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Ellipsometry of hybrid noble metal-dielectric nanostructures

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Abstract. Angular ellipsometric measurements of thin Ag, Cu films covered by HfO_2 protective layer were performed. The ellipsometric parameters ψ and Δ were measured in θ = 43°…85° light incidence angle range, where ψ is the azimuth of restored linear polarization, Δ is the phase shift between *p*- and *s*-components of reflected light. For comparison, thin Au film (traditional sensor for surface plasmon resonance (SPR)) was examined as well. The curve Δ(θ) for all the samples investigated falls down with increasing angle of light incidence, while ψ(θ) changes relatively weakly. It has been ascertained that the increase in the thickness of HfO_2 layer affects the tan(ψ) value, while tan(ψ) deviation is mainly determined by the type of metallic film. With the growth of HfO_2 layer, the minimum position of tan(ψ) shifts to smaller angles. From these angular dependences, one could choose the appropriate SPR-compatible structure due to maximal deviation of tan(ψ). To optimize layer thickness for a high SPR-response, spectral measurements and additional calculations are required.

Keywords: ellipsometry, thin film, noble metals, surface plasmon resonance, hafnium oxide.

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1. Introduction

Thin metal films attract considerable interest in both science and technology. They often have optical properties different from the same bulk material. Partial transparency and conductivity allow using them as electrodes for solar cells [1] and other optoelectronic devices [2, 3]. Thin metal films are widely used in optical instrumentation (mirrors, beam splitters, different specific coatings and so on).

But, perhaps, the most extensive field of their modern application is electrochemistry and bioanalysis [4]. Gas sensors acting due to conductivity changes upon interaction of molecules with the metal film surface are developed [5]. In surface acoustic waves or electrowetting process, thin metal films are used for precise manipulation of liquid microdroplets [6]. Electrosensing is notable for its sensitivity, relative simplicity and low power consumption. It is used for detection of simple molecules. Conductivity-based thin-film sensors react to molecules adsorbed on the surface and are used for gas detection, for direct detection of DNA and in food quality controlling [6].

Of particular importance are sensors based on surface plasmon resonance (SPR), which are the subject of this work. SPR sensing has established itself as an important tool in characterization of biomolecular interactions [7, 8]. Such instruments allow real-time detection of various chemical and biological substances and their combinations. However, there still remains a considerable space for the improvement of these devices, particularly, increasing their resistance to external and explored environments as well as lifetime. The aim of this work is to examine hybrid multilayer noble metal-dielectric structures by using the optical ellipsometry method to propose the physical and technical approach for developing more efficient SPR-sensors.

2. About SPR

The surface plasmon-polariton (SPP) is a quasi-particle corresponding to the quantization of the collective plasma oscillations of the electron gas in solids under action of *p*-polarized light. The area of their localization is near the interface of media, where surface charges are concentrated. Surface plasmon-polariton waves are the waves of changes in the electric charge density, which can arise and propagate in the electron plasma of metal along the interface of metal film surface. Surface plasmon (SP) is the extreme case of SPP, which is a two-dimensional wave localized at the surface.

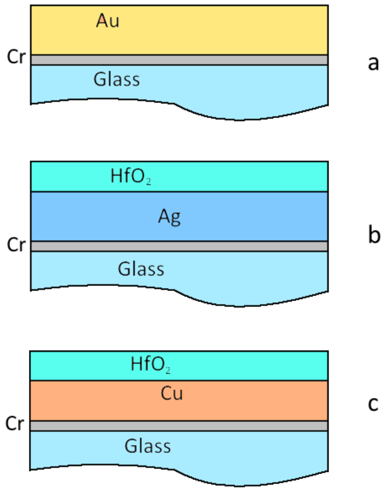

Fig. 1. Hybrid multilayer structure of the investigated samples based on Au (a), Ag (b) and Cu (c) thin films.

Surface plasmonic resonance (SPR) usually occurs with total internal reflection when an electromagnetic wave propagates along the reflecting surface at a rate that depends on the angle of incidence. The resonant phenomenon consists in the transfer of energy from the photon flux to the electron plasma of the metal when light falls at a certain angle onto surface. In this case, a decrease in the intensity of the reflected light and a change in the azimuth of the restored linear polarization are observed [9].

Surface plasmons are extremely sensitive to their local dielectric environment. Adding nanoparticles of a certain size and shape, one can configure such a sensor to detect a given type of the adsorbed objects. That's why SPR-sensors are so perspective in biotechnology.

Gold has long been known as the highest quality plasmonic material for the visible and near-infrared applications. It does not oxidize, has a large value of the refractive index and a small imaginary part of the dielectric function, high adhesion and affinity for organic molecules. Thin Ag and Cu films has also similar SPR properties, sometimes even better [10], and lower cost. But they oxidize relatively quickly, limiting long-term device applications [11]. A potential solution to this is to use HfO_2 very thin layer as a protection of the copper/silver plasmonic film. It was chosen HfO_2 as a dielectric layer because of its very stable chemical behaviour and high refractive index about 1.9…2.0 in the visible spectrum [12]. Combination of plasmonic film with such dielectric layer has yielded significant advances in SPR sensing due to the interference of reflected waves on interfaces metal/dielectric and promotes the path extension of the plasmon wave propagation along thin surface layer.

3. Samples and experiment

All metal films studied in this work were deposited using electron-beam evaporation onto glass substrates of the thickness 1 mm. The films were grown in a commonly available deposition apparatus with base pressures within 10^{-5} to 10^{-6} Torr range. The growth of metal films was monitored using a calibrated quartz crystal microbalance (QCM). Before deposition of Au (Ag, Cu) films, thin adhesive layers with the thickness about of 1.5 nm (Cr) were also deposited onto the clean glass substrates by using electron beam evaporation. To achieve the best adhesion and smooth surface with good optical performance sputtering rates were selected as follows: 0.14 nm/s for Au, 5…7 nm/s for Ag and 1 nm/s for Cu. On the top of Ag (Cu) films, HfO_2 layer was deposited with the small rate 0.05…0.1 nm/s. The structure of the samples is shown in Fig. 1 schematically.

Table 1. The list of samples investigated.

#	Substrate	Layer 1	Layer 2	Layer 3
1	glass	Cr (1.5 nm)	Au (47 nm)	–
2	glass	Cr (1.5 nm)	Ag (45 nm)	HfO_2 (7 nm)
3	glass	Cr (1.5 nm)	Ag (45 nm)	HfO_2 (8 nm)
4	glass	Cr (1.5 nm)	Cu (43 nm)	HfO_2 (7 nm)
5	glass	Cr (3 nm)	Cu (35 nm)	HfO_2 (10 nm)

In this paper, we will consider five heterostructures with different thicknesses of layers. The detailed list of samples investigated is given in Table 1.

The research was carried out on a multifunctional automated goniopolarimetric installation, built on the basis of the goniometer Г5 [13]. The experiment is controlled by a personal computer using the NI6221 Data Acquisition Card manufactured by National Instruments®, our own electronic automation system and the LabVIEW graphical programming environment.

The scheme of the experimental instrument is shown in Fig. 2. The radiation source is LED with λ = 625 nm, $\Delta\lambda$ = 10 nm. The collimator lens forms a parallel beam of light, which then passes through the polarizer P and falls on the sample to be studied. After the reflection from the sample, light passes through the analyzer A and it focused by the chamber lens onto the surface of the sensor (photodiode).

The ellipsometric studies are carried out as follows. The sample is installed on the table of the goniometer for performing its alignment and positioning. The polarizer P

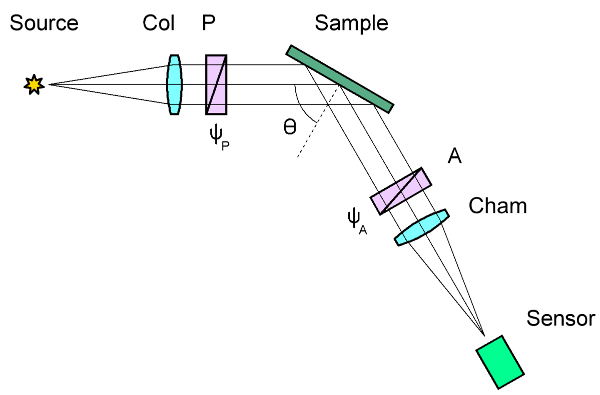

Fig. 2. Scheme of the experimental setup: collimator lens – Col, polarizer – P, analyzer – A, chamber lens – Cham.

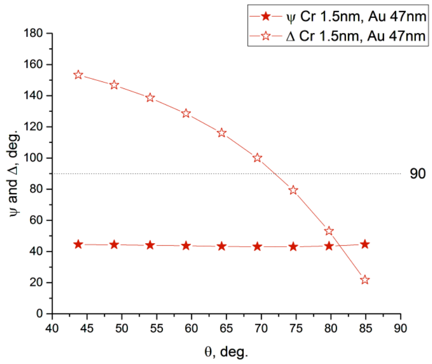

Fig. 3. Angular dependences of parameters ψ and Δ for the Au (reference) sample.

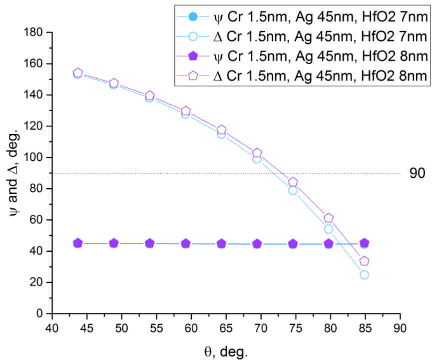

Fig. 4. Angular dependences of parameters ψ and Δ for Ag-based samples.

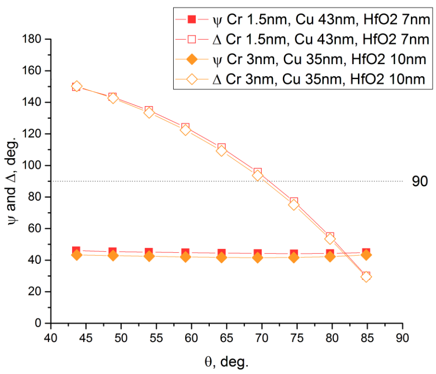

Fig. 5. Angular dependences of parameters ψ and Δ for Cu-based samples.

is set to 45° relatively to the *p*-plane. With an automatic drive, the sample turns to the required incidence angle θ, and after that the analyzer A begins to rotate. During rotation of the analyzer, the signal from the photodetector is permanently recorded. Then, the sample is positioned at a subsequent angle of incidence, *etc.* Measurements are continued until all the required range of light incidence angles has been passed. Using the obtained data, the special computer program reproduces the shape of the polarization ellipse of the reflected light and displays the angular dependence of the ellipsometric parameters ψ and Δ in the plot.

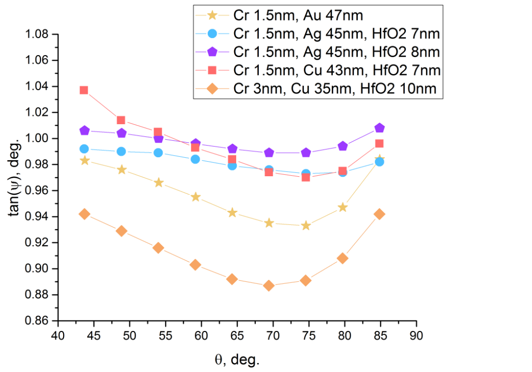

Fig. 6. Angular dependences of tan(ψ) for all the samples investigated.

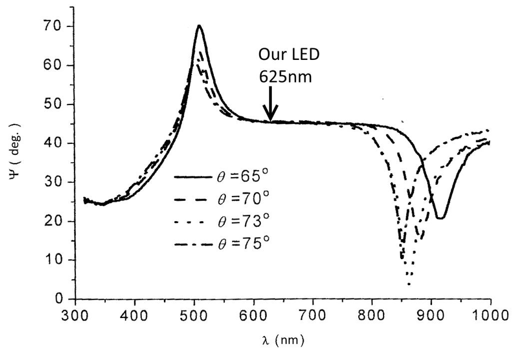

Fig. 7. Spectral dependences of ellipsometric parameter ψ of the heterostructure Cr (3 nm), Au (30 nm), HfO_2 (45 nm) for different angles of light incidence.

4. Results and discussion

For the above-mentioned samples (Fig. 1), the angular measurements of the ellipsometric parameters were performed within 43°…85° range. ψ is the azimuth of restored linear polarization, Δ is the phase shift between *p*- and *s*-components of incident light. The samples were probed from the upper side (not through glass). The results of the measurements are shown in Figs. 3 to 6.

As one can see from these plots (Figs. 3 to 5), the optical properties of these metal heterostructures are similar. There is slightly different principle of light incidence angle (the angles, where phase shift Δ between *p*- and *s*-components is equal to 90°) for these samples. The curve Δ(θ) falls down with increasing angle of light incidence while ψ(θ) changes relatively weakly.

Usually surface plasmon resonance manifests itself in the form of a sharp decrease in the intensity of the reflected *p*-polarized electromagnetic wave in the vicinity of the specific angle of incidence. The reflection efficiency for SPR depends on the thickness of dielectric (HfO_2) and noble-metal films due to the former changes the electromagnetic field distribution of the surface plasma oscillations. The reflectivity spectra *R*(λ) of the sample reach the minimum at plasmonic resonances. To increase SPR efficiency, one should minimize the *p*-polarized reflection spectra and its full width at half maximum (FWHM) [14].

Table 2. Characteristics of the samples and measurement data.

Sample	Principal angle*, deg.	tan(ψ), minimal value	Angular position**, deg.	tan(ψ) deviation
Cr 1.5 nm, Au 47 nm	71.9	0.933	73.2	0.051
Cr 1.5 nm, Ag 45 nm, HfO_2 7 nm	71.5	0.973	76.3	0.019
Cr 1.5 nm, Ag 45 nm, HfO_2 8nm	72.9	0.989	72.0	0.019
Cr 1.5 nm, Cu 43 nm, HfO_2 7 nm	70.8	0.970	74.8	0.067
Cr 3 nm, Cu 35 nm, HfO_2 10 nm	70.2	0.887	69.8	0.055

* Principal angle of light incidence
** tan(ψ) minimal angular position, deg.

The angular dependence of the reflection coefficient $R(\theta)$ as a shape of the resonance curve, in particular, the angular position of its minimum, depends on the wavelength λ, the optical constants n and κ of the sample and the ambient, as well as a film thickness d and optical characteristics of the film deposited on the top of this heterostructure. So, if we plot tan(ψ), which is expressed as a reflected *p*- and *s*-components ratio, these curves should demonstrate a depression at the resonant angle of light incidence.

On the plots in Fig. 6, there are actually observed minima, but they are comparatively small in their amplitude (at the resonance, reflection must typically decrease close to 0). It is seen from Fig. 7, where appropriate minima are observed for spectral dependences ψ(λ) of similar specimen presented at [15], then it becomes obvious that the reason for the occurrence of such weak minima in Fig. 6 consists in the difference of our source wavelength ($\lambda = 625$ nm) from the resonant ones for the samples investigated.

To create some effective SPR-sensor, it is necessary to optimize the thickness of appropriate layers. It is optimal near $d = 47.5$ nm for the film based on gold [16]. Hence, one should also explore the spectral dependences of ψ for this selection. From angular dependences, one could only choose the appropriate SPR-compatible structure due to a minimal value of tan(ψ).

One can compare behavior of ellipsometric parameters for Au-, Ag- and Cu-based samples with different thicknesses of films of these metals (see Table 2).

In Table 2, the principal angles of light incidence in appropriate heterostructure investigated, the angular positions and the values of tan(ψ) minima, as well as tan(ψ) amplitude deviations are presented. We can notice at comparison Au-based and Cr (3 nm), Cu (35 nm), HfO_2 (10 nm) samples that the increase of the thickness of the HfO_2 layer only weakly independently of selected metal for film affects the ψ amplitude. Namely, tan(ψ) deviation is mainly defined by the type of metallic layer of that film. With the growth of HfO_2 layer, the minimum position of tan(ψ) for these structures shifts to the smaller angles θ.

5. Conclusions

The HfO_2-protected Ag and Cu layers provide a possible alternative to the conventional noble metals (usually, pure Au) in plasmonics applications. In this case, they are relatively stable and high-quality plasmonic materials, which is suitable for effective sensor fabrication that requires low plasmonic losses.

A few nm thick HfO_2 layer on the top of Cu or Ag film improves its SPR stability and lifetime, though it changes SPR-response. From angular ellipsometrical measurements, one can suppose that the samples with greater tan(ψ) deviation are the best candidates for SPR-sensors among the heterostructures examined.

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