EFFECTIVE PERMITTIVITY MATERIAL MODEL OF GOLD NANOPARTICLES LAYERS FOR SPECTROSCOPIC ELLIPSOMETRY

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1. Introduction

Gold nanoparticles are historically known as colourants in stained-glass windows and ceramics. Their color properties follow from the localized surface plasmon resonance (LSPR) with the natural frequency in visible spectra of electromagnetic radiation. Other noble metals also perform LSPR, but the main frequency is mostly shifted to the UV region. Detectable changes of the plasmonic properties is a basic principle in many nowadays practical applications, e.g. chemical sensors, surface enhanced Raman spectroscopy (SERS), photonic circuits, light-emitting diodes, photovoltaics, etc. [1,2]The information on material properties is essential in the design of functional elements based on nanoparticles. Usually, it is quite difficult to find an appropriate theoretical approach to describe behavior of the real surfaces covered with layers of nanoparticles. Many methods exist for each specific application, which are more or less close to reality [3]. In this work we propose the material model of effective permittivity with two Lorentz oscillators to evaluate spectroscopic ellipsometry measurements. The model was verified on samples prepared by chemisorption deposition.

2. Samples preparation

Gold nanoparticles PlasmaChem with a diameter of 6–7 nm and coated with a hydrophobic surfactant were deposited by chemisorption onto substrates of two types: Si wafer with 110 nm thermal SiO_2 and microscopic glass. Pure substrates with a monolayer of mercaptosilane, (3-mercaptopropyl)trimethoxysilane, were immersed in the concentrated solution of nanoparticles in chloroform for approx. 30 min. Covalent binding of a metal nanoparticle on mercaptosilane'ssulfur atom ensures formation a monolayer on the substrate surface. Next layers were deposited step-by-step using 1,6-hexanedithiol as a binding material between the adjacent layers with two sulfur atoms located at the opposite sides of the molecule. Both, mercaptosilane and hexanedithiol were deposited on substrates in an evaporation bank with saturated steam for approx.10 hours.

Repeating these steps of evaporation and chemisorption in the nanoparticles solution, the samples of 1, 3, 5, 7, 10, and 12 cycles of deposition were produced. One new monolayer should appear on the sample after each step. The thickness of the sample corresponds to the number of cycles, as it is shown on Fig. 3.

3. Material model of metal nanoparticle layer

Relative permittivity of the organic ambient environment surrounding the nanoparticles in the layer (bounding molecules, nanoparticles surfactant polar molecules and their residuals from the deposition solution) is modeled by the Lorentz oscillator [4]:

$$\varepsilon_{\mathrm{a}}(\omega) = \varepsilon_{\infty} + \frac{f_{\mathrm{a}}\omega_{\mathrm{a}}^{2}}{\omega_{\mathrm{a}}^{2} - \omega^{2} + \mathrm{i}\gamma_{\mathrm{a}}\omega} \tag{1}$$

where ε_{∞} is the high frequency permittivity, f_{a} is the Lorentz oscillator strength, ω_{a} is the oscillator natural frequency and γ_{a} is the damping factor – the width of the Lorentzian peak.

The interaction of incident light with metal nanoparticles at resonance conditions leads to the localized surface plasmon generation. Such a resonant process can be described by means of the Lorentz oscillator approximation as well:

$$\varepsilon_{\mathrm{p}}(\omega) = \frac{f_{\mathrm{p}}\omega_{\mathrm{p}}^{2}}{\omega_{\mathrm{p}}^{2} - \omega^{2} + \mathrm{i}\gamma_{\mathrm{p}}\omega} \tag{2}$$

Consequently, the complete material model of the nanoparticle layer is obtained as a sum of the two said models

$$\varepsilon = \varepsilon_{\mathrm{a}} + \varepsilon_{\mathrm{p}} = \varepsilon_{\infty} + \frac{f_{\mathrm{a}}\omega_{\mathrm{a}}^{2}}{\omega_{\mathrm{a}}^{2} - \omega^{2} + \mathrm{i}\gamma_{\mathrm{a}}\omega} + \frac{f_{\mathrm{p}}\omega_{\mathrm{p}}^{2}}{\omega_{\mathrm{p}}^{2} - \omega^{2} + \mathrm{i}\gamma_{\mathrm{p}}\omega} \tag{3}$$

Usually, the index of refraction of common organic materials changes slightly in the region with normal dispersion. It is the case of visible light and the dispersion relation is described by the Cauchy or the Sellmeier formula. Nevertheless, in the absorption curve of the nanoparticles layers, in addition to the plasmon resonance maximum located in the visible part of the spectra another peak in UV region appears. The growth of absorption in the UV region (Fig. 1) can be caused by the nanoparticles themselves, moreover this effect is gained for non-spherical nanoobjects elongated in one direction (ellipsoids, sticks, etc.) [5]. The phenomenon would not occur in the ellipsometry model, if only the last plasmonic Lorentz term in Eq. (3) was taken into account.

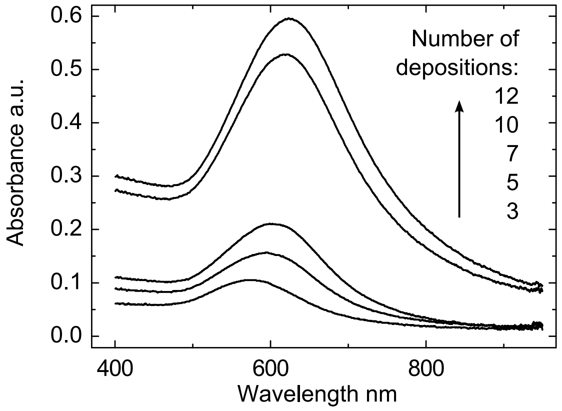

Fig.1: *Absorbance spectra from transmission measurements of the Au nanoparticle layers on glass substrates. The growth of absorption in UV region is clearly seen for multiple depositions.*

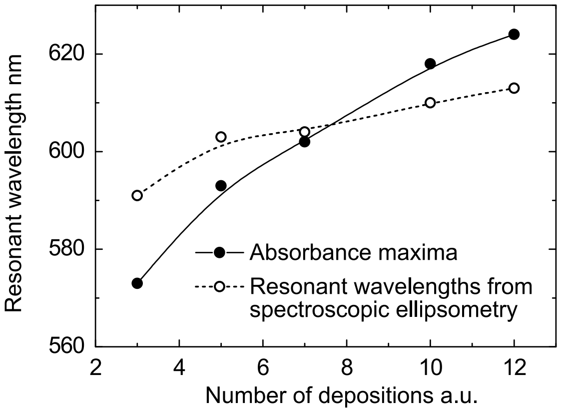

Fig.2: *Comparison of absorbance maxima wavelengths vs. resonant wavelengths of the plasmon peak obtained by spectroscopic ellipsometry. Maxima in the absorbance spectra are dependent on layer thickness because of interference on thin layer, while the plasmon resonant peak changes with the layer thickness slightly.*

4. Results and discussion

The nanoparticles from PlasmaChem are shipped as a powder of gold spheres coated with an organic hydrophobic surfactant which enables their deposition from the water surface by traversal of the substrate through the interface (e.g. Langmuir-Blodgett or Langmuir Schaefer) and prevents the nanoobjects from aggregating into huger clusters. To ensure the complete covering of the sphere, the amount of the surfactant molecules is mostly higher than needed. The residual material which is not bound to the particles is dissolved in the deposition solution and prevents from creating a continual self-assembled monolayer of nanoparticles. Thus, the resulting layer consists of separately stochastically distributed gold nanoparticles with the organic surfactant and the binding molecules of mercaptosilane or hexanedithiol, perhaps residual surfactant and air in between.

Table 1 summarizes the material parameters obtained from spectroscopic ellipsometry measurements on Horiba Jobin Yvon MM-16 ellipsometer. Initial values for the data fitting were estimated from the absorbance spectra (Fig. 1) and the known dimensions of particles. At a brief glance, the first layer is slightly different from the others. This is comprehensible if taking into account the method of samples preparation. The first layer of nanoparticle was adsorbed on substrates via mercaptosilane, whereas the higher order depositions were formed using 1,6-hexanedithiol. This means that the structure of the surrounding medium at the first layer is not the same as at the next ones.

Tab 1. *Parameters of the two-oscillator effective material model from spectroscopic ellipsometry.*

Deposition	Thickness	$n_\infty = \sqrt{\varepsilon_\infty}$	Plasmon resonance			2nd oscillator		
no.	nm	a.u.	f_p a.u.	ω_p eV	γ_p eV	f_a a.u.	ω_a eV	γ_a eV
1	6.1	1.38	0.19	2.31	0.72	0.07	2.99	0.39
3	9.8	1.58	0.73	2.13	0.52	0.42	3.09	1.19
5	12.0	1.64	1.08	2.08	0.48	0.58	3.06	1.29
7	13.6	1.65	1.08	2.08	0.47	0.57	3.05	1.27
10	28.7	1.68	1.25	2.06	0.47	0.67	3.13	1.58
12	37.7	1.69	1.28	2.05	0.47	0.62	3.14	1.73

A comparison of wavelengths corresponding to absorbance maxima of samples from Fig. 1with the maxima of material absorption from spectroscopic ellipsometry is shown on Fig. 2. The shift of absorbance maxima with the layer thickness is determined by thin film interferometry. Even though the layers are rather thin (less than 40 nm), the effective index of refraction in the resonant maximum reaches relatively high value – up to 2.6. That is to say the interference effect is significant. On the other hand, the shift of the material absorption maximum is small. Either there is no shift indeed and the effect is caused by a measurement error, or the shift is caused by creating a linear chain of nanoparticles during the growth of subsequent layers. The idea from the chemical point of view is that the metal particle of the next layer binds onto the metal particle of the previous layer. As it was previously said, the particles in the first layer are distant from each other and the next chemisorption deposition creates separated groups of nanoparticles connected by hexanedithiol. Such clusters could exhibit special plasmonic behavior determined by localized plasmon coupling of the group members, which can eventually leads to the shift of resonance frequency [3,5].

Using permittivity of gold layers by Johnson and Christy [6] and the Froehlich relation the plasmon wavelength from quasi-static theory [7] comes out approx. 550 nm, if the index of refraction of the surrounding medium is 1.5.The measured values according to the formula for the resonant frequency of a damped oscillator $\omega_{\mathrm{R}} = \sqrt{\omega_{\mathrm{p}}^2 - \gamma_{\mathrm{p}}^2/2}$, corresponds to the wavelengths in the range 550 nm – 612 nm.

The measured thicknesses of each layer are shown on Fig. 3, where the dependence on the number of depositions is clearly visible. The dotted line is a linear fit with the intercept at 0 nm. The slope 2.8 nm per one layer is a consequence of the fact, that we were not able to prepare continuous monolayers of nanoparticles. Hence, the diameters of the spheres is 7 nm, the effective thickness of each deposited layer is smaller, of course. This discrepancy allows us to make a picture of the nanoparticles stocking density.

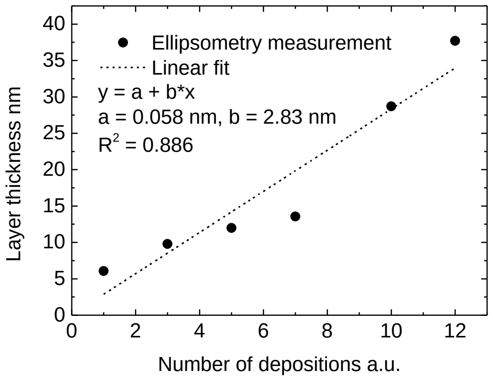

Fig.3: *Graph of nanoparticle layers thickness vs. number of depositions (black circles). The expected linear dependence is shown as the linear fit (dotted line) with the intercept near to 0 nm and the slope 2.8 nm per one deposition cycle.*

5. Conclusion

Multilayers of gold nanoparticles on solid substrates were prepared and measured to determine their optical properties. It was shown that such a composite material can be described by the proposed double-oscillator effective permittivity material model. The resulting resonance frequencies are in good agreement with expected theoretical values and also correspond to the resonances from absorbance measurements. Explanation and quantitative evaluation of the second Lorentz oscillator requires further investigation exploiting other advanced experiments, such as atomic force microscopy, scanning and transmission electron microscopy, etc.

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