Improvement of Sensor Glass Substrates for Surface Plasmon Resonance Devices

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***Abstract*— Possibility of increasing the sensitivity of sensors based on surface plasmon resonance phenomenon by electron beam processing of glass sensor substrates is shown. This is a consequence of the reduction of losses in the propagation of surface plasmons along the metal-air boundary. In this case the thickness of heterointerface gold–air was lowered from 3.26 down to 1.37 nm. Glass substrates treatment increased sensitivity by 1.7 times from 1.425 deg^{-1} up to 2.396 deg^{-1}. It was ascertained using X-ray reflectometry that the film density increased from 17.2 up to 19.3 g/cm^3 and reached the value typical for the bulk gold. As a consequence of resonance characteristic shift to the side of lower angles, the range of measurements is additionally widened by 0.37 deg, which extends the range of measurement of refractive indices. The results of the study can be applied to develop new devices based on the phenomenon of surface plasmon resonance.**

Keywords—surface plasmon resonance, sensitivity, electron-beam treatment, X-ray reflectometry.

I. Introduction

It is the most widely used in the world laboratories for monitoring a wide range of physicochemical processes that cause changes in optical parameters and the geometry of the studied objects refractometric method based on the phenomenon of surface plasmon resonance (SPR). The devices based on SPR are mostly equipped with on chemical and biological nano-dimensional sensors that consist of a sensitive element and physical transducer. SPR devices allow analysis real-time without the use of markers and fluorescent labels, require small sample volume of the studied substance (less than 10 µl) and have high sensitivity to changes in nanoscale layer of sensors [1].

The sensitive element in SPR devices with the prism method to excite surface plasmons contains a thin layer of metal with high electrical conductivity. The layer of metal, mainly it is gold, is applied onto a glass substrate. The roughness of metal influences on propagation of surface plasmons and causes the scattering of energy and premature decay of plasmons [2]. The principal factors influencing the structure and properties of metallic layers made of thermal evaporation in vacuum are the speed of deposition and temperature of substrate. At the same time, low speeds of deposition results in fine dispersed, rough and friable structure of deposited layers, while high deposition speeds lead to the coarse-grained structure of surface. An alternative way to act on the structure and properties of metal layers is the temperature annealing at the temperature 120 °C to provide a minimal roughness [3]. Lowering the mean-square surface roughness from 2 down to 0.8 nm causes increase in the sensor sensitivity in the analysis, when depositing the metal layer under the angle 45° to the glass substrate [4].

The main factor influencing on the properties as well as on nano-roughness of metal layers is effect of the substrate nano-relief. To reduce this effect on the surface nano-roughness of the deposited metal layers, the surface substrate is usually prepared using the optical traditional technology [5]. The actual problem is preparation of qualitatively polished, defectless and homogeneous in its chemical composition substrates for SPR devices. These defects cause losses of electromagnetic wave energy and birefringence.

It is known that the most common methods of surface treatment of glass parts (mechanical, chemical, chemical-mechanical and electrochemical polishing), which are used in the optical industry, do not allow to avoid defects of the treated surface and changes in its chemical composition. Traditional technologies do not allow preparation of optical surfaces meeting the requirements of the International standard ISO 10110-1/14, namely: homogeneous surface layers characterized by guaranteed typical micro-inhomogeneities less than 5 nm [6].

A promising method of processing the working surfaces of precision glass parts, which significantly reduces the roughness of the glass surface without the formation of a broken layer and significant changes in its chemical composition, is the method of electron-beam treatment. This method provides ecological cleanness, possibility to control

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the respective technological process and simplicity in realization. Investigation of goods after electron-beam treatment shows that the mean-square surface roughness is close to R_q = 3...5 nm [7]. The mean-square surface roughness for the glasses К8, К108 is reduced from 4…9 down to 1.5…2.2 nm after electron-beam treatment [8]. After processing glass, there takes place the increase in the value of spectral transmission coefficient in the infra-red range as a result of decreasing the amount and sizes of unwanted defects on the surface. The method of electron-beam treatment the surface of glass substrates used in SPR devices is very promising, if taking into account the reduced nano-roughness of the glass surface.

The nano-roughness of substrates affects in process formation of the metal film in SPR devices. Therefore, it is necessary to investigate the effect of electron-beam treatment on optical characteristics of the metal film, its density and surface nano-roughness. In this work performed investigations influence of electron-beam treatment the surface of glass substrates for SPR devices on their characteristics by X-ray reflectometry (XRR), X-ray diffraction (XRD) and the method based on SPR phenomenon.

II. Materials and Methods

Thin glass substrates of sensitive elements with electron-beam treatment (irradiate with the power 27.84 W/mm^2 (sample 1) and 36.62 W/mm^2 (sample 2)) and without electron-beam treatment (sample 3, 4) were selected for the study. The substrates were made of optical glass (brand of glass flint F1 with the refraction index n_D = 1.6128±0.0001) with the overall sizes 1×20×20 mm with a possible deviation ±0.1 mm. Previously the surfaces of the plates were polished mechanically. Mean-square roughness of surface after polished mechanically was R_q = 3,18±2 nm.

Electron-beam treatment of glass samples was performed using the equipment based on the multi-purpose installation УВН-74П3. Mounted in the vacuum chamber of it were: a silica infrared oven providing preliminary heating and final cooling, Pierce electron gun with a special optics to form a strip electron flow (accelerating voltage 1…12 kV, cathode heater current 10…30 A). With the aim to avoid thermotensions in surface layers caused by temperature drops the samples were heated up to the temperatures 700…800 K before and after treatment.

After mechanical and electron-beam treatments the glass substrates were cleaned in the ultrasound bath containing the mixture of solutions of hydrogen peroxide and ammonium hydrate in the relationship 1:1. The samples were then washed with distilled water and dried. After cleaning the surface, one of the substrate sides was covered with the gold layer of the thickness 48±4 nm by using thermal evaporation in vacuum. Deposition was providing with the installation ВУП-5М. During deposition, the thickness of the gold layer was controlled using the quartz microbalance device КИТ-1.

To study condition of surface the samples, we used the method of X-ray reflectometry with the diffractometer Philips X'Pert PRO–MRD (CuK$_\alpha$ radiation, λ = 0.15406 nm). The tube anode voltage was 45 kV, current – 40 mA. The samples were scanned in the symmetric geometry, when the angle of incidence is always equal to the angle of reflection. The step of scanning was 0.0008°, data acquisition time in one point – 1.5 s. The density and root mean square nano roughness of the glass-air transition layer were determined from the measured reflectance characteristics of the fit using the Reflectivity software. The presence of interference oscillations on the reflectograms and different values of the critical angles made it possible to estimate the thickness of the films and their density.

The refractometric characteristics of the studied samples were determined using the SPR refractometer "Plasmon-6" designed by V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine [9]. This device (Fig.1) is based on the prism method for excitation of plasmons in the Kretschmann optical geometry [10].

Fig. 1. Appearance of the refractometer "Plasmon-6".

To excite surface plasmons, there used is a semiconductor laser with the wavelength 650 nm. The refractometer was used in the regime of angular periodical scanning with the simultaneous registration of the reflection curve. By their turn, the samples were mounted onto the operation face of glass (K8, n_D = 1.514) semipentaprism inside "Plasmon-6" with using the immerse liquid (polyphenyl ether Н-ПФЭ possessing the refraction index n_D = 1.63025±0.0007), and their refractometric characteristics were measured. As a reference substance, we used ambient air. SPR investigations were carried out under normal conditions (P = 10^5 Pa, T = 293 K).

III. Results and Discussion

Estimation of the decay velocity for the reflected X-rays enabled to determine the mean-square roughness. In Fig. 2 presents four reflectograms of two glass samples before electron beam treatment, which were taken on both sides of the glass substrate.

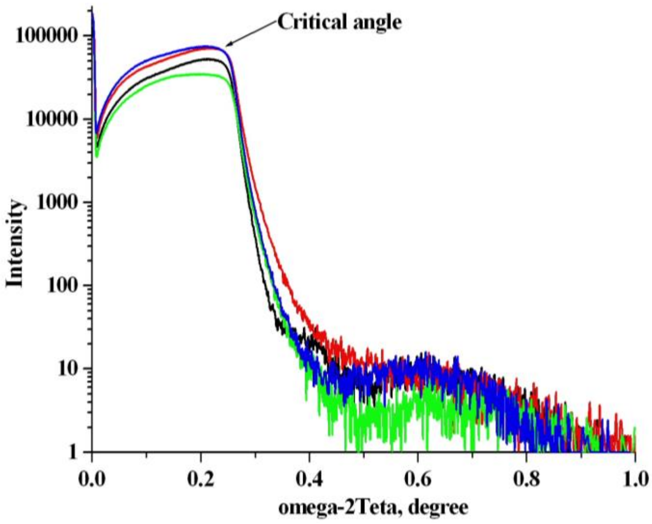

Fig. 2. X-ray reflectivity profile of glass substrates surfaces before electron-beam treatment.

Mean-square roughness of glass substrate surface before electron-beam treatment was from 3,5 nm to 4,8 nm. The fitting of the measured reflection characteristics showed that the density of the surface layer of the glass substrate (up to 200 nm) varies in the range from 3.0 to 3.1 g/cm^3 and slightly less than the passport value of the monolithic material of glass brand F1 (3.56 g/cm^3). The presence of additional scattering in the region of 0.5… 0.8 degrees indicated the existence of a thin surface layer with practically zero nano roughness (less than 0.1 nm). According to the measurement results, it can be assumed that the samples of glass substrates after polishing were additionally chemically etched in the acid by the manufacturer to remove the disturbed defective surface layer.

After electron-beam treatment of the glass substrate surface, the mean-square roughness of the deposited on it metal film is reduced by 2 times from 2,6 down to 1,3 nm (Table 1). Wherein, the mean-square roughness at the SiO-Au heterointerface increased by 2,4 times from 0,5 up to 1,2 nm for the irradiation power 27.84 W/mm^2.

Availability of interferential oscillations on the characteristics of X-ray reflections (Fig. 3) from the samples studied using the XRR method enabled to estimate the thickness of metal films.

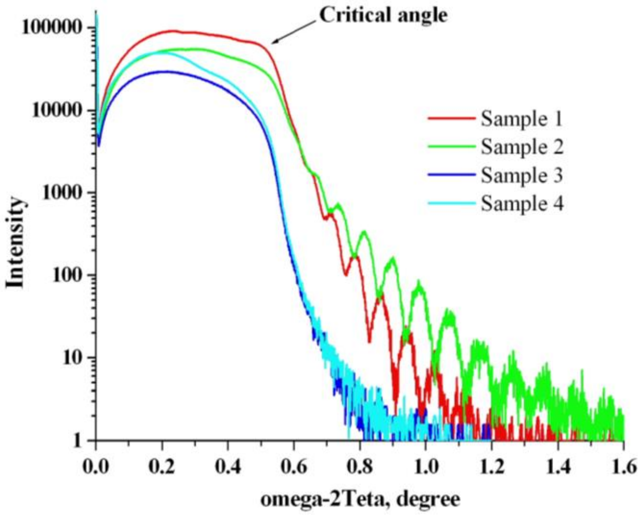

Fig. 3. X-ray reflectivity profile [12].

Different values of critical angles are indicative of their different density (Table 1). The density of gold films is increased from 17.2 up to 19.3 g/cm^3 after electron-beam treatment.

TABLE I. XRR MEASUREMENT RESULTS

Structure	Irradiate power, W/mm^2	XRR method			
		Rq Au-Air, nm	*Rq SiO-Au, nm*	*Density of metal film, g/cm^3*	*Thickness of metal film, nm*
Sample 1	27,84	2,0	1,2	19,3	43,00
Sample 2	36,62	1,3	0,8	19,2	43,46
Sample 3	0	2,6	0,5	17,4	-
Sample 4	0	2,6	0,5	17,2	-

A finer-dispersed structure and higher compactness between the grains were provided, due to the advantage of the rate of grain formation over their growth rate. The density value reached that of bulk gold – 19,32 g/cm^3 [11]. On the reflectograms of samples 3 and sample 4 without electron beam treatment there are no oscillations due to the significant heterogeneity of the properties both in thickness and in the plane of the films. In this regard, the thickness of these layers was not determined by this method (Table 1).

The diffraction patterns of the samples after deposition of the gold film were additionally measured (Fig. 4). This allowed the half-width of the measured peak of the reflex (111) of gold to be estimated by the Scherer formula (1) for the size of the regions of coherent scattering [13].

$$D = 0{,}94 \cdot \lambda \cdot \beta^{-1} \cdot \cos(\theta)^{-1} \qquad (1)$$

Where, D – dimension of coherent scattering region, nm;
λ – X-ray irradiation wavelength, nm;
β – half-width of peak of reflex, rad;
θ – Bragg angle, deg.

With some approximation, the size of the coherent scattering regions can be considered the size of nano-clusters on the surface, which determines the fineness of the film structure. The average size of nano-clusters on the surface of the metal layer after electron beam treatment decreased from 17.7 nm to 15.8 nm, which reduced the surface roughness.

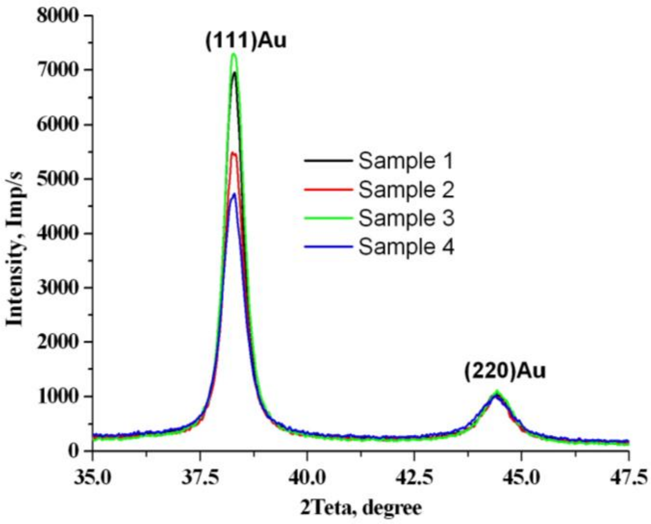

Fig. 4. Diffractograms of three samples of glass substrates of brand F1 with a precipitated layer of gold after electron-beam surface treatment and without surface treatment of the substrates.

The reflectance characteristics (SPR curves) of the respective test four samples measured by the refractometer "Plasmon-6" are shown in Fig. 4. The figure shows that for samples with substrates that have undergone electron-beam treatment, the minima of reflectance characteristics are shifted toward smaller angles. This is a consequence of the reduction of losses in the propagation of surface plasmons along the metal-air boundary.

The measured characteristics of SPR show that the intensity of reflected light increased in the minimum of refractometric characteristics as a result of electron-beam treatment. This is due to the fact that the absorption of glass after processing has increased. The shift of the SPR minimum towards smaller angles is a consequence of the decrease of the refraction index the heterointerface "glass–

gold" and "gold–air". The shift towards smaller angles and the increase in the intensity of reflected light in the minima of reflectance characteristics are also a consequence of changing the composition of the surface area of the substrate due to the thermal evaporation of the volatile components.

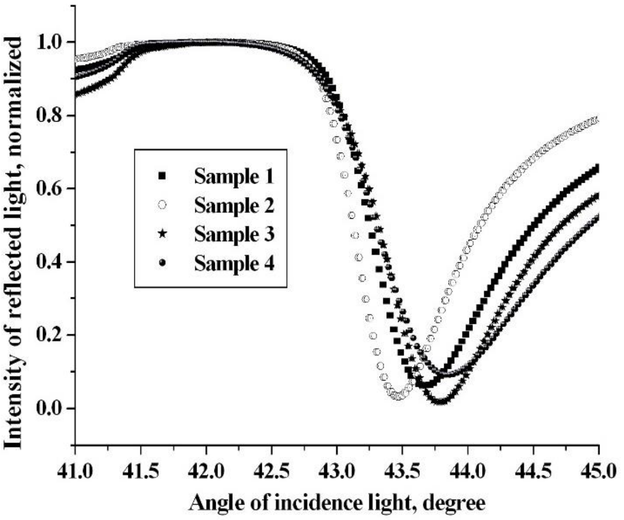

Fig. 5. Measured refractometric characteristics of the samples: with different specific powers of electron-beam treatment of glass substrates 27.84 W/mm^2 – sample 1, 36.62 W/mm^2 – sample 2, and without this treatment – samples 3 and 4 [12].

The measured characteristics SPR were used to determine the following parameters: critical angle θ_C, angle corresponding to the reflection minimum θ_{spr}, half-width of the refractometric characteristic $W_{0.2}$ and the sensitivity S at the point of refractometric characteristic where the slope reaches the highest value on the left wing S_{slope}.

TABLE II. RESULTS OF MEASUREMENTS AND CALCULATIONS.

Structure	θ_{spr}, deg	θ_c, deg	S, deg^{-1}	$W_{0,2}$, deg	S_{slope}, RIU^{-1}
Sample 2	43,462	41,268	2,396	0,453	2,511
Sample 1	43,676	41,346	1,948	0,648	2,034
Sample 3	43,804	41,360	1,578	0,622	1,703
Sample 4	43,829	41,346	1,425	0,867	1,516

The half-width value defines the error of approximation that is used for determination of the SPR minimum in the course of measuring the kinetics with the SPR device "Plasmon-6". As a result of electron beam treatment of the glass surface, the half-width $W_{0.2}$ is practically two-fold decreased after electron-beam treatment from 0.867 down to 0.453 deg. (table 2). The sensitivity S_{slope} grows due to the 1.7 times increases in the slopes of resonance curve from 1.425 up to 2.396 deg^{-1}. As a consequence of resonance characteristic shift to the side of lower angles, the range of measurements is additionally widened by 0.37 deg, which extends the range of measurement of refractive indices.

Thus, the use of electron-beam treatment of the glass substrate surface of the sensing element allowed by reducing the nano-roughness of the surface of the metal film on this substrate to increase the sensitivity of the SPR sensor and extend the range of measurement of the refractive index.

IV. CONCLUSION

Experimentally proved is the efficiency of electron-beam treatment the surfaces of glass substrates for sensitive elements of SPR devices, which resulted in 1.7 times increased from 1.425 deg^{-1} up to 2.396 deg^{-1} and the extension of the measurement range by 0.37 deg, which extends the range of measurement of refractive indices. The reason for this extinction of surface plasmons is related to higher surface uniformity of the gold metal film, its higher density as well as lower nano-roughness of the glass surface and the thickness of heterointerface "gold–air". The film density increased from 17.2 up to 19.3 g/cm^3 and reached the value typical for the bulk gold. Thus, the performed analysis of optical characteristics, density and surface micro-roughness showed that electron-beam treatment the glass substrates of sensitive elements for SPR devices is able to efficiently enhance their sensitivity and to widen the range of measured resonance SPR angles.

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