



# Ultra-thin films on transparent conductor oxides for the development of spectro-electrochemical transducers



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## ABSTRACT

Transparent C, Au and Pt films with thickness in the 5–10 nm range have been deposited by a DC magnetron sputtering system on commercial ITO (indium tin oxide) coated glass substrate for evaluation as electrode of spectro-electrochemical transducer. The transmission, over the investigated spectral range, is superior to 55% with the best transmission values obtained for C films (higher than 80%). The deposited films have been characterized by AFM, XPS and electrochemical methods. Results showed a low roughness, improved in comparison with uncoated electrodes. Electrochemical properties of the Au and Pt films evidenced a metallic behavior, which allowed qualifying them as conductive optically transparent electrodes for spectro-electrochemical devices.

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## 1. Introduction

Surface modifications of materials by functional groups using electrochemical methods proved to be a promising alternative able to open wide opportunities in the field of electrochemical transducers, bioelectronics or manufacturing junctions for molecular electronic devices [1–3].

The grafting by electrochemical method of an electrode surface with a biological platform endowed with selective recognition properties represents a major breakthrough in the field of biosensors. The establishment of a direct electron transfer between biological molecules and the electrochemical transducer represents the key element in developing biosensors applications. One method successfully applied for modification of carbon, metal or semiconductor is represented by the electrochemical reduction of diazonium salts [4–9]. This method allows the covalent bonding of organic molecules to the substrate through the formation of an aryl radical. The possibility of grafting the gold electrodes was demonstrated first time by Ahlberg [10] in the 80s and relatively recently the gold modification by diazonium salts gained an increased interest [11,12].

Although the modification seems to be straightforward in the case of carbon based materials, the mechanism for grafting gold electrodes by diazonium salts are not completely disclosed. Recent

studies showed that the surface properties can influence the mechanism of grafting [13].

On the other hand in a combination with a spectroscopic technique, one can detect in situ the chemical species generated, conferring to the sensor platform, beside the quantitative detection capacity of the electrochemical methods, the power of a qualitative analysis method [14]. The availability of conductive optically transparent electrodes makes possible the correlation between electrochemical processes and the optical ones by direct observation and can supply important information concerning the reaction kinetics, intermediary states or analyte diffusion coefficients.

As far it concerns the material for such applications, a good candidate should comply with several requirements. These are related to a good transparency, chemical inertness, long term structural and chemical stability and a relative fast electron transfer with the detection platform. At present there are several possible candidates for optical transparent electrodes. These candidates are noble metals like Au, Pt, carbon or metal oxides deposited in the form of an ultra-thin film on glass, quartz or plastic substrates [15]. A compromise between the thickness and the optical transparency must be accepted: the film thickness must be high enough to provide a low electrical resistance for reasonable electrochemical properties but too thick films lead to an insufficient optical transparency for spectroscopic observations.

The available data indicated that, from an electrochemical point of view, Au and Pt are very stable. Another advantage of Au, is its possible use for biosensors based on surface plasmon resonance methodology. Carbon films are also good potential candidates

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because of the relatively large polarization window especially in the cathodic range [16]. Covalent grafting of the electrode surface (Au, Pt, C, . . .) with functional groups can be easily achieved. Several procedures have been established for surface modification including electrografting [12]. In these circumstances the use of Au, Pt or C in manufacturing transparent electrochemical electrodes seems to be very attractive.

In the present work, the strategy which is followed was to use a multilayer material deposited on glass substrate. The first layer corresponds to a transparent conductor with a low sheet resistance combined with a good transparency. Commercial ITO (indium tin oxide) coated glass substrate was used. The second layer on the top surface was an ultra-thin layer of carbon, gold or platinum deposited by magnetron sputtering. The use of magnetron sputtering process allows the control of the coating properties in terms of thickness, composition, morphology and structure [17]. In our study the influence of deposition conditions on the coatings characteristics was initially evaluated, and then the optimized deposition conditions have been used for electrochemical investigations.

## 2. Experimental

The deposition has been made using an unbalanced DC magnetron sputtering system. Gold (99.99 at.%), platinum (99.95 at.%) and graphite (99.995 at.%) targets of 76.2 mm in diameter have been used as vapor sources. All the films were obtained by maintaining a constant distance of 130 mm between the magnetron targets and substrates. Commercial ITO glass coated samples (25 mm × 6 mm × 1 mm) have been used as substrates for transparent thin films deposition. The low sheet resistance of the ITO film (50 Ω/□) allows the transfer of current between the deposited film and the electrochemical environment.

The substrates were cleaned in ethanol and distilled water ultrasonic baths for 30 min and then were mounted in the deposition chamber.

Before deposition, the base pressure in the deposition chamber was  $6.5 \times 10^{-5}$  Pa, while deposition was performed with an argon plasma at 0.5 Pa. In order to control the film thickness, the power applied on magnetron target was correlated with deposition time. For gold and platinum deposition a power of 15 W has been applied on magnetron target. The temperature during the deposition cycles did not exceed 80 °C.

In order to get a good balance between a high optical transmission and a complete coverage of the ITO substrate by the deposited material (C, Au or Pt), an extensive study has been performed which consequently led to an optimization of the deposition parameters (discharge power and deposition time) as it follows. The deposition time for Au and Pt films was set to 22 s. Due to a low sputtering yield of graphite target, the transparent carbon thin films have been obtained by applying a power of 110 W on the magnetron target while the deposition time was increased to 15 min. During the deposition different RF bias voltages on substrate have been tested. The influence of RF bias voltage on the coatings characteristics has been afterwards investigated.

Monocrystalline silicon (100) substrates, simultaneously coated with ITO substrates, have been used for ellipsometric measurements in order to obtain the thickness of the films. The ellipsometric data measured for each transparent film have been fitted with an appropriate theoretical model. The curve fitting of the ellipsometric parameters ( $\Psi$  and  $\Delta$ ) has been performed up to a minimum value of the Mean Squared Error (MSE) between the measured data and simulated values using the WVASE32<sup>®</sup> software (J. A. Woollam Co., Inc.).

Ex situ X-ray photoelectron spectroscopy (XPS) investigations were performed using a Kratos Axis Nova spectrometer with an

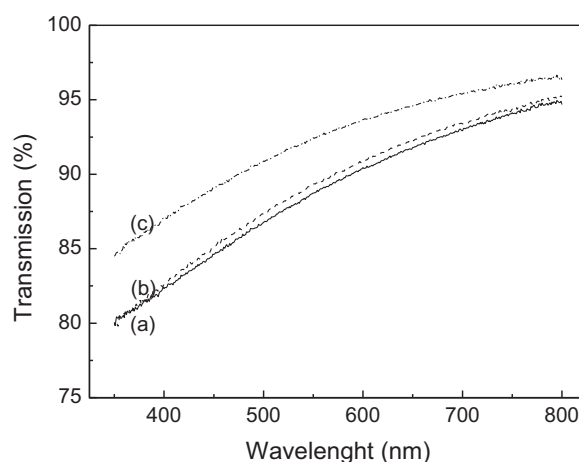


Fig. 1. Influence of the substrate bias on the optical transmission of the C films: (a) 0V (no bias); (b) -70V; (c) -120V.

Al  $K_{\alpha}$  radiation (1486.6 eV). The XPS survey scans were acquired using the following parameters: pass energy = 126 eV, energy step size = 0.5 eV. The survey spectra were taken over a binding energy (BE) range from -4 to 1000 eV, and a scan time of 120 s. High-resolution spectra for the elements of interest such as O 1s and C 1s core levels have been obtained by performing ten scans at pass energy of 40 eV with a step energy of 0.1 eV. CasaXPS 2.3.15 software has been used for the analysis of all XPS spectra. High-resolution XPS spectra have been used in evaluating the chemical composition of the coatings and the chemical states of each element. Chemical state of the elements have been analyzed by fitting the spectra with Gaussian-Lorentzian line profiles defined in CasaXPS as GL(30).

Optical transmission measurements in the spectral range 350–800 nm have been used to evaluate transmission response of the films. A Cary UV-VIS-NIR spectrometer was used in this purpose.

Surface morphologies were evaluated using atomic force microscopy (AFM) in tapping mode. An AFM Veeco equipment has been employed in this respect.

Electrochemical characterizations of the films have been performed by cyclic voltammetry and electrochemical impedance spectroscopy. A SP300-Biologic-potentiostat was used in this respect, and measurements were carried out in a standard three electrodes electrochemical cell (with a saturated calomel electrode (SCE) used as reference electrode and a Pt-wire electrode used as auxiliary electrode). For this purpose, sulfuric acid ( $0.1 \text{ mol L}^{-1}$ ) or ferri/ferrocyanide ( $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ ;  $5/5 \cdot 10^{-3} \text{ mol L}^{-1}$ ) solutions have been examined in order to assess the electrochemical reactivity of a series of prepared ultra-thin film surfaces. The resulting electrochemical performances were then compared to those obtained with uncoated ITO substrates taken as a reference surface.

## 3. Results and discussion

The evaluation of optical transparencies of the coatings was the first step in the characterization of these materials. The transmission increases with the substrate bias voltage for carbon (Fig. 1), gold (Fig. 2) and platinum films (Fig. 3).

A particular evolution of the optical transparency was observed for transparent gold films where the green region of the visible spectra showed the highest transparency, as it can be observed in Fig. 2.

Compared with carbon films, the transmission of platinum films decreases with wavelength (Fig. 3). These preliminary investigations demonstrated on one hand that the deposited films have

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