SURFACE PLASMON RESONANCE AS A TOOL FOR RESEARCH IN NANOTECHNOLOGY AND INDUSTRY

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Abstract: Results of researches are showed, that surface plasmon resonance can be improved for accurate measurements in precision engineering for control state of devices and machines; prospects of using the device on a SPR for the development and monitoring of polymerization processes UV-glue for optical devices, monitoring lubricating fluids in mechanical engineering. The result of the carried-out researches, it was offered to use a thermostabilization not only object of measurement, but also all measuring equipment, allows to increase accuracy of measurements of concentration of studied substances in 5 times.

KEYWORDS: SURFACE PLASMON RESONANCE, NANOTECHNOLOGY, UV-GLUE, POLYMERIZATION PROCESSES, THERMOSTABILIZATION, ACCURACY OF MEASUREMENTS

1. Introduction

The objective of the research is to define the possibility to use surface plasmon resonance (SPR) for accurate measurements in precision engineering for control state of devices and machines, for monitoring lubricating fluids in mechanical engineering and for the development and monitoring of polymerization processes UV-glue for optical devices. Optical measurements are based on the phenomenon of surface plasmon resonance (SPR) is widely used for chemical and biological analyzes based on detection of adsorption of gaseous or liquid media. Surface plasmon resonance is an optical excitation of surface plasmons or a charge density wave on the interface between the conductor (e.g., gold or silver) and a dielectric (insulator may be a gas, liquid or solid). The resonance wave vector related to the optical excitation of surface plasmon waves is dependent on the refractive index of the medium and the dielectric contacting them. SPR occurs in a thin metal film with a negative dielectric constant (high conductivity), which is arranged on a transparent dielectric substrate. The phenomenon of SPR is that at the corners corresponding to total internal reflection within the thin metal film by laser radiation conduction electrons in the metal film are excited, that is observed as a sharp decrease in the intensity of reflected light at a specific (resonance) angle of incidence. For analytical instrumentation is important that the magnitude of the resonance angle depends on the concentration of the substance on the surface of the sensor element. Most sensitive as the metal layer is used as the gold metal layer with a high conductivity and a high chemical inertness. Based on the SPR phenomenon refractometric method has been successfully used for the analysis of the optical properties of a wide range of substances, from gases (e.g., anesthetic gases) [1] to liquids (e.g., analysis of the binary system of methanol in water), [2] and the solids (e.g., inorganic solid particles [3] and the organic film Langmuir-Blodgett [4]). Diagnosing the devices working on the phenomenon of SPR is highly sensitive to low concentrations of analytes, allowing them to be used not only as a gas analyzer [5], but also as high-precision analytical instruments for laboratory analysis in the food, chemical and pharmaceutical industry, in agriculture, medicine, environment [6-11]. At the same time, up to date the temperature influence on accuracy and stability in operation of SPR sensor appliance is investigated insufficiently. As known, change in temperature causes changes in optical parameters of the medium under study, which is able to introduce some errors into results of measurements.

2. Preconditions and means for resolving the problem

Photopolymer curing adhesives are widely used for connecting optical instrument parts in the producing of precision optical devices. This connection method has several advantages compared with other methods of connection of optical components: absence of thermal effects on the items, the ability to control the polymerization process of optical adhesives, the possibility of mutual adjustment of the optical components directly to the polymerization process itself adhesive and the ability to accurately vary the optical and mechanical properties of the compound by introducing fillers into the adhesive mass, which increases the reliability and precision of the optical connection.

As is well known, introduction into the adhesive mass low dispersion adhesive filler reduces shrinkage after polymerization reduces the internal stresses in the connection of optical components and increases the reliability of the connection. Moreover, the dispersion medium affects the polymerization rate increase which is technologically and economically advantageous. By varying the number and quality of the filler can vary the refractive index of the compound to achieve the best optical alignment of the parts.

Thus, the problem arises of controlling the refractive index of photopolymer adhesives and their rate of polymerization depending on the quality and amount of filler.

Lubricants are widely used in modern technology in order to reduce friction in moving mechanisms (motors, bearings, gears, i.e.), and to reduce friction in the machining of structural and other materials on machine tools (turning, milling, grinding, etc. etc.). In terms of production and use of the basic share in lubricants are mineral lubricating oil.

Lubricants consist of a core, a base material, the base oils and supplements - additives to improve its functional properties. Oils are used in industry to carry out various functions and on this basis, divided into:

- lubricating oil to lubricate the moving parts;
- oil heat exchanger, transferring heat energy;
- processing oils;
- electrical energy oil and other purposes;
- protection (conservation) of oil;
- white oils for medical and perfume industries;
- oil for other purposes.

Usually the oil is required not one, but several functions simultaneously. Since motor oil not only lubricates, but also cools and cleans the engine parts. In each case, the oil must have a set of properties that best suit a particular purpose. With respect to the application of the technique of oil are divided into two large groups:

- oil for vehicles (engine);
- industrial oils.

Industrial oils, depending on the area of application are divided into oil general and special purpose. General purpose oil used for lubrication of the most common components and mechanisms of equipment in various industries.

Industrial oils primarily used as lubricants in friction machine tools, forging equipment, textile machinery, fans, pumps and other equipment, as well as hydraulic fluids, base oils for the production of lubricating greases, etc. Appointment of industrial oils - to provide low friction and wear of metal-cutting machines, presses, rolling mills and other industrial equipment. At the same time, industrial oils to remove heat from the friction, protect parts from corrosion, clean the friction surface from contamination, be sealing means to prevent the formation of foam on contact with air, to
prevent the formation of stable emulsions with water or be able to emulsify well filtered through elements be nontoxic and have no unpleasant smell, etc.

Industrial oils are used in many industries. The main end-uses is called metallurgy, metalworking and mechanical engineering, mining companies and the various processing plants, chemical and petrochemical and oil refining. Part industrial oil without additives goes to further modification in improved lubricants.

Given the wide scope of use of lubricants there is a problem of quality control during manufacture and in service. Furthermore, analysis of the spent lubricating oil can determine the degree of durability of the product in which it is applied. Seriously, this is a problem that must be solved using a high-precision rapid control, which can be realized by applying SPR.

The analysis of literature sources [12-16] showed that enhancement of measurement accuracy as well as reliability and efficiency of devices can be provided by temperature stabilization of the measuring cell in which the substance is measured. It means that doing so we stabilize the temperature of studied liquid or gas medium placed above the sensitive element of the analytical device operating as based on the SPR phenomenon. When carrying out these measurements, one of the problems is to provide an allowable error for the measured value. The error value of measurement results is essentially influenced by temperature oscillations both of the investigated object (liquid or gas) and all the measuring equipment. It is related with temperature changes in ambient medium, heating the measuring equipment, and in some cases with chemical processes in the studied substances, when the heat energy can be evolved or absorbed. During measurements, this error can change as a consequence of the difference in temperature at the beginning of measurements and after their completion. It follows from the mentioned above that it is necessary to determine the reasons for temperature errors in optical measurements based on SPR and investigate experimentally the influence of thermal stabilization that provides reducing these errors when performing measurements in various media.

3. Solution of the investigated problem

To solve the problem was used optical measurement equipment developed in Ukraine [17]. The equipment measures the change in the refractive index of the test substances on which to judge the processes of deterioration, polymerization processes, etc. In V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, performed for many years are experimental investigations of applied aspects for designing biosensors based on SPR. One of the designed models is the spectrometer “Plasmon-6” (Fig. 1) suitable for operation in labs of biochemical and biophysical profiles. This device allows you to measure the refractive index over a wide range from 16 RU (relative units) to 150 000RU with an accuracy 2×10⁻⁵ RIU (refractive index unit).

This paper also proposed and experimentally verified a method for determining the optical parameters of photopolymer adhesives and speed of the polymerization process, using domestic appliance "Plasmon-6". Devices based on the SPR allow quickly determining the optical properties of photopolymer curing adhesives and monitoring processes in real time.

Analysis of lubricant (oil) was also performed by an optical method, by measuring the refractive indices of the unused fresh lubricant and the lubricating oil which has worked in the motor vehicle and then comparing them.

Within the frameworks of these investigations, developed and manufactured was the thermostat that enables to keep the set temperature with rather high stability. Offered after performed investigations was thermostating not only of the studied object but also of all the measuring equipment including boxes with the studied substances. This approach enabled to minimize the temperature error in measurement results and, in addition, temperature loading the measuring equipment, which prolongs its functioning term [18].

4. Results and discussion

The object of measurement UV-glues were three samples, each of which is represented by a three-layer structure (glass-glue-glass) and three individually appropriate adhesives. All elements of glass samples were 0.2 mm thick plates measuring 20 × 20 mm glass F1 (refractive index relative to the vacuum n = 1,61). Samples differed adhesive composition. For all samples used adhesives are polymerized by ultraviolet radiation in the wavelength range 340-380 nm (near-ultraviolet). Ultraviolet acts as a catalyst - starts the polymerization of the adhesive. In the sample was pre-polymerized adhesive. Sample number 1 was UV glue without impurities. Sample number 2 had UV glue as number 1 in the sample only silicone acrylate AD1. Sample number 3 was UV glue as in sample number 1 but with a silicone acrylate AD2. Furthermore adhesive number 1 had a greater content of diluent. Adhesives are numbered as well as samples, respectively, 1, 2 and 3.

Each had a different speed glue polymerization rate as pressing a point on the schedule was different and as a result changes the reflection factor too. This is evident by the slope of the kinetic curves. The greatest rate of polymerization of the glue was number 3 (2100 Unit / min.). The smallest adhesive number 1 (300 Unit / min.). Adhesive number 2 (1200 Unit / min.). Thus the rate of polymerization of the adhesive number 3 to 7 times greater than the adhesive number 1 and almost 2 times higher than the number of glue 2. The following parameters were measured for refractive index photopolymer glue before and after the polymerization: glue 1 (before 1,4615 RIU after 1,4628 RIU), glue 2 (before 1,4602 RIU after 1,4816 RIU), glue 3 (before 1,4507 RIU after 1,4655 RIU). It can be concluded that the rate of polymerization depends on the surface or the presence of nuclear polymerization. In adhesives number 2 and number 3 are the following core polymerization silicone acrylates AD1 and AD2 for adhesive number 1 is the interface between gold and glue. The surface area of nuclei polymerization affects the rate of polymerization, confirming graphs in Figure 5. Maybe silicone acrylate AD2 is more dispersed, so the polymerization rate is higher.

![Fig. 1. Appearance of the SPR spectrometer Plasmon-6](image)

![Fig. 2. Measured curve polymerization process](image)
Through the phenomenon of SPR were determined refractive index for motor oil to use (1,4659 RIU) and after driving 3 000 kilometers (1,4621 RIU).

To determine the effect of temperature on the accuracy of measurement spectrometer Plasmon-6 was placed into the thermostat operation chamber where a constant temperature was kept, values of which could be set within the range +10 up to +40°C with the step 0.1°C. Thermostat also been developed V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The volume of termostat chamber was close to 13 liters, which allowed us to place there not only spectrometer but also pump and containers with studied substances. To connect the spectrometer with power and control cables, we provided the thermostat case with special packed openings. Experiments aimed at temperature influence on results of measurements were performed in the Multiple mode of Plasmon-6.

As a result of measurements in the Multiple mode, we took the intensity of light reflected from the sensitive element for the angle of incidence corresponding to the minimum of SPR-curves. It means that in this mode we followed the shift of the angle corresponding to the minimum of SPR-curves $\Delta \theta$. The chamber was filled with air, the temperature of which was stabilized at the level +19°C. It was 1°C above the room temperature. As a sensitive element, we used glass plates with a deposited gold layer of 50-nm thickness. The sensorogram obtained in these experiments is shown in Fig. 3.

![Sensorogram](image)

**Fig. 3.** Temperature drift of the SPR-curve minimum when the cell is filled with air.

Depicted in Fig. 3 are the results of measurements for gas-like medium. In these figures, the abscissa corresponds to the time of observation in minutes, while the ordinate corresponds to the position of the SPR-curve minimum in degrees. At the very beginning, the spectrometer was placed outside the thermostat, air passed through the cell of the volume 30 μl, and we measured the shift of the SPR-curve minimum for 95 min at the room temperature (+18°C). After that, the spectrometer was placed into the thermostat, and measurements were repeated for 85 min at the stabilized temperature +19°C. The measured values of the reflected light intensity were recorded using the special program.

Thus, it is ascertained in this work that thermal stabilization of the measuring equipment based on the SPR phenomenon decreases the temperature error caused by the temperature shift of the SPR-curve minimum by 5 times, which is very important when studying the kinetics of chemical and biological processes.

**5. Conclusion**

Research conducted by the photopolymer adhesives with various fillers has shown the effectiveness and feasibility of utilizing the phenomenon of SPR to monitor the optical parameters of photopolymer polymerization adhesives. Has also demonstrated the ability to control deterioration of lubricating oils with a view to the timely replacement and monitoring of wear and aging mechanisms that use these lubricants. That will allow for the timely replacement of defective parts and components, has decreased in the number of failures will increase the reliability of the devices. The result of the carried-out researches, it was offered to use a thermostabilization not only object of measurement, but also all measuring equipment, allows to increase accuracy of measurements of concentration of studied substances in 5 times.

This will improve precision of measurement and increase the use of surface plasmon resonance in the industry for diagnosis and monitoring structures and manufacturing processes.

**References**


[12] Temperature-dependent sensitivity of surface plasmon


[17] www.plasmon.org.ua