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Sensors

Wear resistance of sensors based on surface plasmon resonance phenomenon

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Abstract. Surface plasmon resonance is used for detecting and measuring various analytes characteristics by sensitive elements in sensor devices. At this, the problem of wear of the sensitive elements, contacting with gaseous and liquid environments whose characteristics are measured, arises during operation of sensor devices based on the surface plasmon resonance phenomenon. Wear of a surface gold nanolayer may be caused by various factors such as maintenance (cleaning before measurements), chemical reactions and abrasiveness of the environment. This problem becomes particularly significant when suspensions are measured. Solid particles in the suspensions have abrasive properties, which leads to modifications of the surface, reduction of the thickness and damage of the sensitive gold layer. As a result, more frequent replacements of sensitive elements are required significantly increasing the measurements cost. In this paper, influence of water suspensions of an optical polishing powder "Polarite" on the wear and the associated changes of the characteristics of a sensitive element is investigated. The need to find solutions of the problem of improving its wear resistance is highlighted.

Keywords: surface plasmon resonance, infrared spectral range, spectrophotometer, suspension, wear resistance.

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1. Introduction

At present, plasmonics is a cutting-edge research field, the technological base of which offers a variety of specific measuring devices, namely spectrometers based on the surface plasmon resonance (SPR) phenomenon. The majority of such devices are designed according to the Kretschmann optical scheme [1]. This scheme usually uses a fixed-wavelength polarized light in the angle scanning configuration, which is necessary to observe excitation in the total internal reflection at the dielectric – studied metal interface. SPR devices can operate in different spectral ranges, one of the promising ranges being the near infrared one (NIR) [2].

Application of SPR in various investigations is universal. It enables reaching a high accuracy of determining parameters of liquid and gas-like substances by measuring their optical refraction coefficients. Use of SPR devices allows one to study various multicomponent environments and identify their components. Besides, such devices enable studying suspensions and determining nanoparticle sizes and size distributions [3, 4].

It is well known that suspension is a dispersed system composed of a liquid dispersing medium and a solid dispersed phase. The latter consists of particles that are large enough to resist Brownian motion. Such systems are widely used in medicine and industry.

With the development of nanotechnology and nanomaterials, suspensions become actively used in industry for obtaining high-quality ceramic materials. A polishing powder named "Polarit" (CeO_2 with rare earth impurities) is widely applied for producing optical components. The particle size and uniformity are particularly important for application of this powder [5]. In the slip casting production technology of ceramic parts, a slip with added nanoparticles is widely used [6]. For manufacturing high-quality and highly reliable products, the problem of its control (homogeneity, particle sizes) arises. Since the slip is a suspension with a moisture content of approximately 30%, its density is usually monitored during the production process [7]. For example, a capacitance sensor that measures the density of suspension flow in the range of solid volume fraction from 0 to 29% is installed [8]. A drawback of this method is its limited ability to treat suspensions with low solid content and to measure only the integrated value of the mixture capacitance without assessing the particle size distribution. Moreover, optical methods for studying slips exist, such as the one presented in [9]. This method applies digital holographic microscopy to investigate droplets of a slurry. It enables measuring the concentration and distribution of solid particles in suspensions with particle sizes of about a micron. Since the SPR method allows one to measure nanoparticles and is fast and highly accurate, it may be promising for research related to its application in this field.

Presence of solid opaque particles in suspensions causes certain limitations for using SPR devices operating in the visible spectral range. Therefore, we performed measurements using an SPR device operating in the NIR range. The experiments were conducted with a toothpaste to model multi-component suspensions containing opaque particles and chemical compounds. The fundamental possibility of such research was demonstrated in [10].

Another feature of the SPR phenomenon is that the frequency of a surface plasmon propagating along the metal-sample medium interface and its damping rate depend not only on the change of the refractive index on the sensitive element surface but also on the nano-roughness of the metal surface in contact with the studied medium. The state of the metal surface in turn depends on the formation technology of the metal layer on the dielectric as well as the substrate surface state, which is defined by its processing technique (mechanical, chemical, *etc*.). Moreover, metallic coatings (typically gold) are made relatively thin, around 50 nm [11]. During the measurements, the surface quality and the layer thickness gradually decrease. Due to the low hardness of gold and the possibility for nanoparticles to enter the pores on the gold nanolayer surface, the service life of the sensitive element decreases. This problem is particularly significant when suspensions are investigated.

Table 1. Technical characteristics of the SPR device "Plasmon-71".

Characteristic	Value
Refractive index measurement range	1.3 – 1.5
Resolution of the refractive index measurements	0.000005
Incident resolution	10 ang. sec
Maximum scanning angle	17°
Measurement time of the entire SPR curve	≤10 s
Number of optical channels	2
Additional channel for electrical measurements	±5 V
Wavelength	λ = 850 nm

2. Materials and methods

To study the effect of only opaque solid particles, a water-based suspension for optical polishing was used. This powder consists of fractions with the particle sizes ranging from micrometers to nanometers. Therefore, a certain quantity of the "Polarit" powder was initially mixed with water and left for 10…20 min to allow the larger and heavier particles to settle, leaving suspended only the smaller ones. Then, both suspensions with small and large particles were investigated using the SPR method. Additionally, water suspensions with a specific concentration of "Polarit" without selecting lighter fractions were also examined. The research was conducted using the "Plasmon-71" device with the characteristics at the wavelength of 850 nm presented in Table 1.

During the measurements, two channels of the Plasmon-71 device with open cells for the test substance were used. To clean the sensitive element, a cell was removed and mechanically cleaned (using cotton swabs) with ethylene. The quality of cleaning and the sensitive element state were evaluated through control measurements after each cleaning with deionized water.

3. Results and discussion

Fig. 1 shows the SPR characteristics of the as-prepared suspension and after separation of the lighter fractions by settling during 20 min.

As can be seen from Fig. 1, the influence of the suspension on the refractometric characteristics is immediately noticed by the reduction of the dynamic range $U_{max} - U_{min}$. The resonance minimum angle is also significantly shifted relative to the one for the reference deionized water, namely 0.19° for the freshly mixed suspension (CeO_2:H_2O = 1:16) and 0.88° for the sample selected from the upper lighter fractions 20 min after preparation with the reduced average size of solid particles in the suspension.

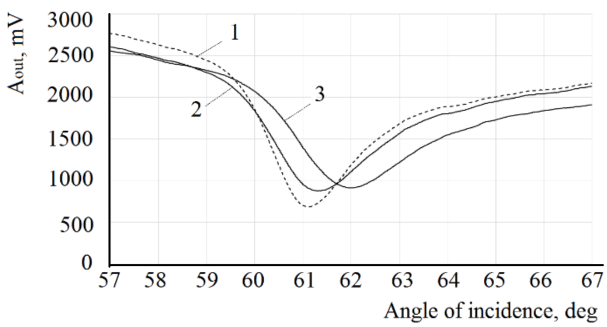

Fig. 1. Refractometric characteristics of SPR for the suspension with the mass ratio CeO_2:H_2O = 1:16. SPR curve for deionized water (*1*), the suspension at the specified ratio (*2*), the suspension after separating the upper lighter fractions by settling during 20 min (*3*).

During the measurements of the suspension (CeO_2:H_2O = 1:16, 10 min after preparation for selecting the lighter fraction, a total of 6 times), both channels of the device were used alternately. Figs 2 and 3 show the results of the control measurements with deionized water before and at the end of the measurements for both channels. The parameters of the sensitive element were monitored through intermediate measurements with deionized water.

The measurements show degradation in both channels, which is primarily manifested as a reduction in the response for the channels 1 and 2 as well as a shift in the resonance minimum angle. Such degradation leads to a decrease in the dynamic range of the sensitive element and, consequently, its sensitivity. Moreover, visible damage of gold and decrease of the gold layer thickness can be observed at the positions of the measurement cells.

Suspensions with different concentrations of “Polarite” (12.5…100 µg/mL) were also measured. The data of the intermediate control measurements with deionized water are presented in Table 2. The maximum (U_{max}) and minimum (U_{min}) values as well as the angular position of the minimum θ_{SPR} were determined from the measured characteristics. Furthermore, the resonance range ΔU ($\Delta U = U_{max} - U_{min}$) and the half-width W of the characteristic at the 0.5 level were calculated.

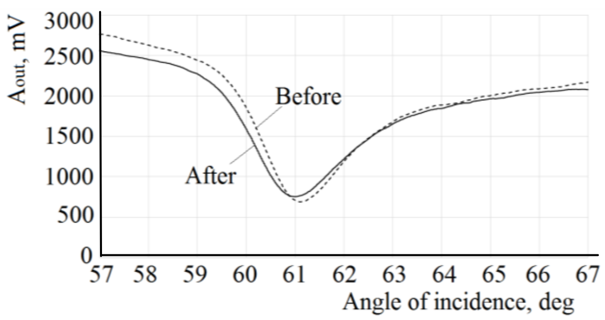

Fig. 2. Refractometric characteristics of SPR for the first channel.

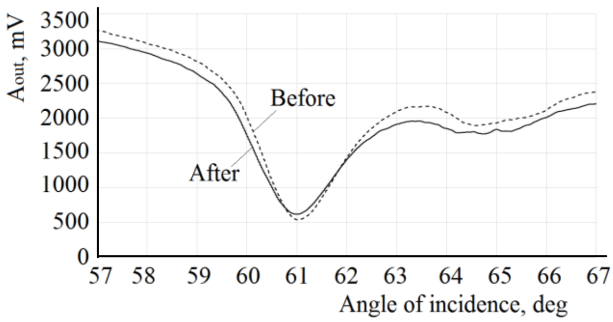

Fig. 3. Refractometric characteristics of SPR for the second channel.

Table 2. Control measurements of deionized water after cleaning from the suspension for the sensitive element with concentrations ranging from 100 to 12.5 µg/mL.

Concentration, µg/mL	Minimum angle, deg	U_{min}, mV	$U_{max} - U_{min}$, mV	W, deg
100	59.46	367	3109	1.47
50	59.48	568	2893	1.6
25	59.36	654	2801	1.76
12.5	59.89	780	2658	1.93

The measurement results showed that the dynamic range decreased by 451 mV and the angle of the minimum shifted by 0.21°. At this, the half-width of the characteristic increased by 0.46°. It may be concluded therefore that the sensitive element of the SPR device became significantly weared.

Comparison of the SPR curves for the sensitive element in the channel before and after the measurements is presented in Fig. 4.

In this case, significantly more wear of the sensitive element is observed compared to the experiment with the selected lighter fractions of “polarite” in the water suspension. This effect may be attributed to larger sizes of solid particles settled in the measurement chamber and their much higher mechanical impact on the gold surface.

Hence, the potential of using SPR devices for monitoring suspensions containing opaque particles with the sizes ranging from micrometers to nanometers in industrial conditions has been demonstrated. The research results show that SPR devices are sensitive to the particle size in the suspension as evidenced by the shift of the SPR angle with decrease of particle size and the reduction of resonance range. During the investigations, negative impact of suspensions on the sensitive gold layers of such devices has been observed. Such impact leads to the necessity of frequent replacement of the sensitive elements. This problem should be addressed in further studies by exploring and applying nanoscale protective coatings.

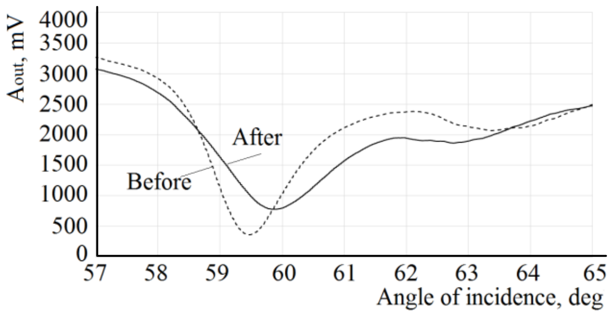

Fig. 4. Refractometric characteristics of deionized water before and after measurements of suspensions.

4. Conclusions

Use of SPR devices for monitoring suspensions containing opaque particles with the sizes ranging from micrometers to nanometers in industrial conditions is relevant. The results of the measurements of wear resistance of the gold nanocoatings on the sensitive elements of SPR devices when investigating water suspensions of “Polarite” have highlighted the importance of this issue. This problem can be addressed by applying nanoscale protective coatings.

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Volodymyr Maslov: conceptualization, methodology, supervising.

Проблеми зносостійкості сенсорів на основі явища поверхневого плазмонного резонансу

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Анотація. Поверхневий плазмонний резонанс використовується для виявлення та вимірювання різних аналітів за допомогою чутливих елементів сенсорних приладів. Під час експлуатації сенсорних приладів на основі явища поверхневого плазмонного резонансу виникають проблеми, пов'язані зі зносом їхніх чутливих елементів, що контактують з газоподібними та рідкими середовищами, параметри яких вимірюються. Зношування поверхневого наношару золота може бути спричинене різними факторами, такими як обслуговування (очистка перед вимірюваннями), хімічні реакції та абразивність середовища. Ця гостра проблема стоїть при вимірюванні суспензій, оскільки тверді частинки в ній мають абразивні властивості, що, в свою чергу, приводить до зміни поверхні, зменшення товщини та руйнування наношару золота чутливого елементу. В результаті чого виникає необхідність заміни чутливих елементів, що значно підвищує вартість проведення вимірювань. Досліджено вплив водних суспензій оптичного полірувального порошку «Полярит» на зношення та пов'язану з цим зміну параметрів чутливого елементу. Висвітлюється необхідність пошуку шляхів вирішення проблеми підвищення його зносостійкості.

Ключові слова: поверхневий плазмонний резонанс, інфрачервоний спектральний діапазон, спектрофотометр, суспензія, зносостійкість.