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Protective properties of ZnO nanofilm against wear and mechanical damage of sensitive SPR sensor element

A. Fedorenko[1], N. Kachur[1], O. Sulima[2], V. Maslov[1]

[1] Institute of Semiconductor Physics NAS of Ukraine, Nauki ave., Kyiv,Ukraine, 03028
[2] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 37, Beresteiskyi ave., Kyiv, Ukraine, 03056

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The effectiveness of the protective properties of ZnO films obtained by sol-gel technology was studied by plasmon magnetic resonance. Amorphous films 10 nm thick with low surface roughness provided an increase in resistance to mechanical wear by more than 2 times. The resistance to film destruction increased by approximately 27 times, which is a significant achievement. Combined with a 5 nm thin layer of chromium to enhance adhesion between gold and glass, amorphous thin films of ZnO have demonstrated excellent protective properties for the sensing elements of sensor devices based on the phenomenon of surface plasmon resonance.
Keywords: Surface Plasmon Resonance, sensitive element, protective coating, zinc oxide, destructive mechanical influence.

Захисні властивості наноплівки ZnO від зношування та механічного руйнування чутливого елементу SPR-сенсора. *А.В. Федоренко, Н.В. Качур, О.В. Суліма, В.П. Маслов*

Методом плазмонного магнітного резонансу досліджено тонкі захисні покриття, одне з яких – оксид цинку – досліджується в цій статті. Дослідження підтвердили ефективність захисних властивостей плівок ZnO, нанесених за технологією золь-гель. Плівки товщиною 10 нм і аморфною структурою з низькою шорсткістю поверхні забезпечували підвищення стійкості до механічного зношування більш ніж у 2 рази. Стійкість до руйнування плівки зросла приблизно в 27 разів, що є значним досягненням. У поєднанні з тонким шаром хрому (5 нм) для посилення адгезії між золотом і склом тонкі аморфні плівки ZnO продемонстрували чудові захисні властивості для чутливих елементів сенсорних пристроїв, що працюють на основі явища поверхневого плазмонного резонансу.

1. Introduction

Surface Plasmon Resonance (SPR) is an effect that arises when free electrons in a thin metal layer are excited by light incident at a certain angle. Electrons on the surface of gold collectively oscillate in response to irradiation with light of a specific wavelength. Consequently, peaks appear in the spectrum of reflected light that were absent in the spectrum of the incident light. The secondary radiation arising on the surface of a metallic film propagates into the substance under study, decaying exponentially as a function of distance. Interactions between molecules lead to changes in surface plasmon characteristics; this manifests itself in changes in the resonance angle and refractive index in the surface layer. This method allows real-time observation of reactions.

The SPR method is universal, allowing high accuracy to determine the characteristics of liq-

uid and gaseous substances by measuring their optical refractive indices. SPR devices make it possible to study a variety of multicomponent media and measure their individual components, in particular, to determine the size of nanoparticles and their size distribution in suspensions [1, 2]. Most of SPR devices are developed based on the Kretschmann optical configuration [3]. In this scheme, a fixed wavelength of polarized light is typically used in angular scan configuration, necessary for observing the excitation of total internal reflection at the interface of "dielectric-sample material."

The sensitive element of the SPR device consists of a gold film with a thickness of 30-50 nm [4], deposited on a substrate of optical glass. Usually, the gold nano-layer is deposited by vacuum sputtering. The sputtered gold layer is soft and has low mechanical strength, thus it wears out quickly during operation. Additionally, gold does not adhere well to glass and requires the application of an additional intermediate chromium layer. However, the intermediate chromium layer does not affect the resistance to mechanical wear and damage of the external surface of the gold coating.

Wear of the surface gold nano-layer can be caused by various factors such as maintenance (cleaning before measurements), chemical reactions, and the abrasiveness of the environment. This problem is particularly acute in the measurement of suspensions [5], since they contain abrasive solid particles which lead to surface changes, reduction in thickness, and destruction of the gold nano-layer of the sensitive element. As a result, there is a need to frequently replace sensitive elements, which significantly increases the cost of measurements. Therefore, extending the service life of the sensitive element by increasing resistance to mechanical wear is the relevant problem. The method chosen by the authors to solve this problem was to use transparent protective nano-layers in the operating wavelength range with higher mechanical properties that would not interfere with surface plasmon resonance measurements. In recent decades, nanomaterials, particularly zinc oxide (ZnO) nanoparticle films, have attracted special interest due to their physical properties [6]. Additionally, ZnO is cheaper and safer for humans and the environment compared to many other semiconductors. Zinc oxide has a wide range of applications, from solar cells and LEDs to sensors and transistors [8-10]. The melting temperature of zinc oxide (1975 °C) is almost twice that of gold (1064 °C), which suggests higher mechanical properties..

The thermochemical sol-gel method is promising for the deposition of ZnO films [11, 12]. This method ensures the production of films of zinc oxide nanoparticles with a high degree of control over their structure and properties. This also makes it possible to achieve uniformity and high surface quality of nanomaterials, which is important for many applications. ZnO has a stronger atomic bond and significantly lower friction coefficient compared to gold [13], and sol-gel technology makes it possible to deposit nano-sized films that are transparent in the visible and near-infrared regions of the spectrum. The protective properties of amorphous nanoparticle films are of particular interest [14].

2. Experimental

Two types of sensitive elements of SPR sensors were studied: with and without an additional top layer of ZnO. Substrates for the sensitive element were plates of optical glass of the TK14 and F1 brands with dimensions: 1×20×20 mm. The chromium and gold films were sequentially deposited (first chromium, then gold) on one side of two rectangular glass plates by vacuum-thermal evaporation on the VUP-5M installation at a rate of 5-6 nm/s, with a residual pressure of $(1\text{-}2)\times10^{-5}$ Pa. The film thickness was monitored during deposition using a KIT-1 instrument with a measurement error of ±0.1 nm. A chromium intermediate layer with a thickness of ~5 nm was deposited on some of the samples to enhance adhesion between gold and glass; the thickness of the gold layer was ~35 nm and ~50 nm.

Then, a ZnO film was deposited using the sol-gel technology [15]. For this, 2.2 mg of zinc acetate was dissolved in 50 ml of isopropyl alcohol and stirred with a magnetic stirrer at a temperature of 50 - 60°C for 30 minutes. 0.6 ml of monoethanolamine was added as a stabilizer. As a result, a sol-type colloidal solution was obtained. The obtained solution was kept at room temperature for 24 hours to form a gel. The samples were placed into a centrifuge, and the synthesized gel was applied to the surface of the glass using a pipette dispenser. The samples were dried by rotating the centrifuge at a frequency of 100 rpm and simultaneous air flow at a temperature of 70°C. The dried samples were annealed in a muffle furnace for 30

Table 1. Technical specifications of the SPR device "Plasmon-6"

Characteristic	Value
Refractive index measurement range	1.0 – 1.43
Resolution in refractive index measurement	0.00005
Angular resolution in incidence angle	10 angular seconds
Maximum scanning angle	17 angular degrees
Measurement time of the full SPR curve	≤ 3 seconds
Minimum time for one measurement:	
- Partial SPR curve measurement mode	1 second
- Fixed angle measurement mode	0.2 seconds
Number of optical channels	2
Additional channel for electrical measurements	±5V

minutes at a temperature of 300°C to remove residual solvent, and then for another 1 hour at a temperature of 500°C to form a zinc oxide film. The thickness of the resulting sol-gel film was 5 nm, and to increase its thickness, the deposition operation was repeated. The thickness of the films was measured using atomic force microscopy. The films were continuous; their surface had a lower roughness compared to the original gold surface. X-ray studies have shown that thin ZnO films are amorphous. Since the thickness of thin ZnO films (5-10 nm) is significantly less than half the working wavelength (650 nm), the effect on the sensitivity and volume of the measured medium is negligible.

To determine the mechanical strength of the nanoparticle coating, atomic force microscopy (AFM) is commonly used [16]. The AFM probe with varying force is pressed against the surface of the film and moved along it. The force at which the film is damaged by the probe is recorded. This method is promising from the point of view of nanotribology, but in our case, it does not provide a comprehensive assessment of the wear resistance and resistance to destruction of the sensitive region of the SPR element. Moreover, this method requires expensive equipment and is quite complex to perform. Therefore, a simple technique was used to evaluate the protective properties of the ZnO nanoparticle film. In this method, the pressing force was determined by repeatedly measuring the mechanical pressure of the index finger in a cotton medical glove on a technical scale. The selected forces ranged from 80 to 100 g/cm^2. With equal force, the experimenter rubbed (dry friction) the surface of a gold-plated sensitive SPR element with and without ZnO. The number of rubs and the results of measurements of optical, electrical, and SPR characteristics were compared.

The optical transmission spectra of the samples were measured on a UV 1600 spectrophotometer from Mapada Instruments. The refractometric characteristics of SPR for the studied samples were measured using the SPR device "Plasmon-6," developed at the V.E. Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine; characteristics are provided in Table 1. The object of measurement was clean ambient air.

The "Plasmon-6" device is constructed in the Kretschmann geometry; it consists of a surface plasmon excitation source (a laser with a wavelength of 650 nm), a total internal reflection prism, a sensitive element, and a photodetector for the light reflected from the sensitive element. The device operates as follows: the prism discretely (under the action of a stepper motor) changes its position within the range of angles of total internal reflection from the prism-metal interface relative to the direction of propagation of the laser radiation. A variable sensitive element is placed on the prism through an immersion fluid. The sensitive element is an optical glass plate (dimensions 1x20x20 mm) onto which a chromium adhesive layer (~5 nm) is deposited, followed by a sensitive gold layer (~50 nm), in which surface plasmons are excited by light. A flow cell, which has inlet and outlet ports for introducing and withdrawing the test substance, is located on the surface of the sensi-

Table 2. Dependence of the transmission coefficient of SPR sensor sensitive elements on the number of wear cycles of this coating.

Sample 1		Sample 2		Sample 1 with ZnO		Sample 2 with ZnO	
Number of wear cycles	T, %	Number of wear cycles	T, %	Number of wear cycles	T, %	Number of wear cycles	T, %
0	18.6	0	15.1	0	18.9	0	16.1
5	29.3	1	13.4	5	20.3	100	18.1
10	49.1	2	14.2	10	20	200	19.6
15	74.4	4	14.8	15	19.8	300	21
20	83	6	16.6	20	20	400	21.7
25	87.2	8	18.5	25	20.2		
30	88.6	10	19.2	30	20.7		
35	89.5	12	21.1	35	21.6		
		14	25.4				
		16	25.4				
		18	27.8				
		20	28.5				
		22	30.9				

tive element so that the test substance contacts the zinc oxide layer. When the photon frequencies of a source of *p*-polarized monochromatic light and electron plasma resonate on the outer surface of the metal, significant absorption of photon energy occurs. This is manifested in a decrease in the intensity of reflected light at a certain angle of incidence of light, which is recorded by a detection system tuned to certain characteristics of the test substances or the result of the interaction of their components. The angular position and shape of the resonance curve are recorded by a control program; this makes it possible to obtain in real time kinetic curves that reflect the processes of adsorption and interaction of molecules present in the test sample of liquid or gas. The measurement results are mathematically processed using a specially developed algorithm. Mechanical scanning of the angle of incidence of radiation on the sensing element provides an angular range up to 17 degrees [17].

3. Results and discussion

The visible wear of the films was monitored using the wavelength of 532 nm. As shown in Fig. 1, this wavelength corresponds to the peak transmission of the sensitive element with gold coating. The obtained values of the transmission coefficient and the number of wear cycles are presented in Table 2.

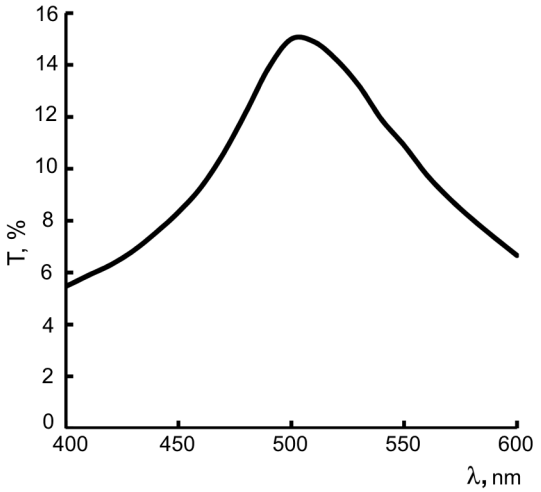

Fig. 1. A typical transmission spectrum for the sensitive element of the SPR sensor (TK-14 glass, gold film thickness ~ 40 nm).

As can be seen from the table, for samples without a protective ZnO coating, the transmittance increases much more intensely. After 5 wear cycles, the film was completely destroyed. For the sample without the protective coating, an increase in the transmission coefficient by 5% occurred after 11 wear cycles, while for the sample with the protective coating, the same increase required more than 300 wear cycles. Thus, we can conclude that applying a protective ZnO coating to the sensitive element increases the wear resistance of gold by at least 27 times. Mechanical wear testing was performed during

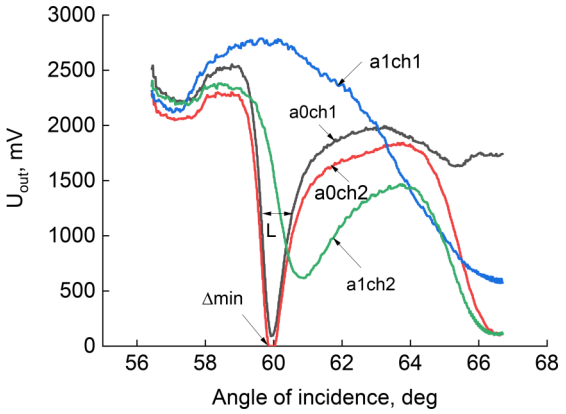

Fig. 2. SPR curves when testing the wear of the sensitive element surface with a ZnO layer of d=10 nm: a_{0ch1}, a_{0ch2} represent the first and second measurement channels before wear testing, and a_{1ch1}, a_{1ch2} represent the first and second measurement channels after 40 wear cycles.

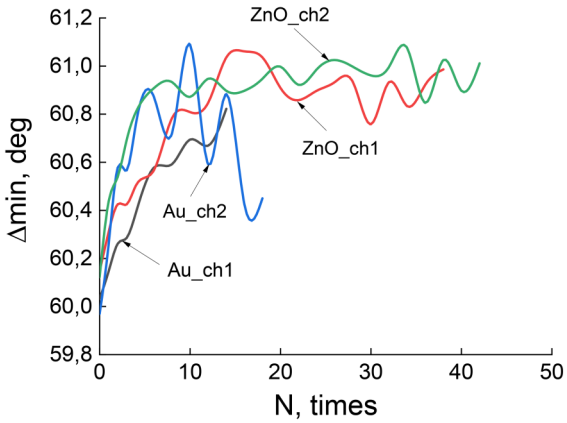

Fig. 3. The dependence of the resonance minimum angle on the number of wear cycles, where A_{uch1}, A_{uch2} represent the first and second channels for the sensitive element without the ZnO layer, and ZnO_{ch1}, ZnO_{ch2} represent the first and second channels for the sensitive element with the ZnO layer.

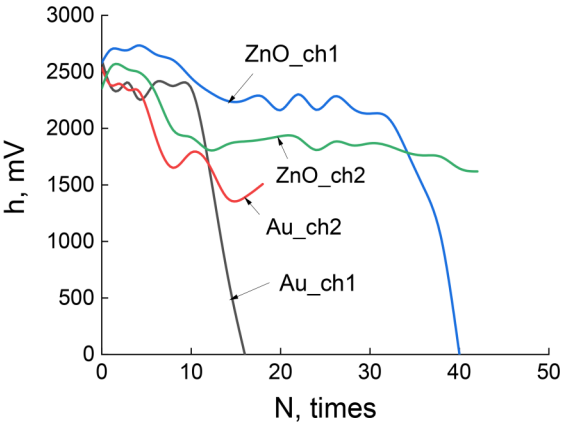

Fig. 4. The dependence of the resonance depth on the number of wear cycles, where A_{uch1}, A_{uch2} represent the first and second channels for the sensitive element without the ZnO layer, and ZnO_{ch1}, ZnO_{ch2} represent the first and second channels for the sensitive element with the ZnO layer.

the measurement of refractometric characteristics on the SPR device. Typical SPR characteristics are shown in Figure 2.

Measurements were carried out until the signal disappeared from at least one channel, as shown in Figure 3. Samples with the applied ZnO layer required an average of 38-44 wear cycles, while samples without the layer required an average of 16-21 cycles. To dynamically represent the changes in the SPR curve after each wear cycle, the following parameters were monitored:

Δ_{min} – angle of the minimum resonance in degrees;

h – depth of output signal drop in mV;

L – FWHM of the drop in degrees.

The dependence of the minimum resonance angle on the number of wear cycles is shown in Figure 3, the depth of the drop in Figure 4, and the half-width of the drop in Figure 5.

As can be seen from Fig. 3, the minimum resonance angle for the sample without ZnO film increased from 60° to 61° in the first channel until the resonance curve completely disappeared after 14 wear cycles. In the second channel, the curve was maintained even after 18 cycles, but the minimum angle increased during the first 5 wear cycles, after which strong periodic oscillations were observed. For the sample with the protective ZnO layer, the minimum angle increased in both channels during the first 10 wear cycles and then stabilized at about 61°. In the first channel, the signal also disappeared after 40 wear cycles, although the curve in this channel had better parameters during the measurements, after which it sharply deteriorated. Periodic oscillations are observed in all parameters; this can be explained by periodic changes in the surface structure, also, slight shifts of the sensitive element or micro-particle tissue residues may introduce errors. The presence of tissue residues is also indicated by the fact that after washing the sensitive element with isopropyl alcohol, the samples only partially return to the original parameters.

The presence or absence of the SPR curve is best seen from Fig. 4. The moment of its disappearance is clearly visible, as well as a more significant decrease during the first 10 cycles and subsequent stabilization. For samples without a protective layer, significant fluctuations are also noticeable.

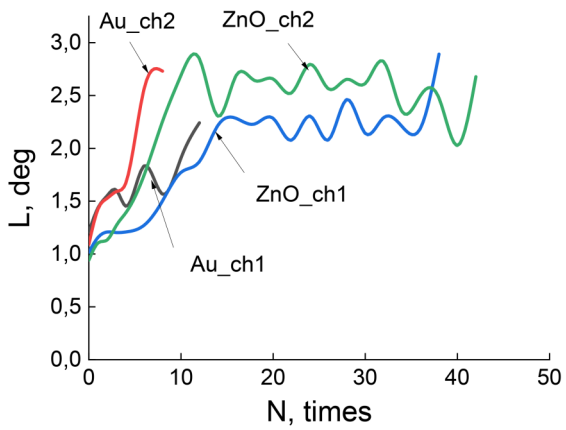

Fig. 5. The dependence of the half-width of the resonance dip on the number of wear cycles, where A_{uch1}, A_{uch2} represent the first and second channels for the sensitive element without the ZnO layer, and ZnO_{ch1}, ZnO_{ch2} represent the first and second channels for the sensitive element with the ZnO layer.

In Fig. 5 we can notice the L value of 2.8°, after which the right branch of the curve did not reach the value $h/2$ and, accordingly, measuring the width became impossible. It should be especially noted that since this parameter is influenced by both the depth of the drop and the slope of the right branch, periodic oscillations are observed much more often. In general, the process was increasing: the minimum angle shifted, then the depth of the drop decreased, and the slope of the right branch increased, and so on in a cycle.

The results of the research have shown that the application of thin zinc oxide films significantly increases the wear resistance of sensitive elements in SPR devices with gold coatings. This can be attributed to the high melting temperature of zinc oxide, 1975 °C, compared to 1064 °C for gold, as well as its approximately twice the hardness. The lower coefficient of friction of ZnO may also play an important role in reducing wear of the films when studying liquids with abrasive elements.

Due to the small thickness of the film, its effect on the sensitivity of the SPR device and the volume of the analyzed material, the refractometric parameters of which are measured, is insignificant. Although much thicker zinc oxide films (150-400 nm) are used in gas SPR sensors depending on the operating wavelength and the specific test subject, the advantage of the proposed thin amorphous ZnO films is increased wear resistance of the element while maintaining the versatility of a gold-coated SPR sensor. The increase in gas sensitivity observed in other measurements may be explained by relaxation and corresponding stress reduction during annealing at 500 °C. Without a protective ZnO film, such annealing becomes impossible, as from our own experience, at 400 °C, the gold film deteriorates and gathers into droplets.

4. Conclusions

The research has confirmed the effectiveness of the protective properties of ZnO films applied using the sol-gel technology. Amorphous ZnO films with a thickness of 10 nm and low surface roughness make it possible to increase resistance to mechanical wear by more than 2 times. Spectrophotometric monitoring showed that the resistance to degradation of the films increased almost 27 times.

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