*Наносистеми, наноматеріали, нанотехнології*
*Nanosistemi, Nanomateriali, Nanotehnologii*
2019, т. 17, № 3, сс. 473–482



PACS numbers: 07.07.Df, 68.65.Ac, 73.20.Mf, 73.21.Ac, 77.55.-g, 78.67.Pt, 78.67.Wj

# Observation of Surface-Plasmon Resonance in Metal–Dielectric Thin Films Covered by Graphene

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The plasmon properties of hybrid metal–dielectric nanostructures on the base of thin Cu films protected from oxidation under atmospheric conditions by dielectric $HfO_2$ layer and/or graphene layer are considered. The ellipsometry experiment and polarimetry with the excitation of surface plasmons into thin films within the Kretschmann's geometry at a probe light wavelength of $\lambda = 625$ nm are fulfilled. The angular dependences of the ellipsometric parameters $\psi(\theta)$ and $\Delta(\theta)$ as well as an internal reflection coefficient $R_{IN}(\theta_{IN})$ are measured. These experimental data are compared to corresponding dependences calculated by using the matrix method in accordance to the proposed theoretical model of the multilayer structure. The numerical values of the heterostructure-layers' optical constants $n$ and $k$, by means of the calculations, are a subject to variation in order to achieve the minimum error deviation between the experimental and calculated data. This gives a possibility for additional control of the optical parameters of the structure layers. The angular dependences of the internal reflection coefficient $R_{IN}(\theta_{IN})$ of the samples investigated possess a typical form of failure (deep minimum) at a certain angle, which is concerned with surface plasmon-resonance excitation. According to the feature of behaviour of these curves, conclusions due to suitability of using these heterostructures as plasmon sensors are made. To estimate the level of such sensors' efficiency, theoretical calculations of the internal reflection coefficient at variation of the refractive index values of the medium, which is in contact with the upper structure surface, are performed. The appropriate graphs possess the inclination, which determines sensitivity of the sensor. Typical sensitivity value for these heterostructures is equal to 100–200 deg/RIU (Refractive Index Unit) in the vicinity of $n = 1.3$ RIU.

Розглянуто плазмонні властивості гібридних металодіелектричних нанорозмірних структур на основі тонких плівок Cu, захищених від окиснення в умовах повітряної атмосфери діелектричним шаром $HfO_2$ та/або графеновим шаром. Експеримент проведено методою еліпсометрії та поляриметрії із збудженням поверхневих плазмонів у таких структурах у Кречманновій геометрії при довжині хвилі зондового світла $\lambda = 625$ нм. Для них виміряно кутові залежності еліпсометричних параметрів $\psi(\theta)$ і $\Delta(\theta)$, а також коефіцієнта внутрішнього відбивання $R_{IN}(\theta_{IN})$. Ці експериментальні дані порівняно з відповідними залежностями, розрахованими матричною методою згідно з моделем багатошарової структури. Числові значення оптичних сталих $n$ і $k$ шарів гетероструктури піддано варіюванню для досягнення збігу з мінімальною похибкою між експериментальними та теоретичними даними. Криві залежностей внутрішнього відбивання $R_{IN}(\theta_{IN})$ досліджених зразків мають характерну особливість у вигляді глибокого мінімуму при певному куті падіння $p$-поляризованого світла, що є однозначним доказом існування у них поверхневого плазмонного резонансу. За особливостями поведінки цих кривих з'ясовано можливість використання таких гетероструктур в якості плазмонних сенсорів. Для оцінки рівня ефективности такого типу сенсорів виконано теоретичні розрахунки коефіцієнта внутрішнього відбивання при варіюванні показника заломлення середовища, яке контактує з верхньою поверхнею структури. Одержано криві відповідних залежностей, за нахилом яких запропоновано визначати чутливість сенсора. Типове значення цієї величини для досліджених гетероструктур становить 100–200/RIU (Refractive Index Unit) в околі $n = 1{,}3$ RIU.

Рассмотрены плазмонные свойства гибридных металлодиэлектрических наноразмерных структур на основе тонких плёнок Cu, защищённых от окисления в условиях воздушной атмосферы диэлектрическим слоем $HfO_2$ и/или графеновым слоем. Эксперимент проведён методом эллипсометрии и поляриметрии с возбуждением поверхностных плазмонов в таких структурах в геометрии Кречманна при длине волны зондового света $\lambda = 625$ нм. Для них измерены угловые зависимости эллипсометрических параметров $\psi(\theta)$ и $\Delta(\theta)$, а также коэффициента внутреннего отражения $R_{IN}(\theta_{IN})$. Эти экспериментальные данные сравнены с соответствующими зависимостями, рассчитанными матричным методом согласно модели многослойной структуры. Числовые значения оптических постоянных $n$ и $k$ слоёв гетероструктуры подвергнуты варьированию для достижения совпадения с минимальной погрешностью между экспериментальными и теоретическими данными. Кривые зависимостей внутреннего отражения $R_{IN}(\theta_{IN})$ исследованных образцов имеют характерную особенность в виде глубокого минимума при определённом угле падения $p$-поляризованного света, что является однозначным доказательством существования у них поверхностного плазмонного резонанса. По особенностям поведения этих кривых установлена возможность использования таких гетероструктур в качестве плазмонных сенсоров. Для оценки уровня эффективности такого типа сенсоров выполнены теоретические расчёты коэффициента внутреннего отражения при варьировании показателя преломления среды, которая контактирует с верхней поверхностью структуры. Получены кривые соответствующих зависимостей, по наклону которых предложено определять чувствительность сенсора. Типичное значение этой величины для исследованных гетероструктур составляет 100–200/RIU (Refractive Index Unit) в окрестности $n = 1{,}3$ RIU.

**Key words:** multilayer structures, dielectric layer, hafnium oxide, graphene, surface plasmon resonance, biosensors.

**Ключові слова:** багатошарові структури, діелектричний шар, оксид гафнію, графен, поверхневий плазмонний резонанс, біосенсори.

**Ключевые слова:** многослойные структуры, диэлектрический слой, оксид гафния, графен, поверхностный плазмонный резонанс, биосенсоры.

*(Received 20 March, 2019)*

## 1. INTRODUCTION

The one of major applications of surface plasmon physics has started from the theoretical prediction and experimental confirmation of the huge sensitivity of surface plasmons to their local dielectric environment to characterise the growth of films [1] and the electrochemical and biological processes [2]. Nylander *et al.* extended this statement to show that surface plasmons could be used as a basis for sensing antibodies in fluids [3]. These experiments paved the way for the first commercial surface-plasmon resonance (SPR) sensors released by Biacore [4]. Strong interactions between the surface plasmon and biomolecules on the metal surface have two important consequences, namely, light can be confined in an area smaller than that predicted by the diffraction limit, and the local electromagnetic-field intensity can be enhanced by many orders of magnitude [5, 6].

Metals as materials with high free-electron density and possible weak interband transitions in the visible range are the most suitable materials for plasmon applications. Traditionally, gold is widely used, though silver and copper are perspective as well [7]. However, these metals have high chemical activity and tend to oxidize in air ambient. It is clear that SPR response of such sensors will decrease in time.

In this work, main purpose is to find a way to prolong plasmon sensors lifetime. A potential solution is to use graphene as a protective barrier on copper or silver thin film as a base for SPR sensor within the broad spectral region, namely, from blue to near infrared [7, 8]. Very stable and flat thin graphene layer can also help to solve such a problem of functionalization of thin metal film with biomolecular recognition elements. Usually, the passive adsorption of receptors to the metal surface represents the most simple and straightforward functionalization method. It may be note that the graphene-protected copper and silver SPR sensors also survive only during 0.5–1 year [7].

We have studied optical properties of plasmon heterostructures of hybrid systems with atomically thin materials such as graphene and thin dielectric layer (< 10nm). The graphene coating can provide not only additional corrosion barrier but also allow the targeted biofunctionalization of its surface. The combination of plasmon film with dielectric layer and graphene has yielded significant advances in SPR sensing due to the interference of the reflected waves on interfaces metal/dielectric and dielectric/graphene and promotes the extension of the plasmon wave propagation. The aim of the work was to find out what will be the surface-plasmons' excitation process in thin copper films protected from oxidation by a dielectric layer, and to evaluate the efficiency of their functioning as plasmon sensors with an additional top graphene layer deposited.

## 2. GETTING EXPERIMENTAL DATA

All metal films studied were deposited using electron-beam evaporation with glass substrates thickness of 1 mm. To grow these films, we used a commonly available deposition apparatus with base pressures in the interval of $10^{-5}$ to $10^{-6}$ Torr. To control growth of the metal film, a calibrated quartz microbalance (QCM) was used. We also deposited Cr adhesive layers about of 1.5 nm thick on clean glass substrates before Cu-films' deposition. For Cu films prepared, the good adhesion and random grains were achieved, when Cu deposition rate was equal to ≅ 1 nm/s. On the top of Cu films, $HfO_2$ layer was also deposited with small rate of 0.05–0.1 nm/s.

The surface morphology and RMS surface roughness of $HfO_2$ layer deposited was characterized by atomic force microscopy (AFM). AFM analysis is performed in the tapping mode on the sample to examine the surface morphology in a scan area approximately of 1.5×1.5 μm$^2$. Cu/$HfO_2$ heterostructure maintains a quiet smooth surface morphology (RMS roughness changes from 2 to 3 nm). It is also worth noting that the investigated hybrid nanofilms exhibit the continuous (without any islands) morphologies.

Chemical vapour deposition (CVD) graphene transfer on Cu–$HfO_2$ surface was performed as follows. CVD graphene grown on copper film was removed by etching the copper in 0.15 Mol ammonium persulfate for ≅ 8 hours. Before etching, graphene was covered by

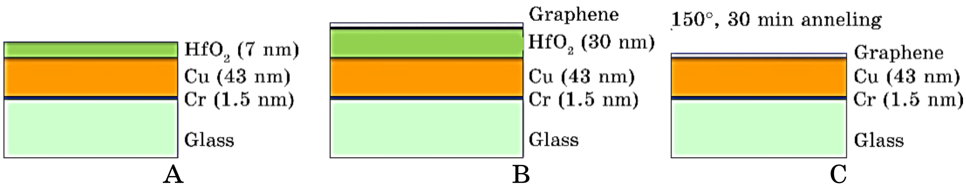


**Fig. 1.** The structure of the samples investigated.

≅ 500 nm of PMMA with a tape window cut out and placed on the PMMA; so, the membrane can be mechanically moved after etching. The free-floating graphene membrane was transferred to a clean dish of deionised (DI) water for 10 min, then to a second dish of DI water for a further 10 min to remove contamination from etchant solution. The PMMA–graphene film was then transferred onto the target Cu–$HfO_2$ films into a desired position. Finally, the PMMA layer was removed in acetone.

A set of three samples was fabricated, the structure of which is shown in Fig. 1. The first (A) consists of a thin copper film coated with a protective oxide $HfO_2$ layer; the second (B) has a similar structure, but still contains an additional graphene monolayer; the third (C) has only a copper film with deposited graphene layer on its surface. The graphene surface of sample C was further cleaned by argon/hydrogen annealing at 150°C for 30 mins.

Optical constants of thin films obtained (refractive index $n$ and extinction coefficient $k$) were firstly verified by ellipsometric measurements (Fig. 2, *a*). In the previous paper [9], ellipsometry was used to check, if there is some optical anisotropy of such heterostructures, and its absence was established. In this paper, the studies were also performed on a multifunctional experimental setup described in [10, 11]. This setup allows one to perform various types of optical research, in particular, polarimetric measurements. Ellipsometric experiment was carried out according to the typical scheme of rotating analyser [12]. The radiation source was a LED with wavelength $\lambda = 625$ nm and spectral FWHM $\Delta\lambda = 10$ nm. The probe ray fell on the top (thin film) side of the samples during ellipsometry.

In order to detect plasmon resonance in the manufactured specimens, an optical polarimetric experiment was conducted in the geometry of surface-plasmon excitation based on Kretschmann's

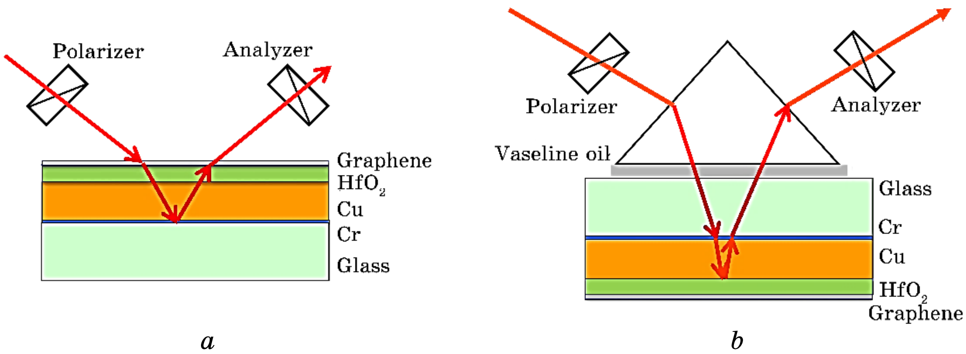


**Fig. 2.** Two methods of conducting an experiment: ellipsometric (*a*) and reflectometric with surface plasmon excitation (*b*).

scheme (Fig. 2, *b*). The sample glass substrate was coupled with internal reflection prism, through which a probe beam polarized in *p*-plane passes. Vaseline oil was applied to create an optical contact between the specimen and the prism. Its refractive index in the spectral region selected amounts $n = 1.464$ (refractive index of the prism is $n = 1.511$, and the glass substrates have $n = 1.506$). When passing inside the prism, immersion and substrate, the beam was subjected to attenuated internal reflection, went outside and was recorded by a photodetector.

Output radiation intensity was being recorded, while scanning the selected external incident angle $\theta_{EXT}$ range (the angle of incidence onto the first prism face). The internal incident angle $\theta_{IN}$ onto heterostructure was changing accordingly. At certain values of $\theta_{IN}$, favourable conditions were created for the occurrence of a surface plasmon resonance in the metallic film, because of which a part of light-wave energy passed into the sample. Thus, it is possible to experimentally register its SPR-curve $R_{IN}(\theta_{IN})$.

The calculation of optical characteristics of thin-film structures was carried out using the matrix method described in [13]. Mathematically, determining the coefficients of reflection, transmission and absorption of multilayer systems was to find the stationary amplitudes of the electric field intensity vectors at all boundaries of the interface medium, taking into account the interference phenomena in each layer. To find the ellipsometric parameters $\psi$ and $\Delta$, such calculations were performed for *p*- and *s*-polarized waves.

**TABLE.** Comparison of layers parameters *n* and *k* obtained from experiments and given in literary sources [14–16].

| Sample | Material, nm | Ellipsometry | | Plasmon excitation | |
|---|---|---|---|---|---|
| | | *n* | *k* | *n* | *k* |
| A | Cr (1.5) | 3.155* | 3.308* | 3.155* | 3.308* |
| | Cu (43) | 0.11 | 3.24 | 0.06–0.55 | 3.26–3.37 |
| | $HfO_2$ (7) | 2.107* | 0.00* | 2.107* | 0.00* |
| B | Cr (1.5) | 3.155* | 3.308* | 3.155* | 3.308* |
| | Cu (40) | 0.16 | 2.39 | 0.06–0.55 | 3.26–3.37 |
| | $HfO_2$ (30) | 2.107* | 0.00* | 2.107* | 0.00* |
| | Graphene | 2.724* | 1.345* | 2.724* | 1.345* |
| C | Cr (1.5) | 3.155* | 3.308* | 3.155* | 3.308* |
| | Cu (43) | 0.11 | 2.88 | 0.07–0.66 | 3.00–3.16 |
| | Graphene | 2.724* | 1.345* | 2.724* | 1.345* |

*Note*: *The marked values were fixed at variance and accepted to be equal to literary data [14–16].

In obtaining the $R_{IN}(\theta_{IN})$ dependences, the probe beam refraction and reflection during its passing the prism, immersion and sample substrate were also taken into account. Corresponding correction of the reflection coefficient was carried out using the Fresnel formulae.

## 3. RESULTS AND DISCUSSION

At the first stage of the experiment, angular dependences of ellipsometric parameters $\psi(\theta)$ and $\Delta(\theta)$ of each sample were measured. They were compared with theoretically calculated ones, and optimal $n$ and $k$ values, giving the minimum curves difference, were found. Because of the impossibility of simultaneously combining both the curve pair for $\psi(\theta)$ and the pair of dependences for the ellipsometric parameters $\Delta(\theta)$, which can be caused by the scattering of light in the samples, only the limits of the values $n$ and $k$ can be estimated. The results of the corresponding variation of the optical constants $n$ and $k$ are given in Table.

The parameters of thin Cr layer as well as graphene were considered to be known [14, 16], because their change almost did not affect the form of the dependences $\psi(\theta)$, $\Delta(\theta)$ and $R_{IN}(\theta_{IN})$. Neither dominant was influence of $HfO_2$ constants. To compare the results of the optical constants $n$ and $k$ variation, we note here the corresponding data [17], according to which Cu has $n = 0.113$ and $k = 3.484$ at the selected wavelength.

For each sample, the $R_{IN}(\theta_{IN})$ SPR-curve was also being measured in $p$-polarized light. The corresponding graphs are presented in Fig. 3. They demonstrate a good qualitative agreement between the experimental data and numerical results, with the exception of sample B.

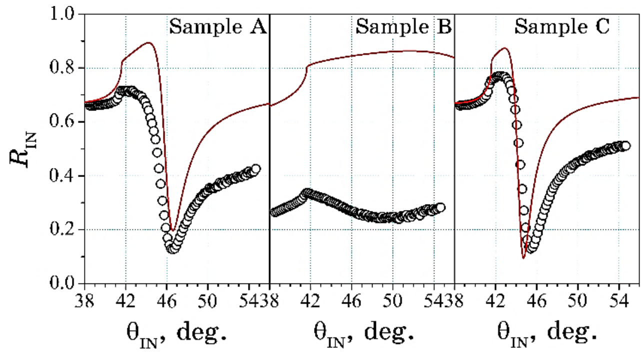


**Fig. 3.** Experimentally measured (circles) and theoretically simulated (lines) SPR-curves of the samples studied.

All these obtained dependences are characterized by a slightly smoothed form and a smaller amplitude of experimental-curves' deviation compared with the theoretical ones. In the corresponding spectral range, such 'blurring' of the contours may be caused by an insignificant statistical spread of the thin-film layers' thickness on different parts of their surface, to which theoretical calculations are sensitive. Because of this, the interference conditions for optical radiation that passes through these layers are violated. As far as sample B is concerned, the deviation of data for which is the most significant one, it is possible to assume significant heterogeneity of its $HfO_2$ oxide layer, which, moreover, has a maximum thickness in comparison with other samples. This is confirmed by the variation in the optical thickness of the $HfO_2$ layer ($nd$, where $n$ is refractive index, $d$ is the layer thickness) used in the theoretical model from 30 nm to 13 nm. Then, the minima position of $R_{IN}(\theta_{IN})$ curves and their depth are almost identical, although their general shape in this case is still different.

Similar to ellipsometric data, for the experimental and simulated $R_{IN}(\theta_{IN})$ curves shown in Fig. 3, fitting with optimal $n$ and $k$ constants, search was also been performed. Variation of $HfO_2$ layers' refractive index within $n = 2.00–2.25$ range, as it turned out, only leads to the curve minimum bias approximately ±0.5 without significantly altering its shape. Therefore, this parameter also left fixed. The resulting values of the layers $n$ and $k$ obtained are presented in Table.

The aforementioned theoretical model was also been applied to assess efficiency level of the investigated structures, when used them as plasmon sensors. For each of the samples, angular position of the SPR-curve minimum was computed as a function of an ana-

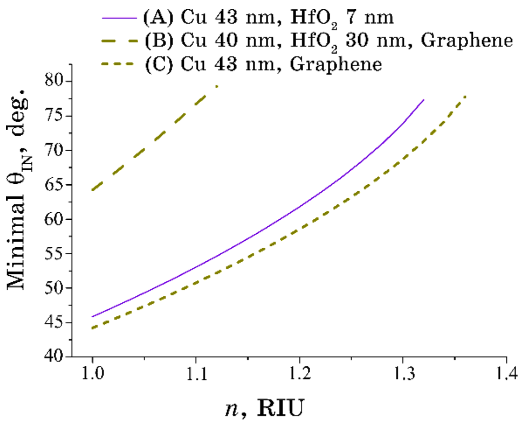


**Fig. 4.** Dependences of the SPR-minimum angular position from the analyte refractive index $n$ for the sensors considered.

lyte refractive index (the medium contacting with the top layer of the sensor). Such dependences are presented in Fig. 4.

It can be seen that the curve for sample A protected by $HfO_2$ layer has a certain bias relative to the curve for graphene-protected sample C. At the same time, for the sample B, this shift is very significant. Although its functioning as a plasmon sensor in this case is possible, the available range of analyte refractive indexes for determining will be limited to ≅ 1.12 RIU (Refractive Index Unit).

The criterion for the effectiveness of SPR-sensors based on the structures considered may be their sensitivity to the analyte refractive index change, which should be determined by the corresponding curves' inclination. As one can see from Fig. 4, the inclination changes somewhat at different of refractive index values. Thus, in the vicinity of $n = 1.05$ RIU, the sensitivity is about 71 deg/RIU for sample A, 125 deg/RIU for sample B, and 65 deg/RIU for sample C. In the vicinity of $n = 1.31$ RIU, one has 173 deg/RIU for sample A and 130 deg/RIU for sample C.

The obtained dependences have shown that the available refractive index range to determine and the sensitivity of the A and C sensors, coated with oxide and graphene layers, respectively, differ insignificantly.

## 4. CONCLUSIONS

Thin Cu films protected from atmospheric oxidation by dielectric $HfO_2$ and/or grapheme layer are characterized by surface-plasmon excitation at an angle of internal reflection $\theta_{IN} \approx 46°$ (probe light wavelength $\lambda = 625$ nm). They can be effectively applied as plasmon sensors, if the oxide-layer thickness does not exceed 30 nm. An overly thick $HfO_2$ layer causes a decrease in the range of analyte refractive indexes available for registration by such sensors. The typical sensitivity value for optical diagnostics of condensed media using these structures will be about 100–200 deg/RIU near $n = 1.3$ RIU.

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