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Hydrogen Treatment of Surface Layer of a Gold Film on Glass

A.G. Vasiljev[1,*], T.A. Vasyliev[1†], R.O. Zhelezniak[1], V.V. Kryvytskyi[1], T.P. Doroshenko[2]

[1] *Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., Kyiv, Ukraine*
[2] *V.E. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, 41, Nauki Ave., Kyiv, Ukraine*

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This work is devoted to the effect of pulse hydrogen saturation on a gold film on glass used as a surface plasmon resonance sensor of the "Plasmon-6" spectrophotometer. Due to electrolysis in a 10 % solution of H_2SO_4 in water, the film was saturated with hydrogen. The surface of the gold film was the cathode, and the carbon electrode was the anode. Electrolysis current pulses lasted 2 s when the time interval between pulses was 1800 s. In this way, several samples were processed. The consequences of the action of five, ten, fifteen and twenty pulses on a gold film were examined as the experimentally obtained spectral curves for treated samples. The surface plasmon resonance is sensitive to changes occurring in the surface layer of the surface plasmon resonance sensor. It is applicable to control and analyze the changes induced by the proposed hydrogen treatment. In the experiments, the plasmon resonance curves shifted to larger angles. Therefore the optical properties modifications of the surface layer of the gold film were recorded. The observed changes gradually increased with the increase of the number of pulses of the electrolysis current. The mathematical approach to light reflection from the gold film was performed to analyze changes in the surface layer of the gold film. The dielectric properties of the surface layer of the gold film were estimated using the effective medium model. It made it possible to simulate changes in the surface layer of the film induced by hydrogen treatment. As a result, theoretical curves of plasmon resonance were obtained. A qualitative correlation between the experimentally observed changes and the theoretical ideas about the processes occurring during hydrogen treatment in the surface layer of the gold film on glass was achieved.

Keywords: Electrolysis, Hydrogen treatment, Hydrogen embrittlement, Gold film, Surface plasmon resonance.

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1. INTRODUCTION

It is impossible to imagine the modern world without nano-technologies. Nanoparticles and nanostructured surfaces are applicable in many fields, including biology and medicine. The therapeutic effect of nanoparticles on cancer cells same as improving the immune system and many other positive effects on living organisms have been proven many times [1, 2]. In many cases, the basis of the positive influence of nanoparticles is physical phenomena. For example, the destruction or blocking of nanoparticles of biological objects (viruses or bacteria) is due to electromagnetic interactions [3, 4]. Therefore, searching the technologies to create nanoparticles or nanostructured surfaces is an important task today.

Due to hydrogen embrittlement [5], the hydrogen treatment of metal surfaces can be used to develop nano-technologies in creating a nanostructured metal surface. Hydrogen embrittlement is a long-known phenomenon that causes hydrogen destruction of metal products and can be practically helpful.

Under appropriate conditions, surface plasmons are excited on the surface of the gold film. Therefore, the gold film on glass is used as a surface plasmon resonance (SPR) sensor. SPR spectroscopy is a sensitive diagnostic method in biological, chemical and medical research. In addition, the influence of the state of the surface of the gold film on SPR provides an opportunity to use it for rapid analysis of the result in the process of creating nanostructured surfaces. In their previous work, the authors prove that hydrogen saturates well a gold nanofilm on the glass during electrolysis in a sulfuric acid solution. This hydrogen saturation changes the physical properties of the film [6, 7]. Studies of [8] were also devoted to the hydrogen treatment of gold films. The authors [8] concluded that the hydrogen plasma treatment of samples containing thin gold film reveals an issue for technological applications. But from an optimistic perspective of theirs, the hydrogen treatment suggests an efficient cleavage technique for such films. The film surface properties change significantly affects the SPR spectrum [9]. Therefore, the idea arose to process the gold film with short-term pulses of electrolysis current. With this treatment, hydrogen will penetrate mainly into the surface layer of the film. It will change the properties of the surface layer. Such processing is easy to control. A significant accumulation of hydrogen in the surface layer causes hydrogen embrittlement of the surface layer of the film. It could become the basis of the technology for creating a nanostructured surface of a gold nanofilm. Therefore, the main goal of these studies is to describe the capabilities of a well-controlled pulsed hydrogen treatment regime applied to the surface layer of a gold film on glass (SPR sensor).

2. HYDROGEN TREATMENT OF GOLD FILM ON GLASS

2.1 The Samples for Research

* a.g.vasiliev56@gmail.com
† taras.a.vasiliev@gmail.com

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Let's briefly talk about the creation of the samples. In this work, gold films are grown by the Volmer–Weber mechanism [10]. SPR sensors were manufactured in batches of several dozen pieces. At first, glass blanks with dimensions 20 × 20 mm and 1 mm thick were inserted into the cassette. Then the cassette was placed into the VUP-5M vacuum station. The residual pressure of gases in the vacuum chamber VUP-5M was 10^{-6} Pa. Metals evaporated in the vacuum station and precipitated onto glass plates at room temperature, making a layer. Gold has poor adhesion with glass. So at first, a layer of chromium was deposited onto the glass plates. Then a layer of gold was precipitated onto chromium. Corresponding masses of chromium and gold were loaded into the tungsten evaporator consequently.

With such a sensor manufacturing technology, samples have slightly different properties. But with some accuracy, it is possible to state that the sensors have very similar characteristics. The thickness of the chromium layer was approximately 5 nm. The thickness of the gold layer was 50 nm. The dimensions of the gold film were 18 × 20 mm.

2.2 The Pulse of Hydrogen Treatment

Before hydrogen treatment, we need to determine the time of the electrolytic current pulse during which hydrogen will saturate the gold film. Due to diffusion, hydrogen must penetrate the surface layer of the film. But the depth of hydrogen penetration can be different for different pulses lasting. At first, we approximate the diffusion coefficient of hydrogen in gold. It is a specific characteristic that can significantly depend on film production technology. To estimate the value of the diffusion coefficient, we decided to rely on the previously published experimental data [7] and solved a simple problem of diffusion theory. Since the dimensions of the film significantly exceed its thickness, it was a simple problem of one-dimensional diffusion of hydrogen through the thickness of the film under the following boundary and initial conditions. The boundary conditions of this problem were as follows: during electrolysis, the surface concentration of hydrogen was constant $c(0, t) = c_0$; the flow of hydrogen atoms at the metal-glass interface was zero. Initial conditions: there was no hydrogen in the gold film before hydrogen treatment, that is, $c(x, 0) = 0$. The solution to this problem, as a function of the relative concentration $c(x, t)/c_0$ of hydrogen in the gold film, has the form

$$\frac{c(x,t)}{c_0} = 1 - \sum_{m=0}^{+\infty} e^{-\frac{(2m+1)\pi^2 Dt}{l^2}} \sin\left(\frac{(2m+1)\pi x}{2l}\right), \quad (1)$$

where x is the distance from the surface of the gold film to the point where we determine the hydrogen concentration; t is the time; D is the diffusion coefficient of hydrogen in the film; l is the thickness of the film. We used solution (1) to determine the diffusion coefficient. We know from previous studies [7] that 30 seconds of electrolysis is enough to separate the film from the glass when currents are high. Therefore, due to the diffusion of hydrogen through the film, the relative concentration at the metal-glass interface was approximately 0.5 and could reach a value of 0.95. At such relative concentrations of hydrogen at the metal-glass interface, the diffusion coefficient changes from 0.316×10^{-12} cm²/s to 1.093×10^{-12} cm²/s.

Then, based on this range for the diffusion coefficient, we calculated the value of the relative concentration of hydrogen in the sample two seconds after the start of electrolysis. The results of these calculations are in Fig. 1. It is clear that after two seconds of the electrolysis, the concentration of hydrogen in the sample as a function of distance x from the surface of the film decreases rapidly. In the middle of the film thickness, the relative concentration is near 2.6 % of the surface concentration for a smaller value of the diffusion coefficient. For a higher value of the diffusion coefficient, the relative concentration in the middle of the film is 23.2 %. So, we chose the electrolysis current pulse time of 2 s. In this case, only the surface layer with a thickness of about 10 nm was expected to be effectively processed.

The electrolysis was performed in the 10% solution of H_2SO_4 in water. The gold film was the cathode, and the carbon electrode was the anode. The strength of the electrolysis current was 5 μA. From previous works, it is known that this current had the highest effect on the physical properties of the gold film. The current impulse time was 2 s. The time intervals between impulses were 0.5 hours.

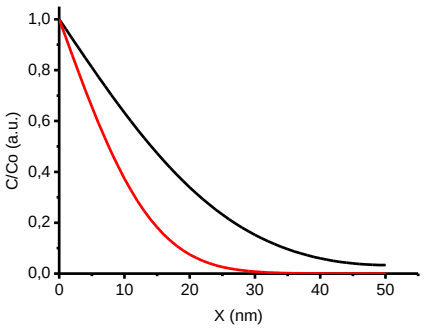
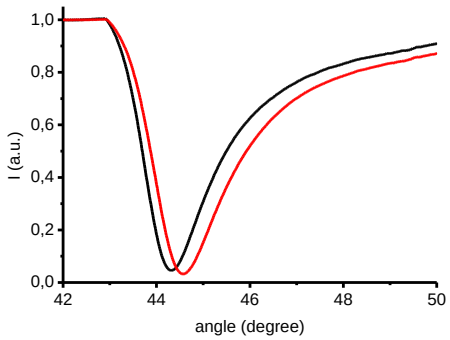


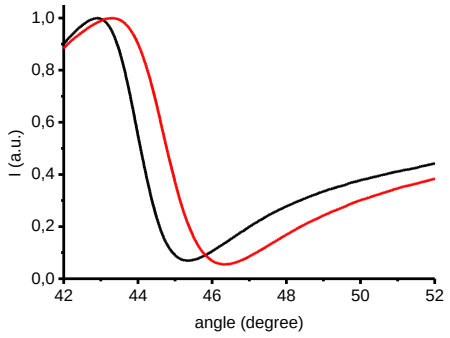
Fig. 1 – Distribution of hydrogen concentration in the film at the end of the 2 s from the beginning of electrolysis: red curve corresponds to $D = 0.316 \times 10^{-12}$ cm²/s; black curve corresponds to $D = 1.093 \times 10^{-12}$ cm²/s

3. CHANGES IN THE SPR SPECTRUM CAUSED BY HYDROGEN TREATMENT

The investigated films on glass are applicable as a PPR sensor in the Plasmon-6 spectrometer. Plasmons in the Plasmon-6 spectrometer are excited by the Kretschmann method. In a spectrometer, a beam of light from a laser passes through the glass of the prism and plate onto the gold film and is reflected from it. The angle of incidence of the beam on the film changes in a directed manner. By spectrometer, we measured the intensity of light reflected from the gold film. When the conditions of plasmon resonance, which depend on the angle of incidence, were met, plasmons were excited at the gold-air interface [11]. Therefore, Plasmon 6 registered the surface plasmon resonance curve. The SPR curve is the dependence of the intensity of light



a



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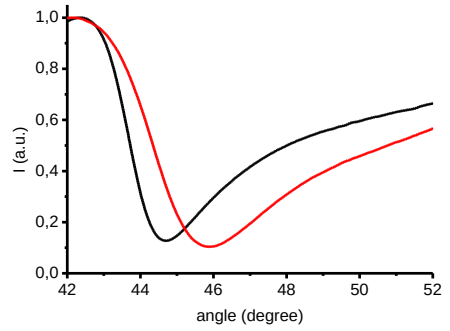

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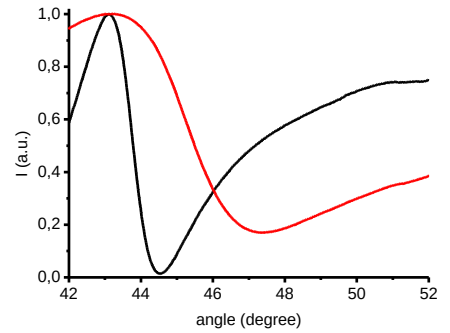


d

Fig. 2 – The SPR curves: black curves obtained before hydrogen treatment; red curves – after hydrogen treatment. a) 5 impulses of electrolysis current; b) 10 impulses of electrolysis current; c) 15 impulses of electrolysis current; d) 20 impulses of electrolysis current

reflected from the film on the angle of incidence of light on the film. Before hydrogen treatment, we obtained SPR curves for each sample. Then, we did the same after treating them. Obtained curves were normalized to the maximum intensity of light reflected from the film.

Fig. 2 shows the SPR curves before (black curves) and after hydrogen treatment (red curves). The black ones are slightly different from each other. This difference is related to the initial sample differences (differences in the thickness of the metal layer and differences in the surface roughness).

Four samples were treated with hydrogen by a different number of impulses of electrolysis current. Namely, this was five, ten, fifteen, and twelve impulses applied to the corresponding films. Seven days after hydrogen treatment, we obtained SPR curves again. From previous studies, we know that one week is the time when property changes occur with attenuation.

Fig. 2 shows the SPR curves for each sensor. We see that after hydrogen treatment for all cases, the SPR curves shifted relative to the position of the SPR curves before treatment towards larger angles. The shift of the curve increases with the increasing number of impulses of the electrolysis current. For the sample treated by five impulses, the SPR curve shift after hydrogen treatment was 0.26°. In the case of hydrogen treatment by ten current pulses, the SPR curve shift was approximately 1.00°. For the third sample (fifteen impulses), the SPR curve after hydrogen treatment shifted by 1.15°. For the fourth sample subjected to twenty pulses, the corresponding shift after hydrogen treatment was 2.39°. The changes in the shape of the SPR curves for the first three samples are small. Changes after hydrogen treatment in the SPR spectrum of the fourth sample are significant. In this case, the width of the SPR curve increased significantly, and the depth of the resonance minimum decreased.

4. RESULTS AND DISCUSSION.

In the present work, a gold film saturation with hydrogen occurred across the solution-gold interface. It was a one-sided saturation of the film with hydrogen since the metal-glass boundary is not a penetration point for hydrogen. It is clear [12] that the one-sided saturation of metal with hydrogen causes significant mechanical stresses. The top layer of metal stretched. Mechanical stresses in the upper layer of the gold film contribute to the emergence of additional defects and increase the size of existing defects (formation of cavities). During the first five pulses, this was the leading mechanism for changing the physical properties of the film. The cavities volume was small, and the shift of the SPR curve was insignificant (Fig. 2 a).

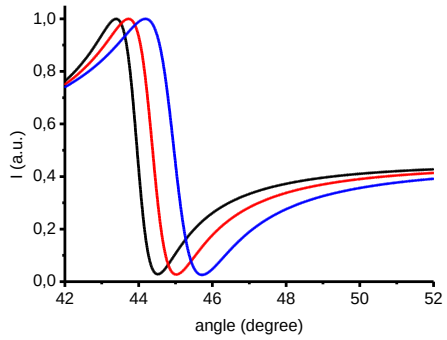
During the further five pulses, there was an active capture of defects of hydrogen atoms. It significantly increased the volume of the cavities. In the SPR spectrum, we observed a significant shift of the SPR curve by 1° (Fig. 2b). The following five impulses of electrolytic current also guided to active hydrogen uptake, but the cavities volume increased slowly because more hydrogen was needed to grow larger cavities. During this processing period, we observe a relatively small shift of the SPR curve (Fig. 2c).

After saturating the sample for twenty pulses, the hydrogen pressure in parts of the cavities exceeded the limit of the mechanical strength. Since these cavities were in the surface layer, they opened to the surface.

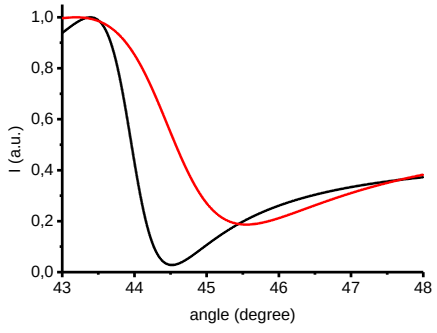
The surface roughness increased. The changes in the SPR spectrum of the sample after twenty pulses of electrolysis current confirmed this (Fig. 2d).

4.1 Theoretical Modeling

The SPR curves in the first three cases of hydrogen treatment (five, ten and fifteen impulses of electrolysis) retain their shape. The resonance amplitude is almost unchanged because the surface of the gold film changed insignificantly. The changes occur only inside the gold film. From theoretical modelling [8], it is clear that the formation and increase of nanopores with hydrogen in the middle of the gold film lead to a shift of the SPR curve towards larger angles, and it somewhat reduces the intensity of reflected light. Therefore, we decided to repeat the based on the transfer matrix approach [13, 14] theoretical calculations of the SPR curves [8]. The cavities with hydrogen were also in the gold film. But in this case, we supposed that they were in the surface layer of the film with a thickness of 10 nm. According to the results of calculations, the SPR curves were built and demonstrated in Fig. 3a.



a



b

Fig. 3 – Theoretical curves of the SPR. a) smooth surface of a film: the black curve in the top layer corresponds to the case with no nanopores; the red curve corresponds to the case of 15 % volume concentration of nanopores in the upper layer of 10 nm thickness; the blue curve corresponds to the case of 30 % volume concentration of nanopores in the upper layer of 10 nm thickness. b) the black curve corresponds to the case when the film surface is not rough; the red curve corresponds to a film with a rough surface of 4 nm

Theoretical computer modelling of SPR curves testifies to the benefit of such a model. Theoretical SPR curves hardly change their shape. The intensity of the reflected light also decreases slightly with the increase in the relative concentration of cavities with hydrogen. It qualitatively corresponds to the experiment, namely to the experimentally observed changes in the SPR spectrum for 5-15 impulses. After 20 impulses of electrolysis current, the sample significantly changed the surface properties. In the case of such treatment, hydrogen cavities, which were in the upper layer of the film, do not withstand the pressure of hydrogen and open to the surface. It changes the surface roughness.

As it is clear from the theoretical modelling [8], the surface roughness increase significantly reduces the resonance amplitude and increases the half-width of the SPR curve. We performed theoretical model calculations for the surface roughness of 4 nm (Fig. 3b). From the figure, one can see that with such an increase in roughness, the curve shifted to larger angles by 1.55°. The width of the SPR curve increased significantly, and the resonance amplitude decreased significantly. Unfortunately, we did not get a quantitative agreement between the theoretical modelling and the experiment. But we obtained good quality correlation.

5. CONCLUSIONS

The paper examines the effect of hydrogen treatment on the surface of a gold film on the glass. For processing, we used electrolysis in an aqueous solution of 10 % sulfuric acid, where the film surface was the cathode, and the carbon electrode was the anode. The electric current of 5 μA was pulsed. Electrolysis lasted 2 s with a time interval between pulses of 1800 s. During the current pulse, the surface layer of the film was saturated with hydrogen. The effect of five, ten, fifteen, and twenty pulses of electrolysis current was studied. It was established that the surface layer of the film gradually accumulates hydrogen in defects. Defects increase in size. It is the reason for the change in the dielectric properties of the surface layer of the film. The surface plasmon resonance spectrum reflects this. As it turned out, twenty current pulses are enough to increase the roughness of the film surface. Therefore, hydrogen treatment of this type can apply to the creation of nanoscale relief surfaces. It will be valuable if researchers use the treated surface in antiviral therapy.

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Воднева обробка поверхневого шару золотої плівки на склі

А.Г. Васильєв[1], Т.А. Васильєв[1], Р.О. Железняк[1], В.В. Кривицький[1], Т.П. Дорошенко[2]

[1] *Київський національний університет імені Тараса Шевченка, вул. Володимирська, 64/13, Київ, Україна*
[2] *Інститут фізики напівпровідників ім. В.Є. Лашкарьова НАН України, просп. Науки, 41, Київ, Україна*

Дана робота присвячена вивченню впливу імпульсного насичення воднем на плівку золота на склі, яка використовується як сенсор поверхневого плазмонного резонансу спектрофотометра «Плазмон-6». Внаслідок електролізу в 10 % розчині H_2SO_4 у воді плівка насичується воднем. Поверхня золотої плівки була катодом, а вугільний електрод – анодом. Імпульси струму електролізу тривали 2 с, а часовий інтервал між імпульсами становив 1800 с. Таким способом було оброблено кілька зразків. Наслідки дії п'яти, десяти, п'ятнадцяти і двадцяти імпульсів на плівку золота розглядалися у вигляді експериментально отриманих спектральних кривих для оброблених зразків. Поверхневий плазмонний резонанс чутливий до змін, що відбуваються в поверхневому шарі датчика поверхневого плазмонного резонансу. Він застосовний для контролю та аналізу змін, викликаних запропонованою обробкою воднем. В експериментах криві плазмонного резонансу зміщувались у більші кути. Тому були зареєстровані зміни оптичних властивостей поверхневого шару золотої плівки. Спостережувані зміни поступово зростали зі збільшенням кількості імпульсів струму електролізу. Математичний підхід до відбиття світла від золотої плівки був виконаний для аналізу змін у поверхневому шарі золотої плівки. Діелектричні властивості поверхневого шару плівки золота оцінювали за допомогою моделі ефективного середовища. Це дозволило змоделювати зміни поверхневого шару плівки, викликані обробкою воднем. В результаті були отримані теоретичні криві плазмонного резонансу. Досягнуто якісної кореляції між експериментально спостережуваними змінами та теоретичними уявленнями про процеси, що відбуваються під час обробки воднем у поверхневому шарі плівки золота на склі.

Ключові слова: Електроліз, Воднева обробка, Воднева крихкість, Плівка золота, Поверхневий плазмонний резонанс.