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Optical Properties of Multilayered Metal–Dielectric Structures Containing Silver Nanoparticles

O.A. Yeshchenko[1], I.S. Bondarchuk,[1] S.Z. Malynych[2,3,4,*], Yu. Galabura[3], G. Chumanov[4], I. Luzinov[3]

[1] *Department of Physics, Taras Shevchenko National University of Kyiv, 64/13 Volodymyrs'ka Str., 01601 Kyiv, Ukraine*
[2] *V.E. Lashkarev Institute of Semiconductors Physics NAS of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine*
[3] *Department of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, USA*
[4] *Department of Chemistry, Clemson University, Clemson, South Carolina 29634, USA*

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In this paper we report on fabrication and optical properties of metal-dielectric nanostructures consisting of stacked monolayers of silver nanoparticles. The extinction spectra of the nanostructures were studied as a function of the angle of incidence and polarization state of the incident light. Two collective surface plasmon modes, namely T and P, associated with particle dipoles parallel and perpendicular to plane of the layer were identified for a single monolayer of the particles. The extinction bands of T and P modes exhibit different intensity and frequency dependences on the angle of incidence. More pronounced angular dependences for P mode band indicate the stronger coupling of dipoles for P mode than for Tone. A new N mode was observed for the structures comprising three nanoparticle layers. This new mode originated from surface plasmon coupling between adjacent layers.

Keywords: Localized Surface Plasmon Resonance, Silver Nanoparticles, Nanostructures, Extinction Spectra.

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1. INTRODUCTION

Noble metal nanoparticles and their ensembles attract most researchers' attention due to their remarkable optical properties. Nowadays, it is well established that those properties are caused by the excitation of free electrons oscillations localized within the surface of a nanoparticle termed localized surface plasmon resonance (LSPR). Concentration of the electromagnetic field in the nanoscale due to LSPR results in field enhancement that opens a great potential in various areas of applications such as sensors, optoelectronics, photovoltaics, and metamaterials. Local field enhancement serves as a basis for surface-enhanced Raman scattering (SERS) allowing one to detect a single molecule.

Tendency of modern technology toward miniaturization and integration requires assembling of a large number of nanoscaled elements into various hierarchical systems. An increase in the concentration of the nanoelements in a finite volume leads to the strengthening of the interaction (coupling) between them. In the case of metal nanoparticles, strong coupling results in the collectivization of the surface plasmon excitations associated with individual nanoparticles. Such collective LSPR modes are eigenmodes of the entire nanoparticle cluster. Thus, it is more appropriate to consider optical response of the nanoparticle cluster or array rather than that of individual nanoparticles. Nanoparticle arrays can be characterized by at least two dimensional parameters: the size of the nanoparticles and the distance between them (internal parameters of an array). Varying any of those parameters one can control the optical response of nanoparticle array [1]. In particular, the near-field coupling between closely spaced metal nanoparticles results in a strong shift of the coupled LSPR band. On the other hand, the external parameters such as the angle of incidence of the light beam and its polarization state are also important. The dependencies of the extinction spectra on the external parameters were studied earlier for linear chains and for single two-dimensional (2D) layers of silver nanoparticles.

In the present work, we have experimentally studied the influence of the angle of incidence and azimuth angle of polarization of the light beam on the extinction spectra of metal-dielectric composites consisting of several (n = 1, 2, and 3) parallel dense monolayers of silver nanoparticles, separated by dielectric polymer films.

2. EXPERIMENTAL

2.1 Materials and samples preparation

Silver nanoparticles were synthesized via hydrogen reduction of supersaturated silver oxide aqueous solution. The reaction produces a fairly monodispersed suspension of Ag nanoparticles with typical concentration of ~10^{10} cm^{-3}. The average diameter of the nanoparticles used in this work was 115 nm. Silver nanoparticles were self-assembled onto chemically modified glass substrates forming planar random array of closely spaced Ag nanoparticles. Commercial microscope glass slides were used as a substrate. Prior to self-assembling the slides were cleaned in freshly prepared 1:3 mixture of 30% H_2O_2 and H_2SO_4 (piranha solution) and dried under a stream of nitrogen

* s.malynych@gmail.com

gas. Glycidyl methacrylate (GMA) from Aldrich was polymerized radically to give poly(glycidyl methacrylate) (PGMA), number average molecular weight (M_n) = 176000 g/mole. Carboxyl-group-terminated poly(2-vinyl pyridine), P2VP-COOH (M_n=40600 g/mol), was obtained from Polymer Source, Inc. Chloroform (Aldrich) was used for preparing 2% PGMA and 2% P2VP solutions. Polymer films were characterized by both ellipsometry and AFM techniques. Imaging of the samples was performed employing scanning electron microscopy. A double-grating spectrometer DFS–12 equipped with a tungsten-halogen incandescent lamp as a light source was used for the spectral measurements in the range of 320–800 nm.

2.2 Fabrication of multilayered nanostructures

Clean glass slides were coated with a polymer film via dipping them into chloroform PGMA solution. The slides were then annealed at 140°C for 10 hours in a vacuum oven. The annealing causes cross-linking of the polymer. Afterwards the slides were rinsed with chloroform to remove any unattached polymer, and were dried at ambient conditions. The thickness of the PGMA film was 140 – 150 nm. P2VP solution was drop-cast on the surface of a slide. The slides were annealed again at 150°C during 1 hour in a vacuum oven, resulting in the formation of a 10 – 15 nm P2VP grafted layer.

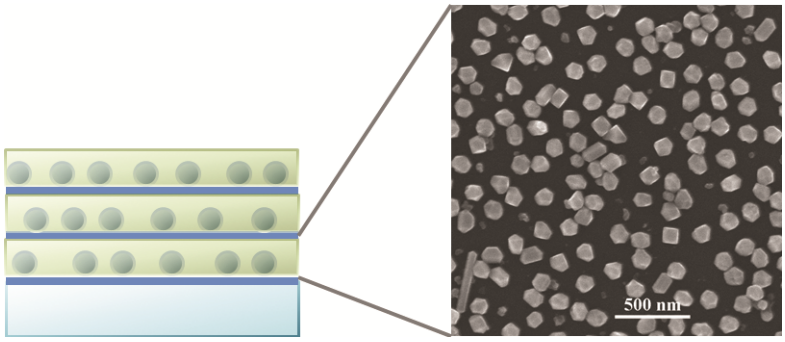

Fig. 1 – Schematics of metal–dielectric structure comprising three Ag nanoparticle layers (left) and SEM image of a single Ag nanoparticle layer (right).

Modified slides were exposed for ~20 hours to an aqueous suspension of silver nanoparticles, while P2VP acted as "glue" providing adherence of the nanoparticles to the surface. Thus, a self-assembled single layer of closely spaced nanoparticles was formed [2]. After drying, the slides with the silver nanoparticles layer was covered with an additional PGMA layer of to obtain the planar 2D layer of the nanoparticles encapsulated into PGMA-P2VP-PGMA film (Fig. 1). Note that PGMA film is used as a spacer between the surface of a substrate and Ag nanoparticle layer. To fabricate 2- and 3-layered Ag nanoparticle structures all the steps were performed repeatedly. The distance between adjacent layers of nanoparticles was 150 – 160 nm.

3. RESULTS AND DISCUSSION

As it was previously shown, planar monolayer of closely spaced Ag nanoparticles exhibit a sharp peak in the extinction spectra associated with a collective LSPR mode [3]. This collective mode arises from electrodynamic coupling between neighboring nanoparticles. Two types of collective LSPR modes exist in the planar nanoparticle layer, namely tangential (in-plane) T mode and normal P mode. Those modes would appear as distinct bands in the extinction spectra at different polarizations of the incident beam. For s-polarization the electric vector of the incident light beam is parallel to the layer plane. So, only tangential T mode can be excited with s-polarization. The electric vector of a p-polarized beam has both parallel and perpendicular components leading to the excitation of both P and T modes. At a certain angle of incidence the decrease of polarization angle will result in the increase of contribution of P mode in the spectra and to the decrease of the contribution of T mode.

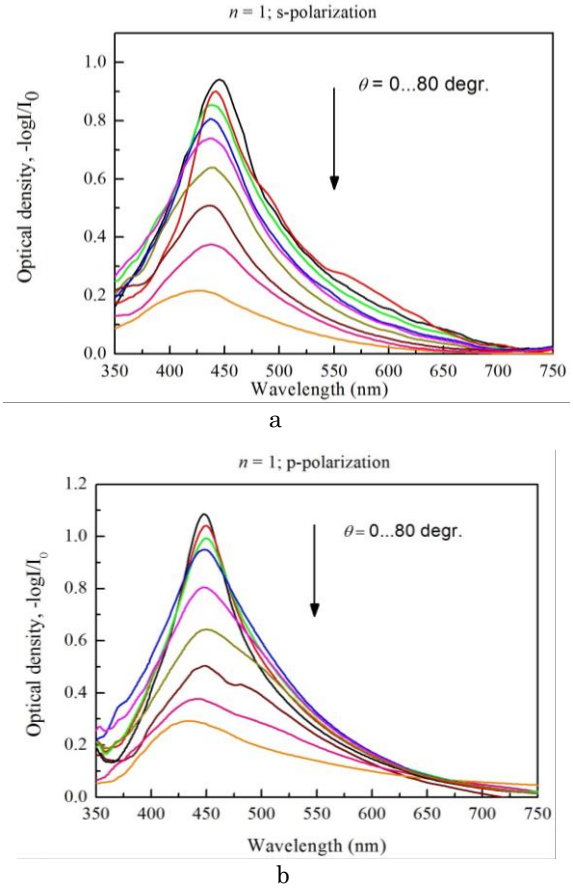

Fig. 2 – Polarized extinction spectra of a single 2D layer of Ag nanoparticles as a function of the angle of incidence θ: (a) – s-polarization, (b) – p-polarization. All spectra are normalized by cosθ.

Experimentally found two-band structure of the extinction spectra proves above expectations. Fig. 2 depicts the dependence of the extinction spectrum of a single planar Ag nanoparticle array on the angle of incidence θ. Only tangential T mode is observed in the spectra for s-polarization, while both P and T modes are observed for p-polarization. The intensity of the tangential T mode band decreases monotonically with increasing θ. Unlike T mode the dependence of spectral band associated with P mode is non-monotonic. At the angles $\theta < 50°$ the intensity of the P mode band increases with increasing of θ, which is in full agreement with the expectations. At larger angles ($\theta > 50^0$) the decrease in intensity of the P band is observed. Such a behavior can be rationalized as follows.

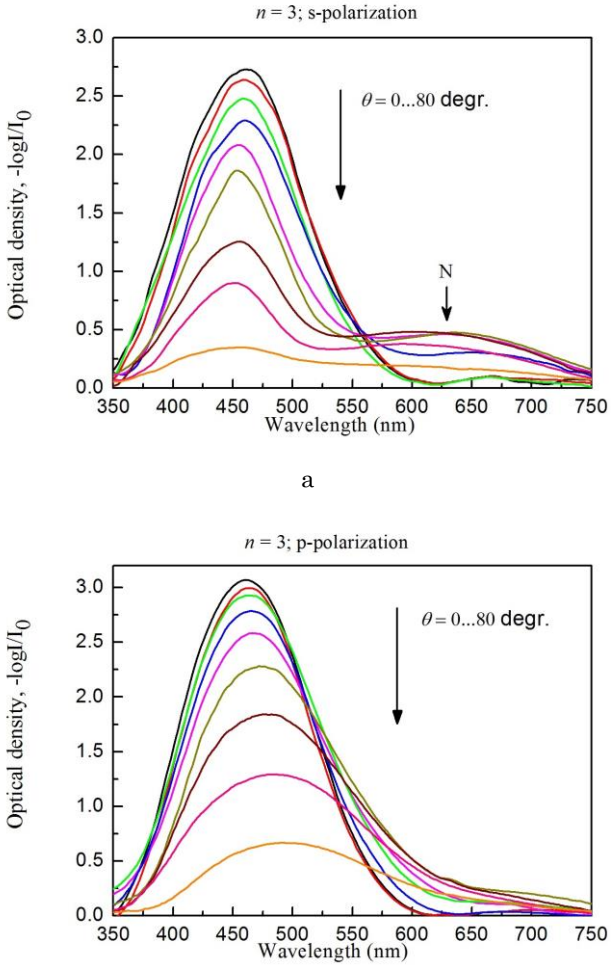

Fig. 3 – Polarized extinction spectra of a three layered Ag nanoparticle structure as a function of the angle of incidence θ: (a) – s-polarization, (b) – p-polarization. All spectra are normalized by cosθ.

At oblique angles, the neighboring particles experience different phases of the incident light wave. As a result, the dephasing of free electron plasma oscillations in neighboring nanoparticles emerges with the increase of the angle of incidence. For s-polarized light, the electric vector of the incident light is parallel to the plane of the layer at any incident angle. So, the efficiency of the coherent coupling of neighboring nanoparticles is the same for any angle θ and the angular dependence of the T band intensity is monotonically decreasing due to the overall decrease of the excitation efficiency of this mode. Note that the spectral position of the tangential T and normal P modes exhibits blue and red shift with the increase of θ, respectively. The spectral shift is more pronounced for the P band than for the T band.

Both P and T modes are also observed in the extinction spectra of multilayered (n = 2, 3) Ag nanoparticle systems. However, the intensity and the spectral shift of P band exhibit more pronounced angular dependence for multilayered structures, while T band behaves similarly for all considered structures. We hypothesize that tangential T modes that belong to different layers actually do not couple with each other.

Noteworthy that new band appears in the extinction spectra of the samples with three layers of Ag nanoparticles in addition to the P and T bands (Fig. 3). Emerging of the new N band in the spectrum indicates the formation of the new collective LSPR mode. Obviously, all three layers should be involved into the coupling and respond to the incident electromagnetic radiation as a whole system. The N band is observed in the extinction spectra only for s-polarization, while the T and P bands are observed for s- and p-polarization and p-polarization, respectively. The angular dependence of the N band intensity is similar to that of the P band; i.e., the increase at the angles $\theta<50^0$ and the decrease at $\theta>50^0$, with an increase of the incident angle. Spectral shift of the N band is opposite to that of the P band, i.e., there is a blue shift of the N band with the increase of θ. This dependence exhibits the same trend (blue shift with the increase of the incident angle) but significantly stronger as that of the T band. Thus, the N band combines spectral features of both P and T bands. The new N band may originate from complex interactions that involve all three layers of Ag nanoparticles, resulting in the mixing of the P and T modes of different layers.

4. CONCLUSIONS

In conclusion, we studied experimentally the dependence of the extinction spectra of metal-dielectric composites consisting of several (n = 1, 2 and 3) parallel dense monolayers of silver nanoparticles on the incidence angle and azimuth angle of polarization of the light beam. The spectra revealed two bands. These bands correspond to the excitation of two different collective plasmon modes that arise from the coupling of LSPR within a single layer of Ag nanoparticles. The tangential T mode corresponds to induced dipoles parallel to the plane of the nanoparticle layer, and normal P mode corresponds to dipoles normal to the plane of the nanoparticle layer. Opposite spectral shift of the extinction bands with the incident angle variations was observed for different SPR modes. Also, different dependencies of the band intensities upon the incident angle were observed for P and T modes. The observed dependencies can be rationalized as a result of different strengths of dipole coupling for different collective LSPR modes. A new additional band was observed for the sample containing three nanoparticle layers. This new N band is observed in the extinction spectra only for s-polarization. The angular dependence of the N band

intensity resembles that of the P band. The N band intensity reaches its maximum at the incident angle of ~50°. As opposed to the P band, the N band exhibits blue spectral shift with the increase of the angle of incidence. The blue shift is also characteristic to the tangential T band. The new N band originates from electrodynamic coupling between all the three layers of Ag nanoparticles.

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