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Hydrogen Treatment of SPR Film Sensors: Experiments and Theoretical Modeling

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The present paper deals with the experimental and theoretical studies of changes of optical properties of SPR sensors under the influence of hydrogen. Theoretical modeling of the SPR sensor treated with hydrogen was performed using the transfer matrix method and effective medium approaches. Different possibilities of hydrogen influence were considered during the modeling. It was established that the accumulation of hydrogen at the glass-chromium interface could not change the SPR spectrum. The experimentally observed shifts in the SPR spectrum were mainly related to the accumulation of hydrogen in all thicknesses of the gold layer by means of the formation of cavities filled with hydrogen. The accumulation of hydrogen in the bulk of the gold film also led to an increase in the SPR resonance value. On the contrary, the theoretical modeling of the increase in the surface roughness of gold predicted a decrease in the amplitude of the resonance. As a result, a complex theoretical description of the processes, which took place in SPR sensors during hydrogen treatment, was proposed. The predictions were as follows. The oscillations of the surface level before hydrogen treatment were 2 nm, and due to the possibility of surface destruction, the oscillations of the surface level increased to 3 nm. The layer of "solid" gold before hydrogen treatment was 48.5 nm, and after hydrogen it increased to 53.35 nm. The average volume concentration of cavities in this layer was about 10 %. The cavities with hydrogen were homogeneously distributed over the volume. The thickness of the chromium layer before hydrogen treatment was 5 nm, and after hydrogen treatment the thickness of this layer increased to 6 nm. The volume of cavities with hydrogen in chromium was 20 %.

Keywords: Hydrogen, Electrolysis, Hydrogen treatment, Hydrogen diffusion, Gold film on glass, Surface plasmon resonance.

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1. INTRODUCTION

Measurements based on surface plasmon resonance (SPR) are hypersensitive. Nowadays, researchers widely use SPR sensors in various fields of chemistry, biology and medicine. Naturally, this induces permanent studies in order to improve SPR sensors [1-4]. The basic part of a SPR sensor is a metal film with a thickness of no more than 100-150 nm. A thin metal film acts as a sensor [5].

Hydrogen is one of the most common elements in nature. It is able to easily penetrate metal. The chemical bonds of metal atoms on the surface of metal are not saturated, i.e., metal surfaces are able to show increased chemical activity. Quite often hydrogen is released from compounds, which are in contact with the metal surface. Then hydrogen dissolves from medium into the metal. The presence of defects in the metal allows accumulation of hydrogen gradually in the bulk of the metal. Hydrogen accumulation can be very significant. Obviously, it changes properties of the metal, and it can even destroy materials [6, 7].

During operation, a SPR sensor frequently contacts with aqueous solutions of various chemical compounds or with solutions containing biological objects like organic molecules, viruses or microorganisms. In many cases, such solutions contain hydrogen ions. The metal film of the SPR sensor interacts with hydrogen. This significantly changes properties of the SPR sensor [8, 9]. In the present study, we try to answer several questions raised in experiments with hydrogen treatment of SPR sensors. What changes does hydrogen cause in the SPR sensor? Does it change the properties of the sensor surface or does it penetrate metal layers and form cavities in the bulk of metals? To answer these questions, a theoretical model was built using the transfer matrix method and the concept of an effective medium [10, 11].

2. HYDROGEN TREATMENT OF SAMPLES

2.1 Experimental Details

The article discusses the effect of hydrogen treatment of a gold film on glass. The film was applied to a glass plate at room temperature. Glass plates with a thickness of 1 mm were approximately 20.0×18.0 mm. The glass plate was first coated with a 5 nm thick layer of chromium, and then a 50 nm thick layer of gold was applied. The gold deposition rate was 0.5 nm/s. As a rule, with this method of manufacturing SPR sensors, the resulting films have a surface with a slight roughness (about 2 nm), and the film itself has many defects in the crystal structure.

Hydrogen treatment was performed by electrolysis. The gold film was connected to the negative pole of the current source through a gold-plated metal contact. The side surface of the metal contact pressed against the film was much smaller than the surface of the film itself. The positive pole of the current source was connected to a graphite electrode. Thus, during electrolysis, the gold

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film was the cathode, and the graphite electrode was the anode. The electrolysis bath was filled with a 10 % solution of sulfuric acid (H_2SO_4) in water. Electrolytic hydrogen saturation took place at room temperature. Series experiments on the electrolysis were performed so that currents were from 2 to 2000 μA. The electrolysis process in each experiment lasted 6 min. Simple calculations allowed to find the number of protons that reach a unit surface area of the sample every second. For example, for 5 μA the number of protons was $8.68 \cdot 10^{12}$ 1/cm²s and for 2 μA it was $3.47 \cdot 10^{12}$ 1/cm²s, while the total number of protons during electrolysis was $1.125 \cdot 10^{16}$ 1/cm²s for 5 μA and $0.45 \cdot 10^{16}$ 1/cm²s for 2 μA. To observe the whole electrolysis process, a video camera was installed on top of the bath.

Surveillance revealed that significant flows of hydrogen to the surface of the gold film destroyed SPR sensors. Small flows of hydrogen to the surface of the gold film did not destroy them. SPR sensors remained operational. Surveillance of electrolysis at small currents of 2 and 5 μA showed that hydrogen bubbles were not formed on the film surface, and most of hydrogen ions were dissolved in it. Since the influence of small flows of hydrogen on SPR sensors is relevant in biological or chemical research, an in-depth study of the effect of small fluxes was performed here.

Experimental plasmon resonance studies were performed by means of a PLASMON-6 spectrometer. It realizes the excitation of plasmons by the Kretschmann method [5, 12]. The device has a goniometer to variate the angle of incidence of light on the surface of the gold film. The accuracy of setting the angle of incidence was 10 angular seconds. Surface plasmons were excited on the gold-air surface. The radiation source was a semiconductor laser, which generated light of the 650 nm wavelength. The spectrophotometer sensor detected the intensity of the reflected light. The obtained dependence of the intensity of the reflected light on the angle of incidence was normalized to the maximum reflected intensity.

The SPR curves obtained before and after hydrogen treatment of SPR sensors by electrolysis with a current of 2 μA are shown in Fig. 1 [8, 9]. As one can see, after hydrogen treatment, the SPR curve shifted towards larger angles by 0.9 °. The shift did not occur immediately after electrolysis. But it lasted for several days with a gradual decrease in the shifting rate.

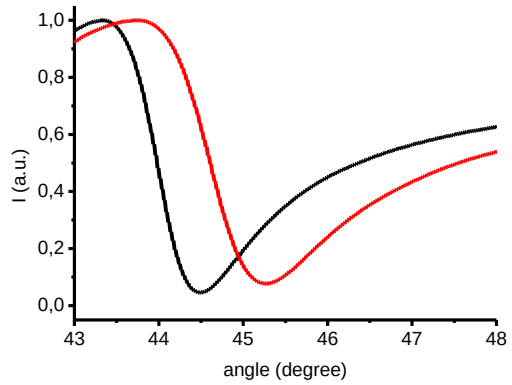

Fig. 1 – SPR curves. The black curve corresponds to the SPR sensor before processing; the red curve corresponds to the SPR sensor after electrolysis with 2 μA

The half-width of the resonance curve increased insignificantly. The amplitude of the resonance decreased insignificantly. Similar changes occurred in the SPR spectrum in case of electrolysis with a current of 5 μA. The SPR curve shifted towards larger angles by 1.3 °.

2.2 Theoretical Modeling of Changes in the SPR Spectrum

To study theoretically the effect of hydrogen on the SPR curves, at first, we must choose a method for calculating the reflected radiation intensity. In [13, 14], using the transfer matrix method, a theoretical description of the excitation of surface plasmons by the Kretschmann method in a multilayer system was successfully provided. This approach was used in the present studies.

Consider a *p*-polarized electromagnetic wave falling at a certain angle of incidence on the surface of a homogeneous metal film. The relation between the amplitudes of the components of the electric and magnetic fields at the input and output of the film is [13, 14]

$$\begin{pmatrix} H_x^0 \\ E_y^0 \end{pmatrix} = \mathbf{M} \begin{pmatrix} H_x \\ E_y \end{pmatrix}, \mathbf{M}_m = \begin{pmatrix} \cos\beta_m & -\frac{i}{q_m}\sin\beta_m \\ -iq_m \sin\beta_m & \cos\beta_m \end{pmatrix}, \mathbf{M} = \prod_{m=1}^{N} \mathbf{M}_m, \quad (1)$$

where $\mathbf{M}_m$ is the transfer matrix of the m-th layer of the layered structure, $\mathbf{M}$ is the resulting transfer matrix of the studied optical system, $\beta_m = \frac{2\pi}{\lambda}\tilde{n}_m d_m \cos\theta_m$, $q_m = \frac{1}{\tilde{n}_m}\cos\theta_m$, $\tilde{n}_m = n_m + ik_m$ is the complex refractive index, θ_m is the angle of incidence, d_m is the thickness of the m-th layer, N is the number of layers in the system, z-axis is perpendicular to the layers, y-axis is directed in the plane of incidence of light. Using matrix $\mathbf{M}$, one can obtain the reflection coefficients of our system [13]

$$R = |r|^2, \quad r = \frac{[M_{11} + M_{12}q_N]q_1 - [M_{21} + M_{22}q_N]}{[M_{11} + M_{12}q_N]q_1 + [M_{21} + M_{22}q_N]}. \quad (2)$$

During modeling, the optical properties of our system used in the experiments were taken into account. Hydrogen treatment of SPR sensors changed their properties. In general, the refractive index $\tilde{n}_m$ of the treated layer became a complex function of spatial coordinates, which made the modeling difficult. But the use of physically reasonable approaches of the effective medium or the effective susceptibility of treated layers simplifies the problem. In the case of the effective medium concept, relations (1) and (2) are applicable with the averaged effective value of the refractive index $\tilde{n}_m$.

The film has many design defects throughout its volume. Defects are known to be good traps for hydrogen. During electrolysis, hydrogen is accumulated in these defects throughout the thickness of the gold layer. At the first moment of time after electrolysis, the hydrogen pressure in defects is high, which contributes to the formation of cavities. But the film state still remains tense, and the hydrogen pressure in cavities

remains high. The resulting cavities with hydrogen increase in volume over time. Mechanical stresses are gradually reduced. This explains the time dependence of changes in the SPR spectrum. We took into account the phenomenon of the origin and growth of cavities. The concept of an efficient environment was used to obtain effective properties of the gold layer with cavities filled with hydrogen. This concept has already been applied to describe the properties of similar porous media [15, 16]. The interaction between the cavities was neglected, because in experiments the concentration of cavities with hydrogen is small compared to the volume of the metal. Under such conditions, the dependence of the effective dielectric function on the internal topology of the system can be ignored. Therefore, we can use Maxwell Garnett approximation. The gold film with a dielectric constant ε_h after treatment with hydrogen with a dielectric constant ε_i can be described as a medium, in which the same spherical cavities filled with hydrogen are evenly distributed. The dielectric function of an effective medium will be as follows

$$\varepsilon_{MG} = \varepsilon_h \frac{\varepsilon_h + \frac{1+2f}{3}(\varepsilon_i - \varepsilon_h)}{\varepsilon_h + \frac{1-f}{3}(\varepsilon_i - \varepsilon_h)}, \qquad (3)$$

where f is the volume concentration of cavities after hydrogen treatment. During and after electrolysis, cavities expand due to the hydrogen pressure in it. The volume of the layer increases due to the volume cavities with hydrogen

$$V = V_0(1+f). \qquad (4)$$

Here V_0 is the initial volume of the layer and V is the volume of the layer treated with hydrogen.

Probably, due to the presence of cavities in the gold layer, one can observe changes in the optical properties of the SPR sensor. The results of the calculations are shown in Fig. 2. It is clearly seen that the more cavities, the greater the offset of the SPR resonance angle. This corresponds to the results observed in experiments on hydrogen treatment. The amplitude of the SPR curve slightly increases, which does not correspond to the experiment.

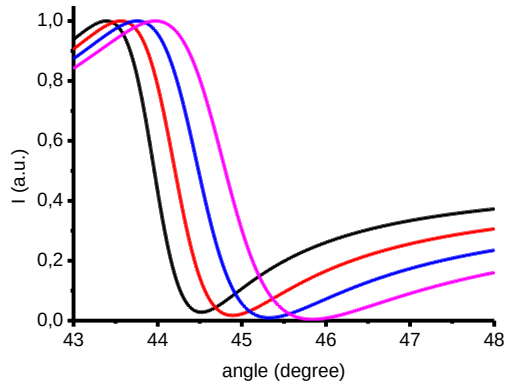

Fig. 2 – SPR curves. The black curve corresponds to the film before hydrogen treatment. Red, blue, and pink SPR curves correspond to the film after hydrogen treatment, the volume concentration of hydrogen in cavities was 5, 10 and 15 %, respectively

The 50-55 nm thickness of metal layers of SPR sensors suggests that the electrolysis time is sufficient for the diffusion of hydrogen through the metal layers. This is confirmed by experiments with powerful hydrogen flows described in [9]. Taking into account that the electrolysis time with high and low flows was the same, it is necessary to estimate the capture of hydrogen by a layer of chromium at the interface of gold and chromium, since the interface between glass and chromium has many defects. Capture of hydrogen by this layer would have led to the formation of cavities at the chromium-glass interface and to an increase in the thickness of this layer. This effect was taken into account when constructing the dielectric function of chromium layer according to the Maxwell Garnett model (3), where ε_h is the dielectric function of chromium. When the relative volume of cavities formed at the chromium-glass interface is significant, the Bruggeman model of the effective medium ought to be used, because it takes into account the phenomenon of percolation [11]. The effective dielectric function in the Bruggeman approximation ε_{BG} in the case of a two-component mixture of chromium and hydrogen is equal to

$$\varepsilon_{BG} = \frac{b \pm \sqrt{b^2 + 8\varepsilon_h\varepsilon_i}}{4}, \; b = (2-3f)\varepsilon_h - (1-f)\varepsilon_i. \qquad (5)$$

Here the solution with the sign "+" will be physically meaningful [14]. The volume of the chromium layer after hydrogen treatment is determined by relation (4).

Calculations of the modified system with a chromium layer with cavities filled with hydrogen revealed a shift of the SPR curve towards smaller angles by 0.15° (Fig. 3) and an increase in the resonance amplitude. As one can see, such changes in the SPR spectrum do not correspond to the experimental results (compare curves in Fig. 1 and Fig. 3). Therefore, we conclude that at low flow rates of hydrogen to the surface of the metal film, the formation of cavities with hydrogen at the chromium-glass interface is not the cause of changes in the SPR spectrum.

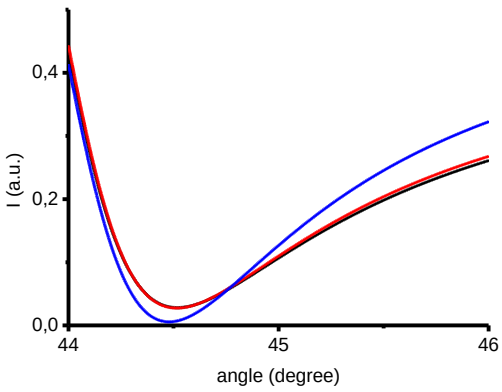

Fig. 3 – SPR curves in the case of cavities at the glass-chromium interface. The black curve corresponds to the film before hydrogen treatment. The volume concentration of hydrogen cavities is 20 % for the red curve and 40 % for the blue one

The real surface of the gold nanofilm is not perfectly smooth. Therefore, the theoretical model must take into account the roughness of the surface of the gold film

and possible changes of its intensity during the electrolysis. If one moves from the air to the middle of the film, the air initially predominates quantitatively. Then, at some depth, the volumes of gold and air become equal. Moving deeper, we reach a surface where gold dominates. To describe this transition layer at the gold-air interface, the Bruggeman approximation (5) is used. In most cases, before hydrogen treatment, fluctuations of the air-gold interface in the direction perpendicular to the film plane are confined within 2 nm. The surface roughness is taken into account by modulating the layer of "gold and air" with a thickness of 2 nm. We assume that during hydrogen treatment, hydrogen is captured by defects in the surface layer of the gold film. The pressure in the cavities formed during hydrogen treatment exceeds the tensile strength. These cavities are destroyed, and the surface roughness of the sample increases. We take this into account in the model by decreasing the thickness of the gold layer and increasing the thickness (or volume) of the "gold and air" layer.

The results of this modeling are demonstrated in Fig. 4. One can see that the increase in roughness from 2 to 4 nm leads to the shift of the resonance angle towards larger angles by 0.55 °. The half-width of the resonance curve increases by 1.22 °. Such changes in the SPR spectrum correspond to the changes that occurred in the experiments. An increase in the surface roughness of the gold film is significantly reflected in a decrease of the amplitude of the SPR resonance. The experiments also show a decrease in the amplitude of the SPR resonance, but this reduction is less than the model calculations. Therefore, it is possible that hydrogen increases the surface roughness. But it is unlikely that changes in the surface relief exceed 3 nm.

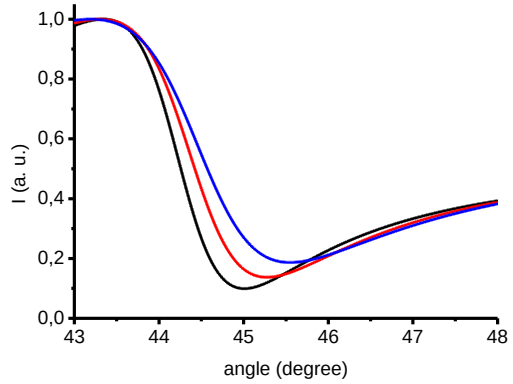

Fig. 4 – SPR curves calculated for different surface roughness of the gold film. The black curve corresponds to a roughness of 2 nm, the red curve corresponds to a roughness of 3 nm, and the blue one corresponds to a roughness of 4 nm

We considered the possible single hydrogen effects during electrolysis. In a real experiment, hydrogen penetrates and accumulates in all layers of the SPR sensor. To create a complex physical model of the SPR sensor treated with hydrogen, we found out how much hydrogen the sample received during electrolysis. The video observation during the electrolysis did not reveal the formation of hydrogen bubbles. Suppose that at least half of the atoms were captured by defects, that is, for a current of 5 μA, this is 5.67 × 1015 atoms. This amount of hydrogen is enough to form cavities at the chromium-glass interface and in the gold film and for partial destruction of the surface. Based on the classical molecular kinetic theory, the estimated hydrogen pressure in the volume of 10 % of the volume of the metal film is $65 \cdot 10^5$ Pa. This pressure does not destroy the gold film. At the beginning of the formation of cavities, the pressure is greater. This pressure decreases over time, the cavities increase in volume.

Table 1 – Changes in the SPR spectrum

		Resonance angle shift, degree	Increase in the resonance width, degree
Experimental	2 μA	0.91	0.62
	5 μA	1.3	1.42
Theoretical	Bruggeman	1.01	1.43
	Maxwell Garnett	0.95	1.47

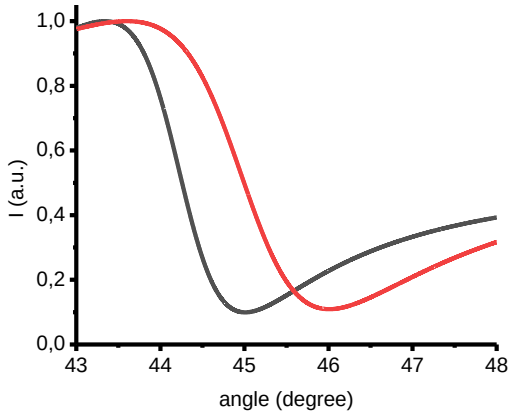

Fig. 5 – SPR curves calculated for a complex model. The black curve corresponds to the SPR sensor before hydrogen treatment, the red curve corresponds to the SPR sensor after hydrogen treatment

Based on the above considerations, we calculate the SPR curve for such a system. The oscillations of the surface air-gold level before hydrogen treatment are 2 nm. After hydrogen treatment, the oscillations of the surface level increase to 3 nm. The calculations of the layer on the surface of the gold film are performed according to the Bruggeman model. Calculations of all other layers are performed using both models. The layer of "solid" gold before hydrogen treatment is 48.5 nm, after hydrogen treatment it increases to 53.35 nm, and the relative volume of cavities in this layer is 10 %. The cavities with hydrogen are homogeneously distributed over the volume. The chromium layer before hydrogen treatment is 5 nm, after hydrogen treatment this layer increases to 6 nm.

The results of these calculations are shown in Fig. 5 and Table 1.

3. CONCLUSIONS

The limitations of experimental studies of the treated SPR sensor do not allow to describe the process and consequences of hydrogen treatment in detail. Therefore, theoretical modeling of the interaction of the SPR

film sensor treated with hydrogen with electromagnetic radiation was considered here. It was performed by means of the transfer matrix method together with the effective medium approaches. Theoretical studies were a step-by-step consideration of possible physically meaningful elementary hydrogen effects, which ended with the synthesis of these effects into a complex qualitative description of the investigated phenomenon. The accumulation of hydrogen at the glass-chromium interface and in all thicknesses of the gold film, as well as changes in the roughness of the gold-air surface, were tested. On basis of modeling results, it was concluded that the observed in the experiments changes in the SPR spectrum are mainly related to the formation in the gold film of cavities filled with hydrogen and to an increase in the roughness of the gold-air interface. The accumulation of hydrogen at the glass-chromium interface does not affect changes in the SPR spectrum.

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Обробка воднем плівкових датчиків SPR: експерименти та теоретичне моделювання

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У роботі наведено експериментальні та теоретичні дослідження змін оптичних властивостей датчиків SPR під впливом водню. Теоретичне моделювання обробленого водневого датчика SPR проведено з використанням методу трансфер-матриць та наближень ефективного середовища. Під час моделювання розглядалися різні можливості впливу водню. Встановлено, що накопичення водню на межі розділу скло-хром не може змінити спектр SPR. Експериментально спостережувані зміщення у спектрі SPR в основному були пов'язані з накопиченням водню у всіх товщах шару золота шляхом утворення порожнин, заповнених воднем. Накопичення водню в об'ємі золотої плівки також призвело до збільшення резонансного значення SPR. Навпаки, теоретичне моделювання збільшення шорсткості поверхні золота передбачило зменшення амплітуди резонансу. В результаті було запропоновано комплексний теоретичний опис процесів, які відбувалися в датчиках SPR під час обробки воднем. Передбачення були такими. Коливання поверхневого рівня перед обробкою воднем становили 2 нм, а через можливість руйнування поверхні коливання поверхневого рівня були збільшені до 3 нм. Шар «твердого» золота до обробки воднем становив 48,5 нм, а після дії водню він збільшився до 53,35 нм. Середня об'ємна концентрація порожнин у цьому шарі становила приблизно 10 %. Порожнини з воднем однорідно розподілялися по об'єму. Товщина шару хрому до обробки воднем становила 5 нм, а після обробки воднем товщина цього шару була збільшена до 6 нм. Обсяг порожнин з воднем у хромі становив 20 %.

Ключові слова: Водень, Електроліз, Обробка воднем, Дифузія водню, Золота плівка на склі, Поверхневий плазмонний резонанс.