Applied Surface Science 278 (2013) 117–121

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Study on the applicability of polytetrafluoroethylene–silver composite thin films as sensor material

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ARTICLE INFO

Article history:
Received 15 June 2012
Received in revised form 6 November 2012
Accepted 8 January 2013
Available online 23 January 2013

Keywords:
Pulsed laser deposition
Composite layer
Silver
PTFE
Fluctuation-enhanced sensing
Cholesterol

ABSTRACT

A study on applicability of conductive high specific surface PTFE/Ag composite layers as active electrodes of a non-enzymatic cholesterol sensor is presented. The composite layers were prepared on one of the two neighboring electrode of a printed circuit board by pulsed laser deposition technique where targets composed of silver and PTFE were ablated by an ArF excimer laser. Cholesterol was dissolved in 0.1 M NaOH in different concentrations in 0–5 mM range. A drop of cholesterol covered the two electrodes and a constant current of 10 μA was forced through the sample while the voltage between the electrodes was measured by means of a high resolution A/D converter with 1 kHz sampling rate for 5 s periods. Instead of the time-averaged signal monitoring we applied the Fluctuation-Enhanced Sensing (FES) method which is based on the analysis of the stochastic component of the signal. The power spectral density of the fluctuation was found to be dependent on the cholesterol concentration of the samples. Principal Component Analysis method was used for quantifying the difference between the recorded spectra. A tendentious variation of the spectral properties as the function of the cholesterol concentration was observed. The results indicate that the FES technique combined with high specific surface composite electrodes may be a useful tool for cholesterol detection.

1. Introduction

Polymer-metal composites are good candidates for sensor materials. Their electrical, optical and dielectric behavior is strongly influenced by the metal content, the size and shape of the particles [1–3]. One of the promising basic materials for composite preparation is the Teflon (polytetrafluoroethylene, PTFE) which has good mechanical, thermal and chemical stability [4,5]. PTFE thin films can be prepared by various techniques depending on the used substrate and quality requirements. The pulsed laser deposition (PLD) allows the deposition of stoichiometric Teflon thin films with compact structure or sponge-like morphology depending on the deposition parameters and post-treatment [6–8]. 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 [9].

Conductive layers with high specific surface can find applications in the field of biosensors, too. Amperometric and potentiometric devices often aiming the detection of analytes with clinical importance (e.g. urea, glucose, cholesterol) are mainly based on incorporation of enzymes into the active electrodes [10–14]. The enzyme-based sensors can have good selectivity and high sensitivity, however, the enzyme immobilization process is the most difficult step of the production process. In the last few years several attempts were made for fabricating enzyme-free biosensors. Wang et al. produced an amperometric glucose biosensor based on the modification of functional nickel hexacyanoferrate nanoparticles [15]. Lee and Park used a macroporous gold electrode with incorporated Pt [16], while Li et al. built porous tubular silver nanoparticles [17] for detecting cholesterol. In these amperometric measurements charges involved in the electrocathalitic oxidation of cholesterol at the electrode surface were detected, therefore the increased specific surface of the electrode is of high importance.

Most of the detection techniques are based on the measurement of the time-averaged value of the sensor signal, however, also the stochastic component (noise) can serve important information on the detector's ambience. For example, in case when detector signal is the result of the desorption of the analyte at the sensing surface the dynamics of the adsorption–desorption and the diffusion properties can serve as a "fingerprint" for a given analyte. In the Fluctuation-Enhanced Sensing (FES) the low amplitude time-varying components are amplified and statistically analyzed to find the "fingerprints" of the analytes [18,19]. While for simultaneous detection of multiple components a number of different sensors

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http://dx.doi.org/10.1016/j.apsusc.2013.01.051

have to be used, with use of proper analysis, pattern database and pattern recognition tools FES can allow their detection using one single sensor [20,21]. The FES method was introduced and mainly used for increasing the selectivity of gas sensors, its usefulness in liquid phase was demonstrated for detection of bacteria [22]. In latter case a voltage fluctuation between two electrodes caused by ions emitted by phage infected bacteria was detected.

The aim of present work is a preliminary study on the applicability of our laser deposited PTFE/Ag composite layers as sensing electrodes for the non-enzymatic detection of cholesterol. Differently from conventional amperometric methods, we intended to study whether the cholesterol concentration can influence the noise of the detected signal which is substantial from the point of view of fluctuation-enhanced sensing.

2. Experimental

2.1. Thin film deposition

PTFE/Ag composite layers were prepared by pulsed laser deposition method onto one of the electrodes of printed circuit sample boards containing two pairs of 2 mm × 2 mm gold plated electrodes as shown in Fig. 1. The experimental parameters were chosen based on the results of our earlier studies [8,9]. The rotating disk form targets were composed of two sectors of circles: 1/6 part PTFE (Goodfellow, grain size 6–9 μm compacted at 520 MPa pressure) and 5/6 part Ag (Goodfellow, 2 mm thickness, purity 99.95%). The target rotated with 10 rpm was ablated with pulses of an ArF excimer laser (λ = 193 nm, FWHM = 20 ns) having 8 J/cm^2 fluence at an area of 0.8 mm^2, the repetition rate was 10 Hz. The relatively low deposition rate does not allow the formation of sandwich structure. Layers were deposited with 7500 and 12,500 pulses, respectively to obtain composite electrodes with different roughness. During deposition the substrates (sample board or glass plate for electron microscopic investigations) were placed onto a 150 °C heatable holder. The base pressure of the PLD chamber was about 2 × 10^{-3} Pa and the distance between the target and the substrate was 4 cm. The morphology of the layers was studied with a Hitachi S4700 scanning electron microscope, while their elemental composition was analyzed with the energy-dispersive X-ray spectrometer (EDX) of the electron microscope.

2.2. The fluctuation-enhanced sensing

Cholesterol was dissolved in 0.1 M NaOH solvent containing 2 v% Triton X-100 (Sigma) in different concentrations: 0.5, 1, 2 and 3.5 and 5 mM, respectively. (The normal cholesterol concentration is below 5 mM in human blood.) A drop of solution was placed onto the sample board to overlap the two adjacent electrodes, one being covered with the PTFE/Ag composite layer, as shown in Fig. 2. Reference measurements on untreated Au electrodes were also carried out. A constant current of 10 μA was drawn through the circuit and the $U(t)$ voltage between the two adjacent electrodes was measured with a sampling rate of 1000 Hz for three consecutive periods of

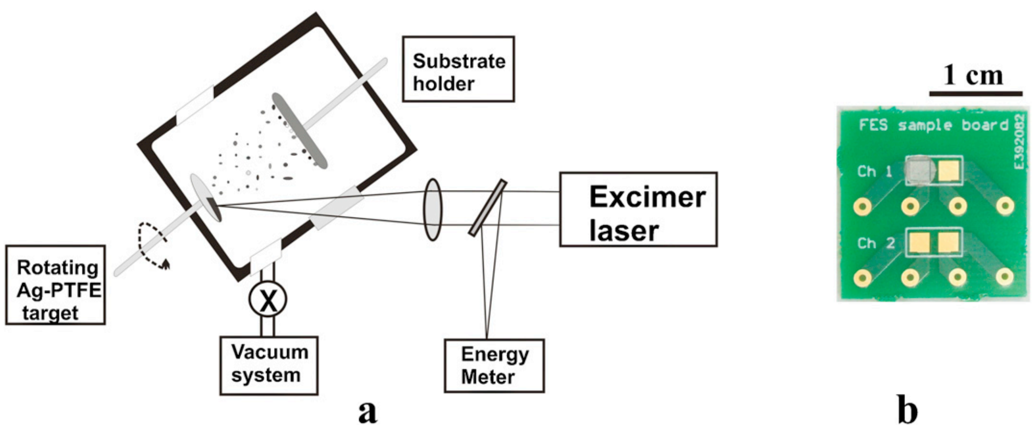

Fig. 1. Set-up used for composite layer deposition (a) and photograph of a sample board with one covered electrode (b).

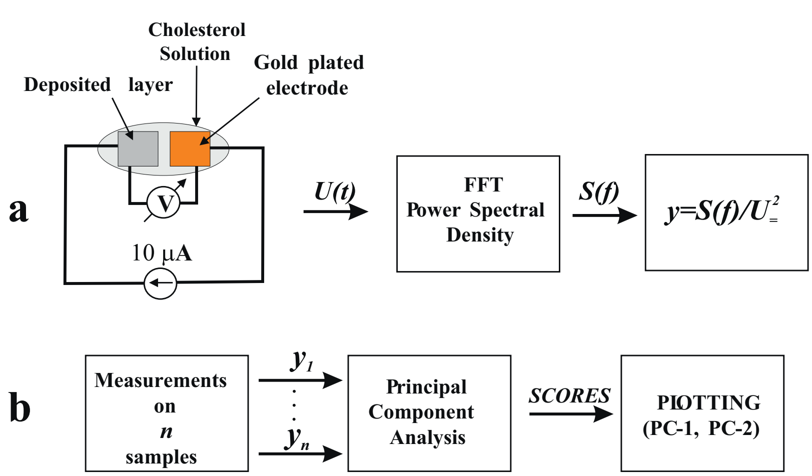

Fig. 2. Scheme of the measurement procedure of FES method: obtaining individual noise spectrum for each sample (a) and comparison of spectra by means of PCA (b).