

SURFACE PLASMON RESONANCE IN Ag NANOPARTICLES DEPOSITED INSIDE POROUS GaP TEMPLATES

L. Sirbu^{*}, V. Sergentu^{**}, V. Ursaki^{**}, I. Tiginyanu^{*}, G. Piredda^{***}, R. W. Boyd^{***}

^{*}Center for Materials Study and Testing, Technical University of Moldova
168 Stefan cel Mare Blvd., MD-2004, Chisinau, Republic of Moldova

^{**}Laboratory of Low-Dimensional Semiconductor Structures, Institute of Applied Physics
Academy of Sciences of Moldova, 5 Academy str., Chisinau MD-2028, Moldova

^{***}Institute of Optics, University of Rochester, Rochester, New York 14627
E-mail: sirbu_lilian@yahoo.de

Abstract—Surface plasmon resonance is studied for Ag nanoparticles electrochemically deposited on bulk GaP substrates and inside porous GaP templates. The size and density of Ag nanoparticles are controlled by the conditions of electrochemical deposition and thermal processing. The experimental data are analyzed in the frame of the Drude theory taking into account the parameters of the metallic nanoparticles and the morphology of the porous template. It is shown that porous templates provide wide possibilities for the control of the surface plasmon resonance frequency.

Keywords: Surface plasmon resonance, Ag nanoparticles, porous GaP templates, Drude theory, reflectance spectroscopy.

1. INTRODUCTION

Today's information technologies are driven by electronics and photonics which use electrons and photons, respectively, to carry, store, and process information. An emerging branch of photonics, called "plasmonics", aims at using nanostructured materials that support "surface plasmons" for these purposes. Plasmonics can potentially achieve highly complex miniaturized devices by controlling and manipulating light on the nanometer scale [1, 2]. Metal nanostructures can exhibit strong local resonances of light-induced electron plasma oscillations. Due to such resonances the electromagnetic field intensity close to the surface of the nanostructures can be strongly enhanced. These electromagnetic fields lead to fascinating enhancement of optical characteristics such as surface-enhanced resonant Raman scattering [3], enhanced transmission through subwavelength apertures [4], enhanced non-linear optical properties [5], etc. The main contribution to this enhancement arises from the excitation of localized surface plasmons (LSP) [3]. Porous semiconductor

templates offer possibility for a wide variation of the effective refractive index by tailoring the morphology and porosity of the template, and consequently for the control of the plasmon resonance in metallic nanoparticles deposited inside the template.

In this work we investigate the influence of the porous semiconductor template on the plasmon resonance frequency of Ag nanoparticles as compared to bulk semiconductor template.

2. EXPERIMENTAL

(111)-oriented n-GaP:S wafers with electron concentration 10^{18} cm^{-3} cut from Czochralsky-grown ingots were used for the fabrication of porous GaP layers. The anodic etching was carried out in a double-chamber electrochemical cell with 4 electrodes as described elsewhere [6]. Electrochemical treatment carried out with the applied voltage of 25 V in a $\text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{SO}_4$ (50:5:20 volume parts) solution at 50 °C during 10 minutes results in the formation of a template with the morphology illustrated in Fig. 1

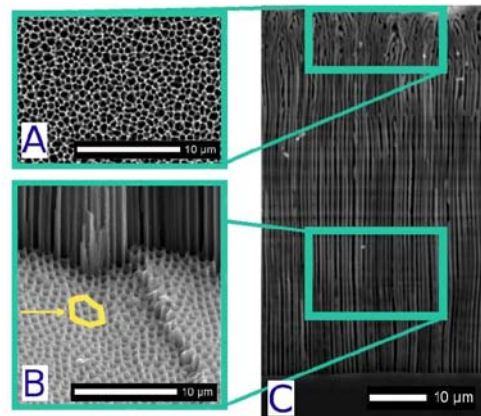


Fig. 1. SEM image of a GaP template taken at the surface (A), in the volume (B) and cross section (C).

It represents a porous layer with pores stretching perpendicular to the sample surface. The growth of pores at the surface of the template is unstable which results in a disordered porous layer as illustrated in Fig. 1A. With penetrating in the depth of the substrate volume, the growth of pores becomes more regular due to a self-organization process resulting in a hexagonal arrangement of pores with diameter around 600 nm and the thickness of walls around 150 nm as shown in Fig. 1B.

Ag nanoparticles have been deposited electrochemically on the surface of the GaP substrate as well as inside porous templates using an AgNO_3 aqueous solution. The deposition was carried out with the application of 4V pulses with the width of 100 μsec and frequency of 0.5 sec. The size and the density of Ag nanoparticles are controlled by the conditions of electrochemical deposition and the subsequent thermal treatment. The deposition during 2 minutes followed by thermal treatment at 400 $^\circ\text{C}$ during 1 hour leads to the formation of Ag particles with the mean size of 30-40 nm and the density around 50 particles per μm^2 as illustrated in Fig. 2.

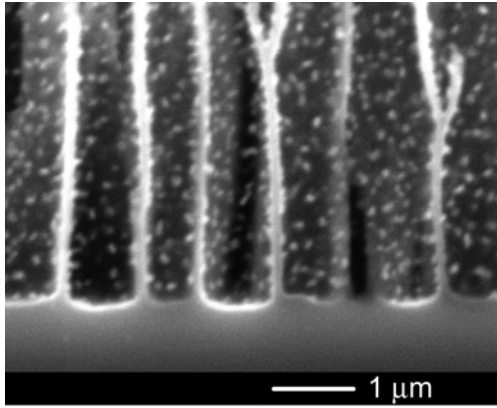


Fig. 2. SEM image of the cross-section of a GaP template filled with Ag nanoparticles.

The morphology and the chemical composition microanalysis of the prepared samples were studied using a TESCAN scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive X-ray (EDX) system.

The reflectance spectra were measured with a PerkinElmer Lambda 900 UV/VIS/NIR Spectrometer with incident beam perpendicular to the surface of sample. The

spectra from samples with metallic nanodots have been calibrated to the respective spectra measured on samples without metallic particles.

3. RESULTS AND DISCUSSIONS

Figure 3 compares the reflectance spectra of a sample with Ag nanoparticles deposited on the surface of a bulk GaP substrate with the one measured on a porous GaP template with similar metallic particles deposited inside the pores.

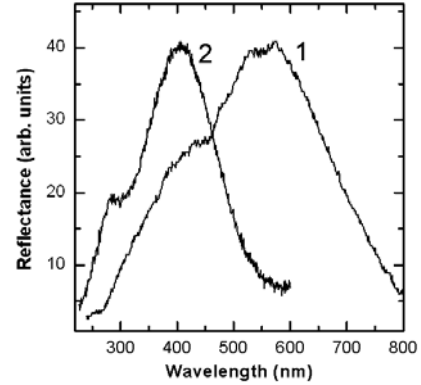


Fig. 3. Reflectance spectra of bulk (1) and porous (2) GaP samples with Ag nanoparticles.

One can observe that the maximum in the reflectance spectrum is shifted from 580 nm to 400 nm when the Ag nanoparticles are deposited inside the porous template instead of the bulk surface. The experimental data are treated in the frame of previously developed theoretical approaches for the scattering of light by metallic particles [7,8] which were successfully used for the explanation of data related to scattering properties of metallic nanoparticles in various transparent media [9]. According to these data, the inclusion of metallic particles into media with the refractive index $n > 1$ leads to the broadening and shift of the plasmon resonance peak to long wavelength as compared to the same particles in air.

The calculations have been performed for small Ag particles incorporated into medium with the effective refractive index n_{eff} using the Drude formula for the dielectric function of the metal

$$\varepsilon(\omega) = 1 - \omega_0^2 / (\omega(\omega + i\gamma)), \quad (1)$$

where ω is the frequency of the electromagnetic radiation, ω_0 is the plasmon frequency of the metal, and γ is the damping constant. The value of $\omega_0 = 3.9\text{eV}$ and $\gamma = 0.02\text{eV}$ [10] have been used.

According to the results of calculations, the maximum in the spectrum at 400 nm and 580 nm is obtained for the n_{eff} value of 1.05 and 2.0, respectively (Fig. 4).

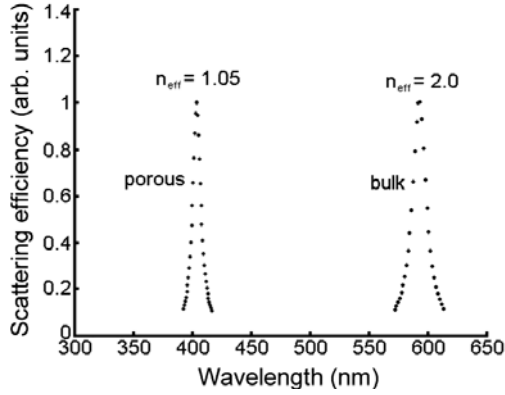


Fig. 4. Spectral dependence of the scattering efficiency of small Ag particles incorporated in media with different values of the refractive index.

One can explain the value of $n_{\text{eff}} = 2.0$ for the case of metallic particles on the bulk GaP substrate by the fact that each particle resides with a half of the surface on the substrate with $n = 3.4$, while another half of the surface is in air ($n = 1$).

The value of $n_{\text{eff}} = 1.05$ obtained for the porous GaP template is in contrast with the one deduced according to the Maxwell-Garnett effective medium theory [11, 12] for a GaP porous medium with the morphology shown in Fig. 1. This is understood, since the effective medium theory is not valid for the characteristic sizes of the porous entity comparable with the wavelength of light. For explaining the too low value of the n_{eff} we used an approach based on the analysis of photon density of states similar to the electron density of states applied in crystals and amorphous solids [13]. Actually, the considered porous template represents a 2D photonic crystal in the depth of the porous layer, and an amorphous photonic crystal in the near-surface regions. One should note that the analysis based on the density of states is applicable both for crystals and amorphous media, while the band-structure is suitable only for crystals. The photon density of states bears enough information for the determination of the wavelength dependence of the effective refractive index of the porous system, including the disordered one.

The photon density of states is determined by “counting” all allowed states with a given wavelength [14]:

$$\rho(\lambda) = (C/\lambda^2) \sum [\delta(\omega - \omega(j,k))] d^3k \quad (2)$$

where C is a constant, $\omega = 2\pi/\lambda$ is the frequency of the electromagnetic radiation, k is the wave vector, and $\omega(j,k)$ are the branches of the photonic band structure. The integral is over the first BZ of a Dirac- δ function, and the sum is over all branches of the photonic band structure.

For a homogeneous medium with the index of refraction n , the wavelength dependence of the density of states is a monotonous function

$$\rho(\lambda) = Cn^3/\lambda^4 \quad (3)$$

where C is a constant.

The local change of the density of states for a certain medium leads to a significant change of the scattering efficiency of the incident radiation, since the variation of the density of states means the respective variation of the effective refractive index:

$$n_{\text{eff}} = C'\lambda^{4/3}\rho(\lambda)^{1/3} \quad (4)$$

The wavelength dependence of the photon density of states for a porous GaP template with the morphology shown in Fig. 1 calculated according to the relation (2) is presented in Fig. 5. The density of states for a homogeneous medium with $n = 3.4$ (a bulk GaP substrate) and $n = 1$ (air) is shown for the calibration.

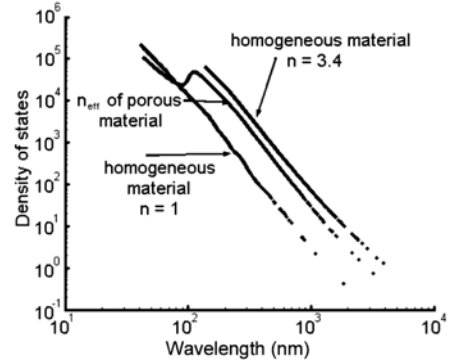


Fig. 5. Wavelength dependence of the photonic density of states for a porous GaP template, a bulk GaP substrate, and the air.

The spectral dependence of the photon density of states for the porous template is represented by a line with a maximum at wavelength nearly equal to the diameter of pores. One should note that the calculations of the photonic density of states in a 2D photonic crystal for the photons propagating perpendicular to the optical axis

revealed a series of features due to van Hove singularities [14]. The rather monotonous dependence of the density of states in our case is due to accounting the photons propagating in all the directions.

One can see that for long wavelength the photon density of states of the porous template, and respectively the refractive index, is in between the values corresponding to bulk GaP and air. For long wavelength the refractive index of the porous template can be deduced from the effective medium theory. With decreasing the wavelength, the density of states for the porous template approaches that of the bulk material, and for the wavelength comparable with the diameter of pores a sharp transition to values characteristic for air occurs. That means that for short wavelength the effective refractive index of the porous template has the value around 1, or it can be even smaller than 1, since the density of states for the porous template for short wavelengths is lower than that of air. The results of these calculations corroborate the low value of the effective refractive index of the porous template deduced from the comparison of Fig. 3 and Fig. 4. The broader shape of the plasmon resonance peak in the experimental spectrum as well as the presence of a shoulder at short wavelengths can be explained by the deviation of the form of the metallic particles from a spherical one, or/and by a partial oxidation of the metallic particle during technological processing. This suggestion is supported by the calculation of the dependence of the position of the plasmon resonance peak on the effective refractive index of the porous template for three types of metallic nanoparticles (Fig. 6).

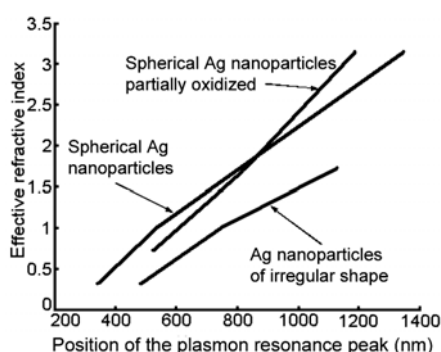


Fig. 6. Dependence of the position of the plasmon resonance peak on the effective refractive index of the porous template for various metallic nanoparticles.

One can see from Fig. 6 that the wavelength of the plasmon resonance is different for the same value of the refractive index of the porous template for different Ag nanoparticles. Therefore, the variation of the shape of metallic nanoparticles as well as their oxidation may explain the broadening of the plasmon resonance peak.

4. CONCLUSIONS

The results of this study demonstrate that porous semiconductor templates provide wide possibilities for the control of the surface plasmon resonance frequency of metallic nanoparticles, since the effective refractive index of the template can be varied from the value of the bulk material refractive index to values around 1 or even lower than 1 by tailoring the morphology and porosity, while the plasmon resonance frequency of metallic nanoparticles is highly sensitive to the refractive index of the medium they are incorporated into.

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