The electrochemically induced processes at the gold-polyaniline film interface: surface plasmon resonance study

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Surface plasmon resonance (SPR) method has been modified to study the electrochemical processes at the surface of a 50 nm thick gold film. Electrochemical SPR (ESPR) enables the electropolymerization and study *in situ* of different polymers, especially materials with expressed redox properties. Electrochemical processes at the surface of bare gold and gold covered by 80 nm thick polyaniline film have been studied using simultaneously SPR and cyclic voltammetry. ESPR measurements were performed upon time-changed application of interfacial electrical potential −0.2 to 1.3 V in acid (pH = 1.1) and neutral (pH = 7.4) electrolytes. The physicochemical mechanism of changing of optical characteristic for Au-polyaniline film system is described.

Метод поверхностного плазмонного резонанса (SPR) модифицирован для целей исследования электрохимических процессов на поверхности пленки золота толщиной 50 нм. Электрохимический SPR (ESPR) обеспечивает возможность электрополимеризации и исследования *in situ* различных полимеров, в частности, материалов с выраженными редоксными свойствами. Электрохимические процессы на поверхности чистого золота и золота, покрытого пленкой полианилина толщиной 80 нм, исследованы с применением одновременно SPR и циклической вольтамперометрии. Измерения ESPR выполнялись при приложении к поверхности раздела изменяемого во времени электрического потенциала в пределах от −0,2 до 1,3 В в кислых (pH=1,1) и нейтральных (pH=7,4) электролитах. Описан физико-химический механизм изменения оптических характеристик системы золото-полианилиновая пленка.

The surface plasmon resonance (SPR) with electrochemical measurements (ESPR) becomes the attractive technique last years [1, 2]. The possibility of ESPR *in situ* to estimate optical constants and thickness of thin films is of advantage for investigation of various electrochemical processes, including the electropolymerization [4, 5]. However, there are problems at the interpretation of the results of SPR-electrochemical measurements. The problems originate from the necessity (usual for SPR method) to separate two main parameters of investigated layer, namely, refractive index n and thickness d, as well as due to influence of electrical potential applied to the layer. The possibility to separate n and d is studied well and can be realized by fitting experimental and theoretical SPR-spectra [4-5], although remains rather complicated for multilayer systems. The influence of the interfacial potential on the angular position and shape of SPR spectra is less studied, only few works being known [6-8].

The anglular shift and changes in SPR-spectra (SPR-curve) form (SPR-response) under applied interfacial potential are due to changes in concentration of free electrons in surface layer of metal carrying the plasmon oscillations [6]. Similar changes are observed also in the forms of oxide layer on the metal [8] as well as in the influence of electrolyte ions [3]. However, at the application of interfacial potential up to 1 V for bare Au placed in electrolyte solution, the environment influence on SPR spectra can be clearly noticed only for case where the electrolyte solution exhibits

redox properties. Acid or base electrolytes usually used in electrochemical experiments do not exhibit such properties. In this case, SPR response depends mainly on formation of oxide layer, that is possible only under specific values of the applied interfacial potential exceeding a certain threshold value [8]. The situation is changed when gold electrode is covered with a dielectric film, especially when the film exhibits pronounced redox properties. At the application of even a low potentials under specific conditions (pH), the SPR response increases significantly and depends mainly on the thickness of studied film, its structure and on the extent of the redox properties. It is known that optical parameters of such materials can be modified by changing the thickness of investigated layers during electrochemical reaction [9]. This fact brings additional difficulties in the SPR examination of the film properties. However, the SPR method give us some advantages at the investigations of similar structures, because this technique is sensitive to concentration of redox molecules in the electrolyte solution as well as to the adsorbed layer thickness. Cyclic voltammetry (CV), at another hand, enables us to estimate the concentration gradient of redox particles at the electrode surface [10]. It seems to be of promise to combine these two methods when studying redox-polymers, especially when the polymer film formed by electropolymerization is insoluble and its structure remains essentially unchanged during CV measurements.

In this work, we discuss the possibilities of electrochemical SPR spectroscopy taking the comparative study of CV and SPR spectra of polyaniline (PA) film as an example. This polymer is a redox material and can be obtained by electropolymerization under conditions of SPR experiment *in situ*. The priority task of this work is the correct interpretation of integrated SPR response at the ESPR study of similar polymers and other redox structures.

All chemicals were purchased from Aldrich and used as supplied without further purification. Double-distilled water was used throughout this work. To synchronize SPR and electrochemical measurements, a classic 3-electrodes cell was utilized. The working electrode was 50 nm film of polycrystalline 99.999 Au where plasmon oscillation can be excited. The gold film was produced by thermal evaporation in vacuum ($5 \cdot 10^{-4}$ Pa) onto F1 glass (20×20 mm^2)

plate. As the counter electrode, 0.5 mm Pt wire was used; Ag/AgCl 0.5 mm wire served as the reference electrode. To improve the adhesion, a thin (up to 5 nm) Cr underlayer was evaporated simultaneously with Au. Before evaporation, the glass plates were treated consecutively in $NH_4OH{:}H_2O_2{:}H_2O$ and $HCl{:}H_2O_2{:}H_2O$ solutions, both of 1:2:2 (v/v) composition during 5 min at boiling temperatures. After chemical treatment, the glass plates were thoroughly washed in twice distilled water and dried in nitrogen stream. To stabilize the drift parameters, the evaporated film was heat treated immediately after evaporation (120°C, 30 min). The material of glass plate was selected exactly the same as for ATR prism to exclude the interference effects. The relatively high refraction index of the prism ($n = 1.61$) together with a broad dynamic diapason (up to 19° in air) of the SPR-instrument Biosuplar-2, (Analytical Microsystem, Germany) enabled to measure the SPR spectra for thick (up to 200 nm) polymer films without changing the initial incidence angle of the laser beam, Fig. 1. Data were processed by a PC using Biosuplar-2 software (version 1.1.30). Cyclic voltammetry and multi-potential step chronoamperometry were performed using an electrochemical analyzer (EG&G, VersaStat) connected to a computer (EG&G software #270/250). The use of a simple open electrochemical cell (230 μL) enabled easy emptying of the cell and thus rapid removal and change of solution above the polymer films if necessary. The Ag quasi-reference electrode was calibrated according to the potential of dimethylviologen, $E_0 = -0.687$ V·vs. SCE measured by cyclic voltammetry and the potentials were reported vs. SCE. The SPR sensograms (time-dependent changes of the reflectance minimum) were measured *in situ* simultaneously with cyclic voltammetry upon application of an external potential to the working electrode. The potential range used in the experiments included the diapason of potentials where the Au electrode is polarized ideally as well as the potential region where a Au oxide layer formation occurs. The measurements were performed with a bare Au electrode and a polyaniline-modified Au electrode.

The polyaniline-modified Au electrodes were used for the SPR *in situ* study using cyclic voltammetry. Polyaniline was generated on the Au covered glass support by the electropolymerization of aniline, 0.1 M, in an electrolyte solution consisting of H_2SO_4,
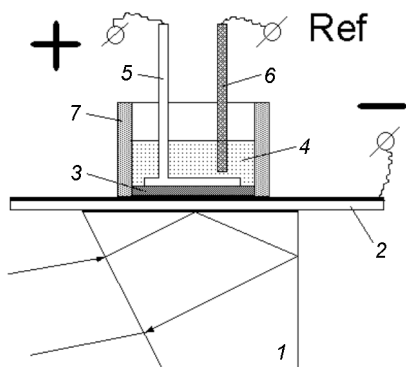
Fig. 1. Scheme of ATR prism and electrochemical cell. *1* — prism; *2* — glass plate with evaporated Au as work electrode; *3* — PA layer; *4* — electrolyte; *5* — Pt counter electrode; *6* — Ag/AgCl reference electrode; *7* — cell wall.

Fig. 2. *1* — kinetic dependences of SPR angular position upon application of time-changed potential for bare Au, pH = 1.1; *2* — cyclic voltammogram at a bare Au-electrode, pH = 1.1; *3* — $\Delta\theta/\Delta t$ dependence (differential SPR).

0.1 M, and Na_2SO_4, 0.5 M, (applied potential 0.8 V) for various time to generate the polymer films of different thickness. The resulting film was washed with background solution of H_2SO_4, 0.1 M, and Na_2SO_4, 0.5 M, to remove the residual monomer out of the cell. The polyaniline film thickness was derived from the computer-aided fitting of the experimental SPR spectrum obtained after electropolymerization and washing the cell with the electrolyte solution free of the monomer to the theoretical spectrum.

It should be noted that some instability of the angular position and shape of SPR spectrum was observed immediately after the electrode modification resulting from changes of the polymer structure. Thus, to determine the film thickness by fitting, the SPR-spectra were taken after the complete stabilization (ca. 1 h after the electropolymerization is over). Also long-time changes of the SPR spectra were observed after each potential cycle applied to the modified electrodes. Such an instability is due to the polymer disturbance and irreversibility of adsorption and diffusion processes during limited time (in our case, 1500 s) of CV cycle, particularly for freshly prepared polyaniline films. In this work, interpreted are data obtained for PA films immediately after electropolymerization, that is important because this makes it possible to observe and discuss the transition processes. The complete stabilization of electropolimerized PA film is possible only after multiple applied potential cycles, the cycle number depending on the potential value and the polymer film thickness as well as on the electrolyte properties (pH).
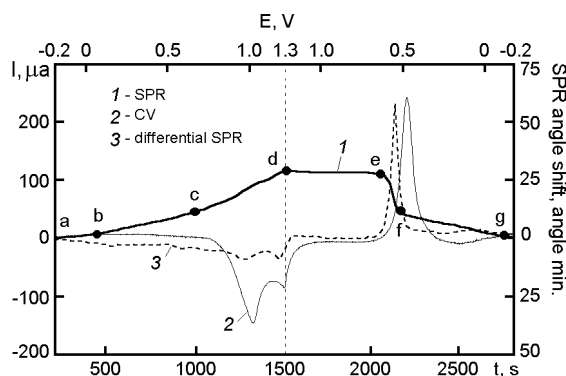
Fig. 2 shows the kinetic dependences of SPR angular position (SPR sensograms) under a time-changed interfacial potential for bare Au. Curve 1 of Fig. 2, shows the SPR sensogram for a bare Au electrode at pH = 1.1. Fig. 2 curve 2, shows the cyclic voltammogram for a bare Au-electrode in the same conditions. Fig. 2, curve 3, shows the $\Delta\theta/\Delta t$ dependencees (differential SPR). Points at the curves denoted as a through g show the respective domains of the curves corresponding to the SPR and electrochemical measurements. Small (up to 10') gradual shifting of SPR position towards larger angles (further-increasing) within the region of anodic scan a–c (−0.2 V to +0.8 V) corresponds to the horizontal part of CV (curve 2, Fig. 2) and could be explained by decreasing concentration of free electrons in the Au layer. Under applied interfacial electrical potential, the distribution of the electronic cloud shifts from surface inside the gold layer, that can be interpreted as changing of dielectric permittivity ε_e of the medium surrounding the electronic plasma [4, 5]. The section a–c corresponds to the ideal polarization region (from −0.2 V to 0.8 V) of the Au electrode at pH = 1.1. This section of the curves corresponds to the ideal polarization of the bare Au electrode when no chemical changes occur at the electrode surface and only small double-layer capacitance current is observed in the cyclic voltammogram (the a–c part of curve 2, Fig. 2). The section c–d (0.9 to 1.3 V) shows a larger slope of the sensogram (shift of the reflectance minimum by about 20'). This region (0.8 V to 1.3 V) corresponds to the forma-

tion of a thin oxide layer at the Au electrode surface.

The electrochemical oxidation of the Au electrode surface in this potential region is reflected by the anodic peak 1V, shown in CV curve 2, Fig. 2. Thus, the chemical change of the electrode surface upon its oxidation results in a significant change of the SPR spectrum. The potential was swept to the opposite direction after the potential reached $E = 1.3$ V (point d). The potential sweep to the negative direction (region d–e, 1.3 to 0.6 V, curve 1, Fig. 2) does not result in any change of the SPR response. This could originate from the screening effect of the oxide layer separating the polarized interface and metal underlying the oxide layer. A further potential sweep to the negative direction (region e–f, 0.7 to 0.6 V) results in electrochemical reduction of the gold oxide layer electrochemically produced before. This is reflected by the cathodic peak in CV curve 2 (peak maximum at 0.5 V), Fig. 2. The region e–f in the SPR sensogram 1 shows the fast diminution of the SPR angles originating from the electrochemically induced stripping of the oxide layer at the Au electrode. The increasing concentration of free electrons in surface layer of metal and the electrode depolarization of (region f–g, 0.7 to –0.2 V) define slow decreasing of the SPR angular position. This region shows only small double-layer discharging current (CV curve 2), and a slow linear shift of the SPR response towards smaller angles until it reaches the initial value (Cf. points g and a, curve 1). It can be concluded that the SPR sensogram and the cyclic voltammogram obtained upon polarization of a Au electrode show the same effects originating from the potential change and oxidation/reduction of the Au-surface. The derivative curve $\Delta\theta/\Delta t$ (curve 3, Fig. 2) derived from the SPR sensogram (curve b, Fig. 2), when being compared with the cyclic voltammogram (curve 2, Fig. 2) shows even better similarity because it reflects the transition processes as well as CV voltammetry.

Similar SPR sensograms in time scale (curve 2, Fig. 3) were obtained upon electrochemical polarization of the Au electrode at pH = 7.4. However, it should be noted that both the electrochemical oxidation of the Au electrode surface and the electrochemical stripping of the Au oxide layer are pH-dependent processes [12]. The SPR sensogram 2, Fig. 3, measured at pH = 7.4 does not show significant difference from
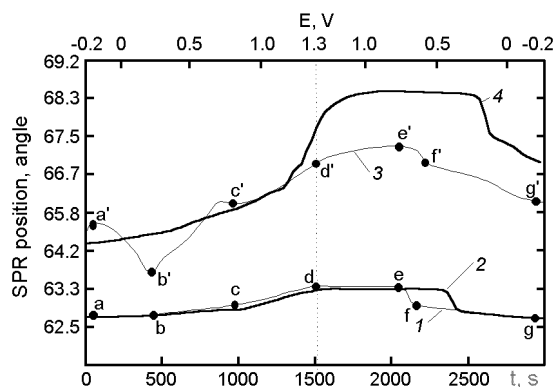

Fig. 3. Kinetic dependences of SPR angular position upon application of time-changed interfacial potential (–0.2 V to 1.3 V). *1* — bare Au, pH = 1.1; *2* — bare Au, pH = 7.4; *3* — polymer, pH = 1.1; *4* — polymer, pH = 7.4.

the curve measured at pH = 1.1 (curve 1) in the region a–d, even if the Au electrode oxidation occurs earlier at lower positive potential. This could originate from the adsorption of phosphate ions from the background solution. At potentials more positive than 0.5 V, the Au electrode is charged positively, thus providing adsorption of negatively charged phosphate ions. Upon formation of the Au oxide layer, the phosphate ions are substituted by Au oxide, that process occurring upon more positive potential than for acid solution. Respectively, curve 2, Fig. 3 shows clearly a fast decrease of the SPR angle at more negative potential than that correlating with the electrochemical reduction potential of Au oxide (Cf. curve 1, Fig. 3).

Fig. 3 (curves 3,4) shows the kinetic dependences of SPR angular position under time-changed potential for Au covered by PA film of about 80 nm thickness. The PA layer thickness was determined from fitting of experimental and theoretical SPR spectra for curves measured after electropolymerization and subsequent removal of the monomer from the cell using the initial buffer solution. The measurements were performed at two different pH values, pH = 1.1 (curve 3) and pH = 7.4 (curve 4). Curve 1 (the same as in Fig. 2) shows the SPR sensogram for bare Au electrode at pH = 1.1. As was noted above and is seen from Fig. 3, application of time-changed interfacial electrical potential to metal layer causes a significantly lower SPR response for bare Au (curve 1) (ca. 25′) as compared to Au coated with redox polymer (ca.145′, curve 3). This fact is explained commonly by changing of

the polymer complex dielectric permittivity $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ induced by the applied potential.

The thick polyaniline layer formed in the course of electropolymerization changes strongly the integrated optical parameters of multilayered SPR structure. It is known that PA is able to absorb light in visible region, including the GaAs laser wavelength used in experiment ($\lambda = 670$ nm). Oxidized and reduced forms of polyaniline differs in optical constants $n = 1.4 + 0.02i$ for reduced form and $n = 1.4 + 0.39i$ for oxidized form [11] (it should be noted that n value for redox materials may depend on the film thickness [9]). The transformation of polymer from usually reduced state to oxidized one is easily reached by application of potential even in range 0 V to 0.4 V, that was shown in our previous work [11]. As is seen in Fig. 3, curves 3, 4, application of a time-dependent potential in the range −0.2 V to +1.3 V results in a significant changes of the SPR position. It is to note a some drift of SPR angular position after finishing of polymerization process due to stabilization of the polymer structure. The complete exclusion of drift processes in the CV-SPR experiments for freshly prepared PA films is impossible due to resumption of long-time drift of SPR-position after the next CV cycle.

Initial part of SPR sensogram (curve 3, −0.2 to −0.17 V) for PA in acid electrolyte shows some (up to 25′) increase of the SPR angular position. The region a–b (−0.17 V to +0.23 V) shows a fast and significant (up to 65′) decrease of SPR position. In point b, the direction of SPR shift changed and we observe the increase in the b–c region (0.23 V to 0.6 V), which continues more slowly in the c–d region (0.6 to 1.3 V) and in the d–e one (1.3 V to 0.61 V). The amplitude of SPR angular positions reaches 170′, i.e. about 3°. Such a large variation of SPR position reflects the respective change of optical constants and is typical of redox materials. Similar changes can be explained only taking into account the orientation polarizability mechanism for polar liquids and solids. [13]. It is known that polyaniline produced by electropolymerization has a porous gel structure [9]. The volume orientation and delocalization of electron band of dipoles in similar media is facilitated. The reversible property of polyaniline molecule to be in two redox states, oxidized and reduced ones, results from the reaction between proton and strongly electronegative

nitrogen atom, with formation of hydrogen bond.

A consequence of this reaction is delocalization of electron bands in polyaniline molecule, a drastic increase of dipole moment upon oxidation and decrease upon reduction. Thus, we observe in this case changing of the molecular polarization due to formation of steady dipoles induced by the electrochemical reaction. Simultaneously with polarization, the group orientation of dipoles results in changes of the polymer refraction in proportion to number of molecules involved in the reaction. Another result of the considered process is shrinking due to more compact packing of dipoles upon oxidation. Upon reduction of PA, the process of dipole relaxation and restoration of previous structure volume is observed [11]. Essentially, we have two states of the polymer which differ in concentration of oxidized and reduced polyaniline molecules. Certainly, we should take in account the processes of electron and ion polarization, however, in this case, it is just the orientational polarization mechanism of polyaniline dipoles that makes the main contribution. As a result, we observe the shift of SPR angular position (range a′ to b′, curve 3, Fig. 3) or change of SPR shift direction (point b′, curve 3, Fig. 3). The curve 3 in the section c′ to f′ repeats essentially the run of curve 1 for bare Au. Thus, the existing Au oxide layer influences the *redox* transformations in polyaniline at this stage of measurements and such influence on the change of optical constant is comparable with the considered polymer thickness.

The hysteresis usual for CV is observed for SPR sensogram also (section d′ to g′, curve 3, Fig. 3). However, unlike CV, the SPR minimum does not return exactly to previous angular position, thus indicating an irreversible change of optical constant during one CV cycle. This could be due to slow kinetic processes for anions moving as well as to stabilization processes in the polymer structure. Similar effect, but more pronounced, is observed in the case of neutral electrolyte (curve 4, Fig. 3). Taking into account the high concentration of large mass ions in neutral electrolyte, it is possible to suppose that it is just the slow movement of anions that mainly defines irreversible character of SPR sensogram. Delay in rotation of induced dipoles of polyaniline in electrical field of surface plasmon results in dielectric leakage that is manifested as
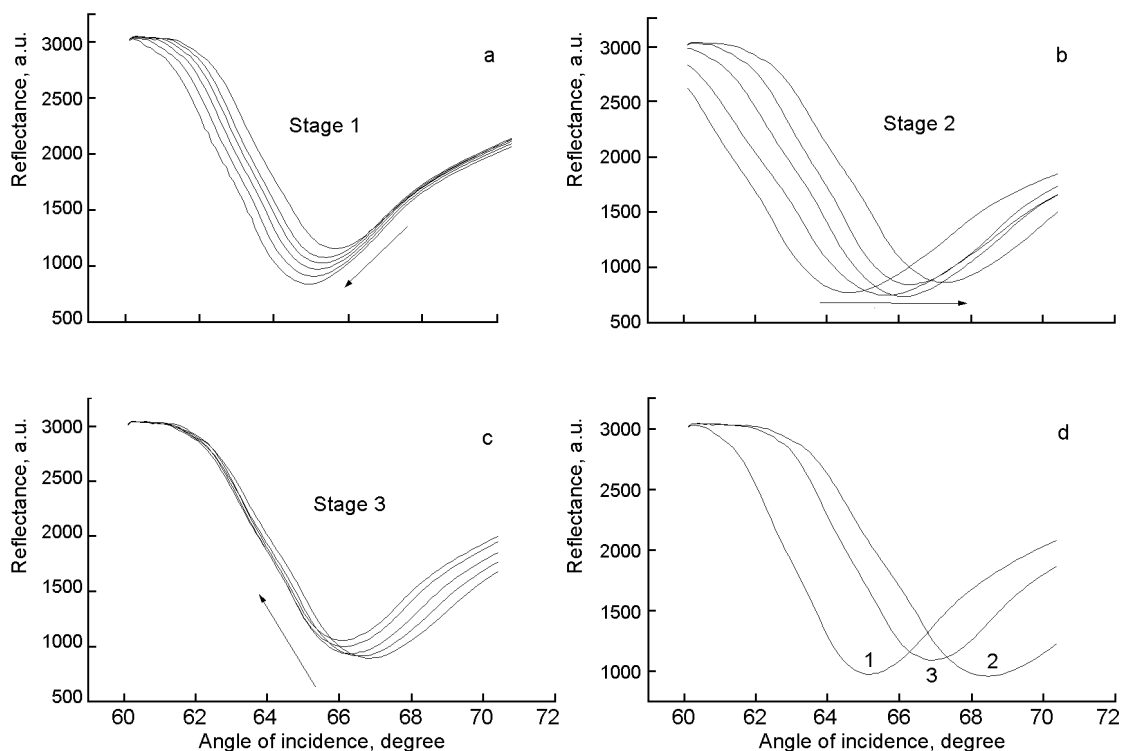
Fig. 4. a–c — Transformations of angular position and shape of SPR spectra upon application of time-changed interfacial potential (polymer, pH = 1.1). a — (–0.2 to 0 V); b — (0 to 1.3 to 0.7 V); c — (0.7 to –0.2 V). d — shifting of SPR spectra during complete cycle of CV (polymer, pH = 7.4). 1— initial position; 2 — top position; 3 — position at the finish of CV.

the imaginary part of dielectric permittivity εe [14]. At the one hand, this causes complex changes of the SPR spectra shape depending on the applied interfacial potential and the state of polyaniline film. In fact, SPR spectra with PA film (pH = 1.1) registered at different stages of CV exhibit a shape typical of each stage (Fig. 4, (a–c)). Three main stages of the SPR spectra transformations can be distinguished. The first one (Fig. 4a), when we observe the fast movement of the spectra to left and down (up), corresponds to process of delocalization and volume orientation of dipole electron bands (section a' to b', curve 3, Fig. 3). Then follows the second stage (Fig. 4b), where after passing zero charge point the slow movement of SPR spectra to right and up are observed (section b' to e', curve 3, Fig. 3). This transformations is due to adsorption processes and formation of oxide layer. And, finally, there is the third stage (Fig. 4c) corresponding to reverse process of delocalization and volume orientation of dipole electron bands again.

At this stage, SPR spectra come back close to initial position (section e' to g', curve 3, Fig. 3). However, we did not ob-

served complete recovery of SPR spectra position and shape due to some saturation of PA film with anions. For phosphate buffer (pH = 7.4), the low concentration of protons in solution as well as high concentration of SO_4^- and PO_4^- anions make shape variations of SPR spectra less expressive and more prevent to a greater extent the recovery of spectra to initial position 1 (Fig. 4d). In this case, the redox processes in PA become slower and SPR response depends mainly on movement of SO_4^- and PO_4^- as well as on adsorption-desorption and oxidation processes on the gold electrode. It should be noted that the above-mentioned processes occur in different extent in both acid and neutral media, thus providing some irreversibility of cyclic measurements. As a result, chemical composition of the medium and optical properties of gold surface change in time, thus resulting in changes of SPR response. So, for next cycles, the shift amplitude of SPR position decreases, the down peak in a'–b' section disappears and the polymer structure comes to a certain equilibrium state. In this state, after optimization of amplitude of applied potential (0 to 0.4 V), the number of cycles

without changing in SPR spectrum shape may be large enough, that could be used in low-voltage optoelectronic modulators [15].

To conclude, the ESPR technique opens a wide possibility to investigate different electrochemical processes as well as to provide preparation of polymers *in situ* and under computer control. The CV voltammetry in the technique under consideration seems to be more sensitive to transition processes, whereas SPR spectrometry, to adsorption-desorption processes, so that there is an excellent example of complementary methods. Additional information to assess the transition processes can be obtained after differentiation of kinetic dependence of SPR angle on the applied potential, because $\Delta\theta/\Delta t$ dependence follows almost all transition processes registered by cyclic voltammetry. The ESPR investigation enables us to estimate the kinetic peculiarities of *redox* materials upon application of interfacial potential, what is important for development of new optoelectronic devices.

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Електрохімічно індуковані процеси на поверхні розділу золото/поліанілінова плівка: дослідження поверхневого плазмонного резонансу

В.І.Чегель

Метод поверхневого плазмонного резонансу (SPR) модифіковано для цілей дослідження електрохімічних процесів на поверхі плівки золота товщиною 50 нм. Електрохімічний SPR (ESPR) забезпечує можливість електрополімеризації та дослідження *in situ* різних полімерів, зокрема, матеріалів з вираженими редоксними властивостями. Електрохімічні процеси на поверхні чистого золота та золота, покритого плівкою поліаніліну товщиною 80 нм, досліджено з застосуванням одночасно SPR та циклічної вольтамперометрії. Вимірюванняя ESPR здійснювалося при прикладенні до поверхні розділу змінного у часі електричного потенціалу у межах від −0,2 до 1,3 В у кислих (pH = 1,1) та нейтральних (pH = 7,4) електролітах. Описано фізико-хімічний механізм зміни оптичних характеристик системи золото-поліанілінова плівка.