

Modeling of the optical properties of a two-dimensional system of small conductive particles.

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Abstract. Software was developed for quick numerical calculations and graphic display of the absorption, reflection and transmittance spectra of two-dimensional systems of small conductive particles. It allowed us to make instant comparison of calculation results and experimental data. A lattice model was used to simulate nearly distributed particles, and the coherent-potential approximation was applied to obtain a solution to the problem of interacting particles. The Delphi programming environment was used.

1. Introduction

Surface plasmons give rise to several unusual optical phenomena, such as changing of optical response of materials at different scales [1], detection of chemical and biological species [2]. Strong interaction between light and surface plasmons in nanoparticles provides for new opportunities of practical usage, such as transportation of energy [3] and spectroscopy [4]. Optical properties of metal nanoparticles can be tuned by changing their shape, size, and environment, creating promising research fields like plasmon-based photonics. Especially interesting for applications are metal nanoparticle arrays and their combinations with semiconductors or insulators [5]. According to calculations [2], sensors created by using such hybrid materials will show extraordinary sensitivity to biological molecules. Theory predicts that those materials can be used to create high-speed switches [6]. In light of the above, there is a need in reliable instruments for instant calculations and modelling of optical properties of such hybrid structures that will allow quick comparison of calculation results with experimental data.

In this work we present a program for calculation of the optical properties of the layer of particles arranged in a plane. Such arrangement is common for different research samples and devices. We compare our calculations with experimental optical reflection spectra for a system of Ag particles on the GaAs surface.

2. Experiment

The samples were semi-insulating GaAs substrates with thin Ag films sputtered on them. The Ag film thickness was 50 Å. In order to obtain Ag nanoparticles the samples were roasted at the temperature of 200°C. Particles thus obtained were randomly dispersed over the GaAs surface. The characteristic particle size was 35-40 nm (characteristic radius 17-20 nm).

Optical reflection spectra were measured at room temperature for *s*- and *p*-polarized light at different angles of the light incidence. The light source was an LS-1 tungsten bulb connected to an



optical fiber. The optical reflection spectra were recorded using an Ocean Optics HR4000 spectrometer and were processed by Spectrasuite software.

In addition to the samples of interest we also measured reflection spectra from a bare GaAs substrate and from a sapphire plate. The latter was used as a reference for normalization since the optical properties of sapphire are well documented and easily described by the Fresnel's law. The reflection of the bare GaAs substrate was subtracted from the optical reflection spectra of the samples in order to reveal the contribution of Ag particles to the total reflection.

An experimental spectrum of light reflection from GaAs substrate with Ag nanoparticles is shown at Fig. 1. The spectrum was recorded at 25° of incidence of p -polarized light.

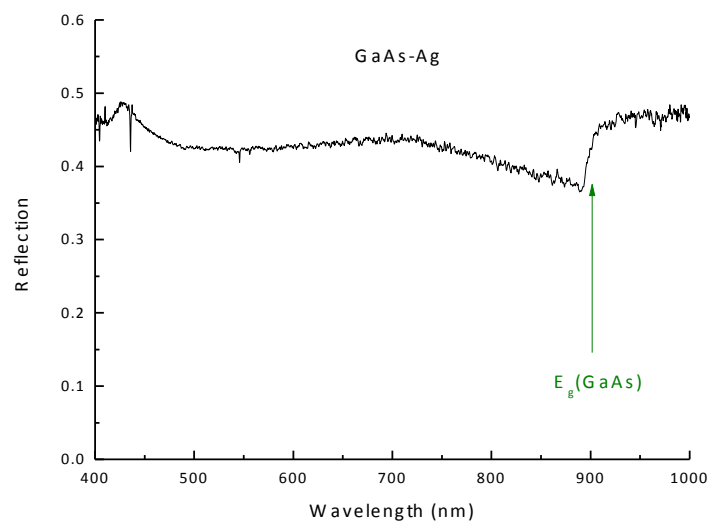


Figure 1. Experimental reflection spectrum recorded for p -polarized light at 25° of incidence. Green arrow shows the location of energy gap of GaAs.

Fig. 2 (a,b) shows experimental reflection spectra recorded with p -polarized light at the angles of incidence taken 25° , 35° , 40° and 45° , from which the reflection by bare GaAs substrate was subtracted. Nevertheless, there is a “step” at 900 nm caused by abrupt changes in optical properties of GaAs near its energy gap (1.4 eV). As the major contribution by Ag nanoparticle array one can observe the maximum at 700 nm and shoulder at about 530 nm on all reflection spectra. The amplitude of the shoulder is increasing with the increasing angle of incidence, whereas the amplitude of maximum at 700 nm is decreasing. Maximum of reflection is about 10% in absolute units. The half width at half maximum (HWHM) of the peak at 700 nm is estimated as 140 nm.

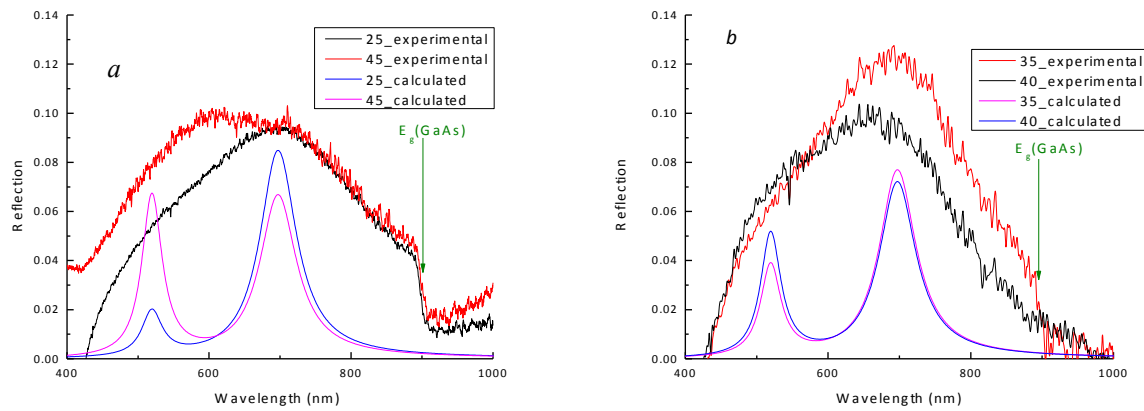


Figure 2. Experimental (noisy curves) and calculated (smooth curves) spectra of optical reflection obtained for angles 25°, 45° (a) and 35°, 40° (b) of incidence of p -polarized light. Green arrows show the location of the GaAs energy gap.

3. Calculations

The system of Ag nanoparticles was considered as a two-dimensional square periodic lattice with period a . The particles were assumed to be spherical with identical radius R . The bulk plasma frequency is given by the following formula [7]

$$\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_{eff}}}, \quad (1)$$

where e is the electron charge, n_e is the electron concentration and m_{eff} is the effective mass of the electron. The dielectric function of plasma then will be

$$\varepsilon(\omega) = \varepsilon_0 - \frac{\omega_p^2}{\omega(\omega + \frac{i}{\tau})}, \quad (2)$$

where τ is the damping constant. In the pure Drude model ε_0 is set to unity. On the other hand, to account for the interband transitions in real metals different values of ε_0 are used.

The polarizability of a single sphere is [8]

$$\alpha(\omega) = R^3 \frac{\varepsilon(\omega) - \varepsilon_c}{\varepsilon(\omega) + 2\varepsilon_c}, \quad (3)$$

where ε_c is the dielectric function of the environment.

Substituting (2) into equation (3) gives

$$\alpha_A(\omega) = R^3 \left(1 + \frac{3\omega b(\omega + \frac{i}{\tau})}{\Omega^2 - \omega(1 + 2b)(\omega + \frac{i}{\tau})} \right), \quad (4)$$

where $\Omega = \omega_p / \sqrt{3\varepsilon_0}$ and $b = \frac{\varepsilon_c}{\varepsilon_0}$. It is more convenient for calculation to use $\gamma = \hbar/\tau$ instead of τ .

In addition to the incident electromagnetic wave there is a secondary field induced by the ensemble of nearby particles. It makes a contribution to the total polarizability. Taking into account the secondary

electromagnetic field the diagonal components of the tensor of polirazability are [9]

$$\alpha_{\parallel}^0 = R^3 \left(\frac{1}{(1 + R^3 U_0)} + \frac{3\omega b(\omega + \frac{i}{\tau})}{((1 + R^3 U_0)(\Omega_{\parallel}^2 - \omega(1 + 2b)(\omega + \frac{i}{\tau})))} \right) \quad (5)$$

$$\alpha_{\perp}^0 = R^3 \left(\frac{1}{(1 + R^3 U_0)} + \frac{3\omega b(\omega + \frac{i}{\tau})}{((1 + R^3 U_0)(\Omega_{\perp}^2 - \omega(1 + 2b)(\omega + \frac{i}{\tau})))} \right) \quad (6)$$

$$\Omega_{\parallel}^2 = \Omega^2 (1 - \frac{1}{2} R^3 U_0) \quad (7)$$

$$\Omega_{\perp}^2 = \Omega^2 (1 + R^3 U_0). \quad (8)$$

Here the contribution of induced secondary field is taken into account in approximation of a regular square lattice of identical nanoparticles. In this approximation the lattice sum gives

$$U_0 = 9.03a^{-3}, \quad (9)$$

where a is the lattice constant.

In accord with (5) and (6) the parallel and perpendicular components of the polarizability are substantially different. They have different resonant frequencies, Ω_{\perp} and Ω_{\parallel} . Hence, there should present two peaks in the reflectance and transmittance spectra.

The total reflectance of the system for light incident at an arbitrary angle θ is [8]

$$r = \frac{-A(\cos^2 \theta \alpha_{\parallel}^0 - \sin^2 \theta \alpha_{\perp}^0) - AB \alpha_{\parallel}^0 \alpha_{\perp}^0 e^{2i\theta}}{1 + B(\alpha_{\perp}^0 - \alpha_{\parallel}^0) - A(\cos^2 \theta \alpha_{\parallel}^0 + \sin^2 \theta \alpha_{\perp}^0) - AB \alpha_{\perp}^0 \alpha_{\parallel}^0 e^{2i\theta}}, \quad (10)$$

$$A = \frac{2\pi\omega i}{ca^2 \cos \theta}, \quad (11)$$

$$B = \frac{2\pi\omega}{ca^2 \sin \theta}. \quad (12)$$

Using this theory we developed a program, which makes quick numerical calculations and graphic display of the absorption, reflection and transmittance spectra. It provides an opportunity to save and load experimental spectra for easy comparison. The interface of the program is shown in Fig. 3.

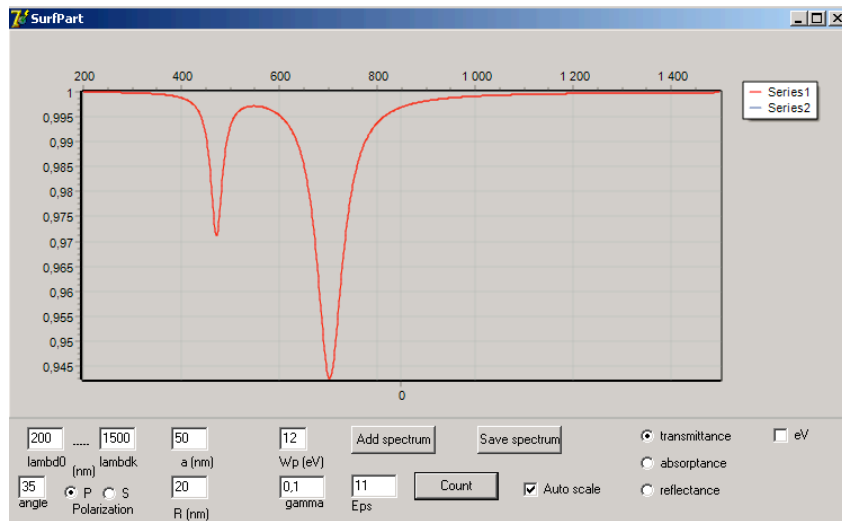


Figure 3. Program interface showing calculation of the transmission spectrum for silver nanoparticles on the surface of GaAs. The lattice constant is $a = 50$ nm. The particle radius is $R = 20$ nm. The angle of p -polarized light incidence is 35° . The transmittance is calculated for the wavelength range from 200 nm to 1500 nm. The material of particles has plasmonic frequency $\omega_p = 12$ eV with damping parameter $\gamma = 0.1$ eV. The ambient dielectric function is 11.

4. Discussion and conclusions

In order to compare the calculations with experiment we should specify the parameters of the system. Based on the sample images provided by scanning electron microscope (SEM) we considered the characteristic particle size R to be in a range from 14 to 22 nm and the effective lattice constant of about $a = 50 \pm 5$ nm. The dielectric functions for Ag and GaAs are well documented [9]. We took $\omega_p = 12$ eV and $\gamma = \hbar/\tau = 0.1$ eV as common parameters of Ag and $\epsilon_c = 12$ as a simple representation of the GaAs substrate.

The calculated optical reflection spectra are shown in Fig.2 along with experimental ones. In this calculation the particle radius is $R = 18$ nm, which provides the best agreement of the two calculated reflection peaks with the features in the experimental spectra. The comparison of calculations with the result of experiment shows that the dominant contribution to the reflection at relatively low angles of the light incidence (25 - 35°) comes from in-plane component of total polarizability. In case of larger angles of the light incidence the experimentally observed major peak shifts to shorter wavelength and a shoulder at around 530 nm becomes pronounced. The calculation shows that this transformation originates from the resonance related to the out-of-plane component of total polarizability. Our simple model shows a reasonable similarity with the experimental results. It predicts the positions of peaks in reflection spectra and their transformation at different angles of the light incidence.

However, the width of calculated peaks is different from the experimental ones. The homogeneous broadening in our model is $\text{HWHM} = 25$ nm with common parameters of Ag particles, whereas the experimental $\text{HWHM} = 140$ nm. This discrepancy may be explained by the fact that in a real sample, particles have different sizes and forms. It is well known that these parameters strongly impact the resonance frequency [10]. Our calculations show that the observed HWHM about 140 nm corresponds to variation of the particle radius from 10 to 25 nm. This dispersion is well consistent to our SEM observations, where a spread of particle radii can be estimated as 15-21 nm. Also our model does not consider the nonlinearity of dielectric function of the substrate. As well, its imaginary part is not included in the calculation. This can result in some broadening of the optical reflection spectra.

However, our estimate shows that the inhomogeneous broadening gives major contribution to the observed reflection spectra.

Thus, the program was developed for quick numerical calculations and graphic display of optical absorption, reflection and transmittance spectra of a layer of plasmonic nanoparticles formed on a dielectric substrate. In overall the calculated spectra are reasonably similar to the experimental ones. The program will be improved in the future by adding the possibility to make calculations by using loaded complex dielectric function of the environment.

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