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MODEL OF THE EFFECTIVE-MEDIUM APPROXIMATION FOR NANOSTRUCTURED LAYERS WITH THE ACCOUNT OF INTERPARTICLE INTERACTIONS AND ITS ELLIPSOMETRIC REGISTRATION

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ABSTRACT. Here we discuss the deficiencies of standard Effective-Medium Approximation in the application to thin layers and propose the model, which overcomes those problems for 2-dimensional case. Ellipsometry of layers of gold nanoparticles reveals the discussed interparticle interactions in such layers.

1. Introduction

The Effective-Medium Approximation (EMA) is a very convenient tool to describe the electromagnetic response of heterogeneous systems with the nonuniformity on the scale smaller than the wavelength [1]. In the case of the size of different constituting parts remarkably bigger than the wavelength, the description of the response should be made on the base of the consideration of uniform fields inside of different parts and boundary conditions for them. If the size of those parts is comparable with the wavelength, the strong scattering exists resulting in band-gap materials in the case of coherent scattering on regular structures. However, if the scale of the nonuniformity is smaller than the wavelength, EMA is very robust approach, as the alternative exact direct description of fields, currents, polarization in each element with the account of their interactions is extremely time and resource consuming task, which should be made for any particular configuration. So, the aim of EMA is to describe some averaged response of a nonuniform system of interest taking into account the distribution of size, shape and dielectric function of constituting parts and their mutual interactions. The main approach to build such models is based on the Lorentz cavity concept for the determination of the polarizability of an individual inclusion and Clausius-Mossotti relation [1]. In such an approach applied for three-dimensional (3D) situation for the case of regular or random uniform distribution of similar inclusions the average near-field scattered by nonuniformities at the place of any of them is zero. So the additional field to the external one at any inclusion is produced by the host medium polarization generated by the scattered far field only. Fluctuations of the distribution would give the corrections to the standard EMA models like Maxwell-Garnett or Bruggeman ones but

it is the zeroing of the average near-field, which is the point of the Lorentz cavity concept. The two-dimensional (2D) situation is principally different. Particles or inclusions are spread only in one plane and the average near-field scattered by closest neighbors is not zero in this case and both near and far scattered fields contribute to the additional polarization. Moreover, interactions of dipoles directed along and across the plane are different producing geometrical anisotropy in the optical properties of such a layer. If the average interaction along the layer is attractive producing red shift of localized resonance, the one across the layer is repulsive resulting in the blue-shifted resonance [2]. It is the reason why, in spite of many applications, the standard EMA models are principally deficient in the description of the optical properties of nonuniform layers. Maxwell-Garnett EMA model, which, in contrary to the Bruggeman one, saves the localized resonance of the inclusions in the mixture and its red shift at the rise of the concentration of inclusions, can be used for the qualitative description of the response of the nonuniform layer for its in-plane excitation. However, with the same constitutive materials, it is impossible to describe by this model the blue shift of the resonance at the excitation of the system across the layer plane.

2. Formalism

To overcome these problems we developed the model based on the solution of the Lipman-Schwinger equation for averaged fields and polarizability, which describes the response for the external field and is the 2D analogue of EMA. The total field E exciting any element of the system can be written as

$$E_i(\vec{R},\omega) = E_i^{(0)}(\vec{R},\omega) - a\sum_{\alpha=1}^{N}\int_{V_\alpha} d\vec{R}' G_{ij}(\vec{R},\vec{R}',\omega)\chi_{jl}(\omega)E_l(\vec{R}',\omega) \qquad (1)$$

where E(0) is the external field, $k_0 = \omega/c$, G is the Green function of the environment where our inclusions are deposited and χ is the polarizability of the individual inclusion [3,4]. The Green function includes all channels of the interactions both direct and indirect ones like reflected field in the case of particles on a surface. In the later case χ is the polarizability of the individual inclusion with the account of its self-action by the image in the surface. This equation after its transformation into 2D Fourier space - so called k-z representation, and averaging for the uniform distribution of inclusions in the layer may be resolved for the polarizability as

$$X_{ij}(\vec{k},z_a,\omega) = \left[(\tilde{\chi}_{ij}(\omega))^{-1} - naG_{ji}(\vec{k},z_\alpha,z_\alpha,\omega)\right]^{-1} \qquad (2)$$

In the case of the plane-wave excitation the back Fourier transformation is trivial as such a field is described by delta function in Fourier space, so after the multiplication of this expression by the concentration of particles or nonuniformities in the layer we receive the expression for the averaging polarizability of our layer, which can be used in different tasks at the determination of the response of the system with such a layer. Thus we receive the 2D analogue of EMA, which accounts both near- and far-field interactions as well as demonstrates necessary optical anisotropy and resonance shift [4]. Experimental measurements were performed by ellipsometry on layers of gold nanoparticles produced by annealing of gold thermally deposited on glass with the mass thickness between 25 and few nanometers

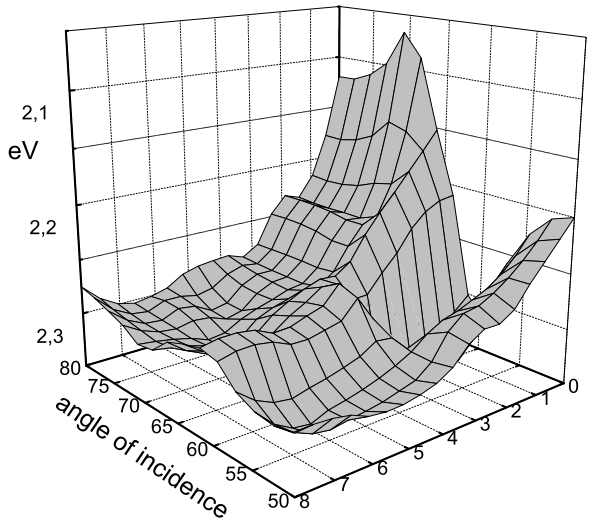

Figure 1. A The position of the resonance versus the angle of incidence and the mass thickness, which increases from N=8 to N=0.

for about 2 hours at 200 C. Spectral ellipsometer of Woollam Co. was used. After annealing spectra of all films demonstrated well-separated feature corresponding to the localized resonance of gold nanoparticles. The position of this resonance versus the angle of incidence and the initial mass thickness is exhibited in Fig.1. Clear red shift of the resonance position with the increasing of the mass thickness and consequently of the interparticle interaction is visible indicating that we monitor the longitudinal resonance. The transverse resonance can not be definitely recognized in measured spectra, as the sensitivity to the elements of the transverse polarizability of thin films is lower than for longitudinal ones. For ellipsometry this difference is about one order of magnitude.

3. Conclusions

So, we can conclude that we developed the analogue of EMA for 2D case with the account of all interactions in the system. Ellipsometric investigations of films of nanoparticles exhibit the localized plasmon resonance in such a system and its dependence on the interparticle interactions.

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References

[1] D. Aspnes, "Local-field effects and effective-medium theory: a microscopic perspective", *Am. J. Phys.* **50**, 704 (1982).
[2] N. J. Persson, "Lateral interactions in small particle systems", *J. de Physique (suppl.)* **44**, C10-409 (1983).
[3] V. Z. Lozovski, "Local field equations in electro-dynamics of systems of small particles", *Optics and Spectrosc* **86**, 96 (1999).
[4] E. G. Bortchagovsky, V. Z. Lozovski, and T. O. Mishakova, 'Theory of the ellipsometry of a layer of semiconductor nanoparticles covering the substrate ", *Ukr. J. Phys.* **55**, 1135 (2010).

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