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**Graphical Abstract**

**Novel Approach to Surface Plasmon Resonance: A Third Dimension in Data Interpretation through Surface Roughness Changes**
Claudiu Constantin Manole, Cristian Pirvu, Francis Maury, Ioana Demetrescu

The SPR data interpretation is usually made from the dependence of the reflectivity angle with the time. We propose a third parameter readily monitored: the reflectivity intensity. Changes in reflectivity intensity are monitored *in-situ* as surface roughness changes. Original implications for pyrrole polymerization with oxalate are presented.
NOVEL APPROACH TO SURFACE PLASMON RESONANCE: A THIRD DIMENSION IN DATA INTERPRETATION THROUGH SURFACE ROUGHNESS CHANGES

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ABSTRACT

In a Surface Plasmon Resonance (SPR) experiment two key parameters are classically recorded: the time and the angle of SPR reflectivity. This paper brings into focus a third key parameter: SPR reflectivity. The SPR reflectivity is proved to be related to surface roughness changes. Practical investigations on i) gold anodizing and ii) polypyrrole film growth in presence of oxalic acid is detailed under potentiostatic conditions. These experimental results reveal the potential of using the SPR technique to investigate real-time changes both on the gold surface, but also in the gold film itself. This extends the versatility of the technique in particular as sensitive in-situ diagnostic tool.

Keywords: Surface Plasmon Resonance, Atomic Force Microscopy, Roughness, Potentiostatic
1. INTRODUCTION

In 1968, A. Otto reported the excitation of the surface plasma waves by total reflection between a dielectric and noble metal [1]. Then E. Kretschmann published a subsequent report for an optical system in which the surface plasma was excited inside the metal and treated its implication on the optical constants [2]. Shortly after, this phenomena named Surface Plasmon Resonance (SPR) was used in technological applications as a versatile technique for gas sensors [3], in the study of optical properties of metals [4], or as a microscopy technique [5]. Recently, the SPR technique was integrated into a powerful biosensing system [6–8].

The optical SPR device is composed of a prism, a thin gold layer (around 50 nm thick) and a sensing layer forming an interface between the gold film and the surrounding medium. Each component has its own refractive index values, noted in Fig. 1a with \( n_p \) for the prism, \( n_m \) for gold (continuous metal thin film) and \( n_s \) for the sensing layer. Different approximations were used to study this phenomenon, with increased accuracy [9, 10]. However using the Fresnel equations [11], we can look at an approach which provides a relationship to the classical Lambert-Beer law while also highlighting practical aspects related to the surface features.

The SPR technique was also coupled with an electrochemical system to simultaneously monitor the electrochemical reactions and the SPR behavior. A previous study described some aspects related to the synergetic use of these techniques [12]. However, in the present paper we followed an original approach which consists in using the electrochemical system only to produce the chemical reactions, while the SPR was used as an in-situ diagnostic tool to investigate them. In order to comply with the theoretical approach, a potential was applied potentiostatically so that its value can be considered as a constant. Practical SPR implication on
in-situ polypyrrole doping is detailed. The changes at the gold interface (i.e. polymerization) and in the gold layer itself (anodizing) is investigated by considering the reflectivity angle change, as described in the fundamental part (usual approach) but also the reflectivity intensity (an original view describing a third parameter), as highlighted in the next section.

2. FUNDAMENTAL PRINCIPLES

When an electromagnetic wave of light is passing from one medium to another, it changes its direction as shown schematically in Fig. 1a, according to the Snell law:

\[
n_p \sin \theta_p = n_m \sin \theta_m
\]

where \( \theta_p \) is the angle of the incident electromagnetic wave and \( \theta_m \) is the emergent one. When the \( \theta_m \) angle reaches the value 90°, the light wave is totally reflected. Under the total reflection conditions, the value of \( \theta_p \) is also called the critical angle, and it can be determined by inserting \( \theta_m = 90° \) in Eq. (1).

The SPR apparatus uses a p-polarized incident light. The total reflected amplitude of this incident light at the prism-metal interface is given by:

\[
r_{pm} = \frac{n_m \cos \theta_p - n_p \cos \theta_m}{n_m \cos \theta_p + n_p \cos \theta_m}
\]

where

\[
\cos \theta_m = \sqrt{1 - \frac{n^2_p}{n^2_m} \sin^2 \theta_p}
\]

Under these total internal reflection conditions, an evanescent wave is formed at the interface of the medium with a magnitude of the wave vector \( k_e \) [13]. This parallel evanescent wave is amplified in the presence of the gold film. This generates collective oscillations of the
plasmons (free electrons in the metal network) at the metal-sensing layer interface. The wave vector of these surface plasmons can be defined as [13]:

$$k_{SPR} = \frac{2\pi}{\lambda} \sqrt{\frac{n_p^2 n_s^2}{n_m^2 + n_s^2}}$$  \hspace{1cm} (4)

Under these conditions, internal reflection will occur inside the metal layer. The amplitude of this reflection is described by:

$$r_m = \frac{n_p \cos \theta_m - n_m \cos \theta_s}{n_p \cos \theta_m + n_m \cos \theta_s}$$  \hspace{1cm} (5)

where

$$\cos \theta_s = \sqrt{1 - \frac{n_p^2 \sin^2 \theta_p}{n_s^2}}$$  \hspace{1cm} (6)

The refractive index is a complex quantity that can be written as:

$$\tilde{n}_j = n_j + i K_j = n_j (1 + i \kappa_j)$$, where $j$ is the $p$, $m$ and $s$ components  \hspace{1cm} (7)

An overview on the total reflection intensity ($R$) of the incident monochromatic light for the whole SPR device is given by [11]:

$$R = \left| \frac{r_p m + r_m s \exp \left( \frac{i 4 \pi \delta h}{\lambda} \sqrt{\kappa_m^2 - \kappa_p^2 \sin^2 \theta_p} \right) }{1 + r_p m r_m s \exp \left( \frac{i 4 \pi \delta h}{\lambda} \sqrt{\kappa_m^2 - \kappa_p^2 \sin^2 \theta_p} \right)} \right|^2$$  \hspace{1cm} (8)

The exponential term in Eq. 8 describes the intensity decrease in the reflected monochromatic light. The parameter $\kappa_m$ is associated to the “internal” intensity loss in the metal, while $\kappa_p$ represents the intensity that is lost into the prism. The thickness of the metal-sensing layers ($h$) has also an important role in the reflection decrease, as evidenced by the Eq. 8 since it is involved in the exponential term.
One of the conditions required for the SPR technique is that \( k_{ev} = k_{SPR} \). Considering this, the SPR resonance angle (\( \theta_{SPR} \)) can be calculated as:

\[
\theta_{SPR} = \theta_p = \sin \left( \frac{n_p^2}{n_m^2} + \frac{n^2}{n_p^2} \right)
\]  

(9)

In the SPR technique we are usually monitoring the changes of the reflectivity intensity and the reflectivity angle as a function of time (in the range of a few seconds). The first one is described by the real part of the refractive index (Eq. 8), while the second one by the imaginary part (the exponents in Eq 8). Punctually, with the SPR apparatus we have a series of constant parameters. For example, by taking \( n_m = \text{constant} \), \( \lambda = \text{constant} \) (with \( C \) as integration constant) and \( n_p = x \), we can define the refractive index rate of change as:

\[
R(\theta_{SPR}) = C \int' \sin \left( \frac{2x^2}{n_p^2} \right) \, dn_s + C \int' \cos \left( \frac{2x^2}{n_p^2} \right) \, dn_s = \int' \frac{\partial n_{SPR}}{\partial \theta_{SPR}} \, d\theta_{SPR}
\]

(10)

Since \( \kappa_p \) and \( \kappa_m \) are intrinsic properties of the prism and of the metal respectively, therefore they are constant, and with in addition \( \lambda = \text{constant} \) one can define the reflectance intensity rate of change as:

\[
R(I_{SPR}) = C \int' Z(h) \, dh = \int' I_{SPR} \, dI_{SPR}
\]

(11)

where \( Z(h) \) represents the height profile function, while \( dh \) represents infinitesimal changes of thickness at the interface. Therefore, the gold film thickness is an important parameter in achieving optimum SPR reflectivity [2]. The thickness profile is directly related to the surface profile, which in turn reflects the surface roughness. In a basic overview, the changes in surface roughness perturb the SPR wave by local changes of the surface normal, and implicitly of the incidence angle from the metal to the sensing layer as indicated in Fig. 1b. This defines practical
implications for another SPR key parameter: the reflectivity intensity. Its relationship with surface roughness will be further detailed with the experimental results of this work.

3. EXPERIMENTAL DETAILS

The experiments were made with an Autolab ESPRIT SPR device. The electrochemical cell is composed of the SPR cuvette with three electrodes: Au working electrode, Pt counter electrode and Ag/AgCl reference electrode. The connection of the electrodes was made to an Autolab PGSTAT 320N potentiostat-galvanostat. Three types of electrolytes were used: i) ultralow ionic solution of deionized water (Millipore 18.2 MΩ cm), ii) Na₂SO₄ 50 mM and iii) oxalic acid (H₂C₂O₄) 50 mM.

For polymerization, polypyrrole PPy 200 mM was added in the oxalic acid electrolyte, and subsequently polystyrene sulfonate (NaPSS), Mw = 70,000, as competing dopant at varying concentrations (50, 100 and 200 µM).

An Atomic Force Microscope (AFM) from APE Research, Italy, was used to obtain the microscopy details on the surface features. The AFM recording had been achieved with a contact mode cantilever of silicon by applying a 5 nN loading force to scan with a rate of 5 µm/sec the 5x5 µm² area and using an acquisition delay of 0.01 ms. The modular program Gwyddion 2.36 was used for data processing.

4. RESULTS AND DISCUSSION
The insight into the third key parameter which provides an expansion in SPR data interpretation will be focused on: (i) the implications of Au anodizing in SPR data; (ii) how anodizing changes the roughness of the Au thin film and (iii) what are the practical aspects when sensing the reactions at the interface during real time monitoring of electrochemical polymerization.

4.1. Gold Anodizing by Oxalic Acid

Chemical reactions can occur at the metal interface with the surrounding medium or the sensing layer, without any changes of the gold surface. An example for two aqueous solutions (ultrapure water and \(\text{Na}_2\text{SO}_4\) electrolyte) is shown in Fig. 2a, from 0 V up to the potentiodynamic range where water electrolysis occurs (1 V). These changes are associated to the refractive index of aqueous solutions which induces a shift of the SPR angle of a few millidegrees, but no significant change in the reflectivity intensity [12].

However, an anodizing process can influence changes in the gold layer, and implicitly in its surface roughness. Such a change in roughness can influence the reflectivity intensity according to Eq. (11) and as shown schematically in Fig 1b. In Fig. 2b such a change in the reflectivity intensity is experimentally observed for an oxalic acid electrolyte at 0.8 V by comparing the curves after 1 s and 95 s. As reported by K. Nishio and H. Masuda [14], in anodizing conditions such as the ones dealt in this paper, the reflectivity increases considerably (roughly four times in our case).

There are two electrochemical processes that can be electrochemically detected at the Au surface, namely the \(i\) oxidation of the adsorbed species and \(ii\) the Au oxidation. The oxidation of the adsorbed OH to O onto the Au surface had been reported up to 0.9 V vs Ag/AgCl [15].
Subsequently, the oxidation of gold to its trivalent state (Au$_2$O$_3$) should occur at around 1.2 V vs Ag/AgCl [16]. The electrochemical mechanism of Au anodizing in oxalic acid at this low potential is a particular case open for clarification. However, after the anodizing process the formation of nanoporous gold was reported [17]. An AFM study was thus made in order to elucidate the changes that occur in this particular case at the Au surface after the anodizing process.

4.2. Surface Roughening

As observed in Fig. 3a, the bare gold surface closely resembles the ones as-deposited by sputtering [18, 19]. After the potentiostatic treatment, a clear surface roughening is observed in Fig. 3b, with the appearance of heightened surface features. In the selected linear profile the surface height varies with around 4 nm (Fig. 4a) for the bare gold, while the roughened one has a selected surface feature of the height of an order of magnitude higher, up to 70 nm (Fig. 4b). Since these local readings do not highlight the overall feature characteristic of the complete area of interest, a general parameter is required for characterization. A standardized statistic parameter which describes the surface features is the Average Surface Roughness (or $R_a$) [20]:

$$R_a = \left( \frac{1}{N} \right) \int_{h_{	ext{min}}}^{h_{	ext{max}}} Z(h) dh$$

where $N$ is the number of points obtained during the evaluation. The close resemblance of Eq. 12 and Eq. 11 emphasizes the close relationship between the surface roughness and the recorded reflectivity. For the bare Au the calculated roughness is 2 nm, while for the anodized gold the surface roughness increased almost 4 fold, to 7.6 nm. The optimum control of the Au surface roughness is reported as an useful tool not only to prevent the unwanted effect of radiation
dampening for SPR [21], but also to obtain the specific SPR-related Enhancement for Raman Spectroscopy, also called SERS [15, 22].

The AFM results coupled with the Reflectivity changes show a practical relationship between the surface roughness and the SPR response. The anodizing implication on the change in reflectivity adds a new dimension to the SPR data interpretation that is to our knowledge unprecedented.

In previous studies we had used the SPR phenomenon as Au nanoparticles marker in a polymeric film as in the paper [23]. Since the oxalic acid behaves also as a marker by decreasing the SPR reflectance, we can monitor its behavior in competing chemical reactions. For this, we can consider as a practical example the in-situ polymerization of pyrrole (Py).

4.3. Practical Approach: in situ Pyrrole Polymerization

Polypyrrole (PPy) polymerizes electrochemically by oxidation at +0.8 V vs Ag/AgCl. During the PPy growth, charge-compensating anions are accommodated. The anion accommodation in the PPy film (also called doping) can be achieved according to the reaction [24]:

\[
PPy + nA \xrightarrow{\text{oxidation}} [(PPy)^{n+} (A^-)^n] + ne^-
\]

where \( A^- \) is the anion that compensates the positive charges generated during oxidation.

The anion involved in the PPy doping can be the oxalate anion (C\(_2\)O\(_4\)\(^{2-}\)). However, the large polystyrene sulfonate ([C\(_8\)H\(_7\)SO\(_3\)]\(_n\); namely PSS\(^-\)) anion can also be accommodated. Consequently, we have set the conditions for a doping competition between the small oxalate anion and the large PSS\(^-\) one, by mixing both species in the same aqueous solution.
The same average number of doping anions was reported for both the small (ClO$_4^-$) and the large (PSS$^-$) anion [25]. Consequently, the density (mass/volume) of the overall film was reported to be 19% higher for the large PSS molecular weight than for the small anion [25]. In Fig. 5a the in-situ SPR angle response shows that the increasing concentration of the large PSS$^-$ anion in the solution leads to an increase in angle. The angle increase implies an increase in weight [6] due to changes in refractive index (see Eq. 9). This confirms that more mass is deposited with PSS$^-$ anion than with oxalate anion. Because of the limiting amount of anions which can be accommodated into the film, a saturation trend at the increased NaPSS concentrations can also be observed (for 100 and 200 µM).

About the ion diffusion in the PPy film, the relative mobility of the ions was reported to be related to their size [26], i.e. the oxalate anion has a high mobility into the PPy film, while the large PSS$^-$ anion has considerable low mobility. In addition, denser films lead to lower ion diffusion. Thus, in the PSS$^-$ denser film, the oxalate diffusion decreases due to low mobility and increased density. Considering the overall PSS$^-$ and oxalate anions competition, the oxalate should dope to a higher degree the PPy film.

The SPR reflectivity in Fig. 5b indicates that, although the PSS$^-$ anion prevented the oxalate doping, the oxalate-favoring decrease in reflectance is still observable. Furthermore, the reflectivity decreases notably in the presence of PSS$^-$ (for instance from 14% to 11% for 50 µM NaPSS$^-$). Between 20 and 80 s of polymerization, PSS$^-$ has the most significant contribution to the doping, with respect to the oxalate (Fig. 5b). In the region until 80 s there are complex processes that occur simultaneously with different rates. Such processes are, for example, pyrrole (Py) adsorption, doping anions adsorption, formation of PPy nucleation sites, continuous polymerization on the already formed sites and film doping [27]. Also, Pt dissolution in highly
acidic media has been previously reported [28, 29]. However the low concentration of oxalic acid, the Pt complexing properties of oxalate [30] and the increased electron density at Pt interface (due to electrode polarization) indicate a potential manner in which the risk of film contamination with Pt is minimized.

After 80 s a relatively stable response is observed for all of the polymerization conditions (Fig. 5b).

Next to the classical increase in weight investigated by the SPR angle dependency, we obtained a complementary insight into the in-situ ion diffusion of oxalic acid during PPy polymerization. This is achieved by monitoring the intensity of reflectivity as a third key SPR parameter.

5. CONCLUSIONS

Beside the already consecrated SPR parameters (e.g. time and SPR angle) we brought into focus a third key parameter: the SPR reflectance intensity. Considering this parameter, we acquired practically two times more analytical results using the same SPR measurements. The reflectivity intensity change was directly related to the changes in surface roughness of the thin Au film.

The highly sensitive SPR was not only used in a classical manner to monitor weight changes at the interface, but also to monitor in-situ changes in roughness. In this manner, any changes (either electrochemically or of any other nature) which occur in the Au film itself can be investigated by SPR. This allowed investigating the in-situ competitive behavior during PPy
polymerization between oxalate and PSS. Consequently, the dependence of ion diffusion on the film density had been confirmed to occur even during the PPy growth.

These results expand the sensing range of applicability not only at the gold surface, but also to the changes in the gold film itself.

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**References and notes**

Captions for Figures

**Fig. 1.** Schematic view of the SPR device in the three layer configuration, for a) planar surface and b) roughened surface. The incident, reflected and transmitted light beam is represented. The various angles are noted $\theta_j$, the refractive indexes $n_j$, the metal thickness $h$ and the infinitesimal change in metal thickness $dh$, where $j = p$ (for prism), $m$ (for metal), $s$ (for sensing layer).

**Fig. 2.** SPR reflectivity vs SPR angle for ultrapure water and Na$_2$SO$_4$ 50 mM at 0 and +1 V (vs. Ag/AgCl) applied potential (a) and the SPR reflectivity in oxalic acid 50 mM for 1s and 95 s of +0.8 V (vs. Ag/AgCl) applied potential (b).

**Fig. 3.** AFM 3D profile for a) smooth and b) electrochemically roughened Au thin film. The vertical line (1) corresponds to the linescan giving the 2D profile represented in Fig. 4.

**Fig. 4.** AFM 2D profile for a) smooth and b) electrochemically roughened Au thin film.

**Fig. 5.** SPR angle (a) and SPR reflectivity intensity (b) response during polymerization of Py/Oxalic acid and Py/Oxalic acid with NaPSS at different concentrations (50, 100 and 200 µM) as competing dopant under +0.8 V.
Fig. 1.

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Fig. 2.

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Fig. 3.

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Fig. 4.

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a)

b)
Fig. 5.

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