.

In an earlier study a quick degradation of the silver based composite electrodes (probably caused by oxidation) was observed during similar experiments and only the spectra recorded in the first 15 s could be used for evaluation. Therefore the stability of the PTFE/gold composite layers and temporal behavior of the recorded spectra were also tested. There was no observable discoloration of the electrodes even after 10 min continuously running experiment. Figure 5 shows an example on the noise spectral stability recorded in case of 5 mM cholesterol solution.

4 Summary

Pulsed laser deposition method was used to prepare conducting PTFE-gold composite layers for sensor electrode purposes. The increased specific surface of the layers increased the sensitivity of the electrodes as compared to the original smooth gold plating, when measuring voltage fluctuations in presence of cholesterol and glucose solutions. While the earlier studied PTFE-silver composite electrodes showed a fast aging due to the oxidation of the silver, the use of gold as conducting element resulted in significant increase in stability. Although there is obvious influence of the concentration on the recorded spectra, in case of two component solution the separation of the components' effect is not straightforward. Similar difficulties were encountered in multicomponent gas sensing with FES method. Further studies on optimization of measuring parameters (electric current value, sampling rate, etc.) and data processing methods are needed for enhancing the cross-selectivity of the method.

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