PLD creation of Au and Ag plasmonic nanoparticles

A.A. Lotin[a], O.A. Novodvorsky[a], L.S. Parshina[a], O.D. Khramova[a],

V.A. Mikhalevsky[a], E.A. Cherebilo[a]

[a] *ILIT RAS - Branch of the Federal Scientific Research Center "Crystallography and Photonics" RAS, 140700, 1 Svyatoozerskaya street, Shatura, Russia*

Abstract

The gold and silver plasmonic nanoparticles have been synthesized on the c-sapphire and silica substrates by the pulsed laser deposition method. It has been demonstrated that the variation of the thickness of as-grown gold and silver films permits producing the plasmon nanoparticles with different size and density. It provides the retuning of the frequency of surface plasmon resonance in wide spectral region.

Keywords: plasmonic nanoparticles; surface plasmon resonance, pulsed laser deposition

1. Introduction

Metal nanoparticles are a subject of study for owing to their unique optical, electrical and catalytic properties [1]. The small values of permittivity of these metals allow observing the effect of the surface plasmon resonance (SPR) in the visible range of the spectrum [2]. The most popular methods of plasmon nanoparticles synthesis are sedimentation from colloidal solutions [3] and the laser ablation of solid-state targets in liquids [4]. However, there are problems for which synthesis of nanoparticles under high vacuum is necessary, for example, production of thin luminescent films [5] and optoelectronic devices on their basis [6] with application of the effect of SPR for luminescence amplification, when the methods of nanoparticles synthesis described above can not be used. Therefore the goal of our work is the fabrication of nanoparticles of gold and silver with controlled sizes and density and the investigation of their optical properties for purposes of nanophotonics and nanoplasmonics.

2. Experimental details

Previously, the step thin films of gold and silver were fabricated on the c-sapphire and p-Si (100) epi-ready substrates by the pulsed laser deposition method. The step variation of metal film thickness was carried out with the special device [7] developed by us. The details of the synthesis of step structures are given in work [8]. The step films were further heated to the temperature of (700±2)° C; as the result of recondensation the gold and silver nanoparticles were formed on the substrate surface [9]. The sequence of nanoparticles formation process is illustrated by fig. 1. The morphology and the cross-sectional sizes of the metal nanoparticles were studied by the scanning electronic microscopy (SEM) in the case of a conductive p-Si substrate. The sizes of nanoparticles synthesized on a dielectric sapphire substrate were estimated by the atomic force microscopy (AFM). The transmission spectra T(λ) of the gold and silver nanoparticles were investigated by the UV-visible spectrophotometer Cary-50 (200−1100 nm, Δλ=1.5 nm). The spectra were measured in the mode of subtraction of the substrate optical density, therefore they only characterize the absorbing and scattering properties of the arrays of metal nanoparticles.

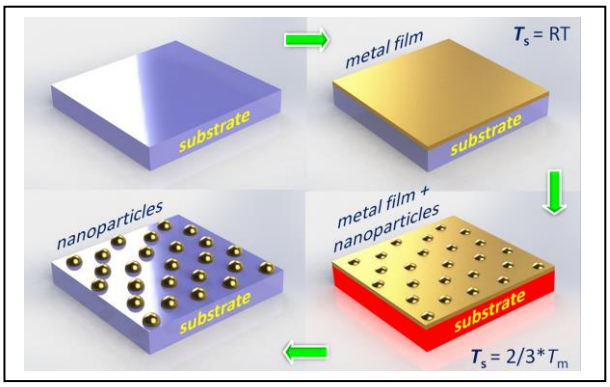
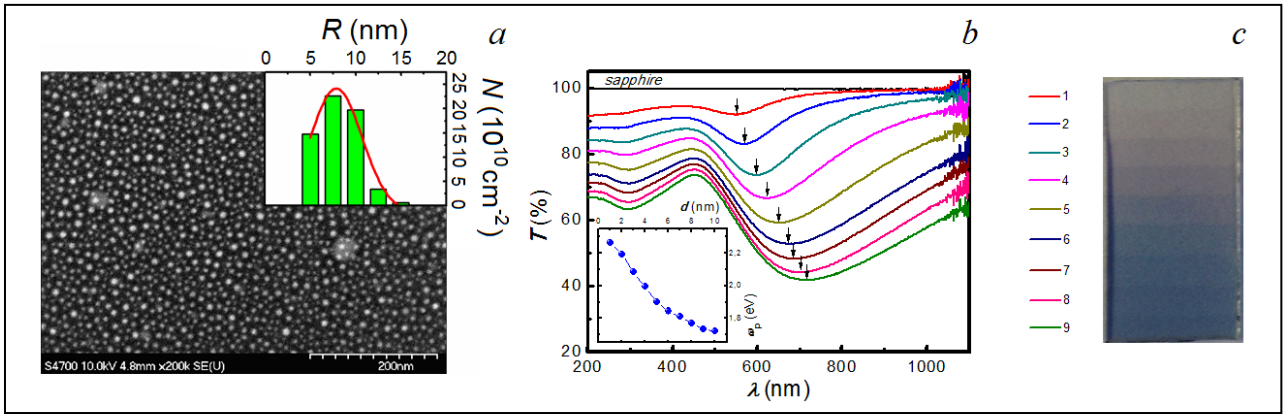


Fig.1. The schematic representation of the stages of nanoparticles formation.

3. Results and discussion

The series of gold and silver thin films in the range of thicknesses from 1 nm to 10 nm have been grown. The nanoparticles were formed from the films on the substrate surface after post-growth annealing. Figure 2 represents the image of gold nanoparticles on a *p*-Si (100) surface obtained by the scanning electronic microscopy (SEM). The histogram of Au nanoparticles size distribution constructed by the results of the statistical analysis of the SEM-image is given in an insert of fig. 2. The

distribution maximum R0, i.e. the average size of nanoparticles, and its dispersion w have been defined by approximation of the histogram by Gaussian function and have made 7.8 nm and 8.9 nm respectively. From fig. 2b it is evident that the extremum in the visible area of the spectrum corresponding to a plasmon resonance monotonously shifts to the red area from ω_p=2.21 eV (561



nm) for d=1 nm to ω_p=1.72 eV (721 nm) for d=9 nm.

Fig.2. *a* - The SEM image and the histogram of the size distribution (an insert) of the gold nanoparticles on a p-Si surface (100). *b* – The transmission spectra of Au nanoparticles synthesized on a c-Al2O3 substrate and the dependence of the spectral position ωp of the plasmon peak on the thickness d of the initial film (an insert). *c* - The photo of the Au nanoparticles step structure.

The AFM-images of the silver nanoparticles synthesized on a sapphire substrate at the thicknesses d 1 nm (*a*) and 10 nm (*b*) of the initial Ag film are presented in fig. 3. As in the case of gold, the cross-section size R of silver nanoparticles increases, and their density N seduces as the thickness of the initial Ag film grows. As illustrated in fig. 3*b*, at the initial film thickness of 10 nm the Ag nanoparticles are densely packed, however the film produced from these particles does not conduct the electric current. The histogram of Ag nanoparticles size distribution approximated by Gaussian function is given in an insert of fig. 3*a*. The maximum of distribution is R_0 = 46.1 nm, and its dispersion is w = 31.6 nm. For the film of silver nanoparticles the SPR band position shifted to the red area from ω_p=2.7 eV (460 nm) to ω_p=2.33 eV (532 nm) with increasing of the thickness d of the initial Ag film and, therefore, of the average nanoparticles size R from 1 nm to 10 nm (fig. 3*c*). The insert of fig. 3*c* shows that the full width on a half maximum of the plasmon band in the transmission spectra is increased while the thickness d of the initial Ag film grows from 0.704 eV to 1.15 eV, is apparently caused by the growth dispersion w of nanoparticles density on the substrate surface.

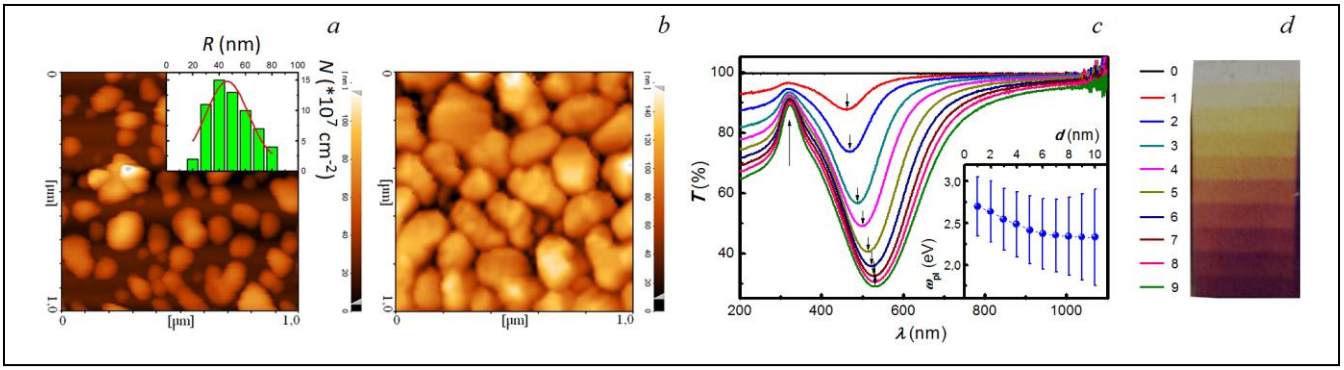


Fig.3. The AFM-images of the Ag nanoparticles on a sapphire substrate surface with the thickness d of the initial Ag film of: a – 1 nm and b – 10 nm. The histogram of Ag nanoparticles size distribution is given in an insert. The red line – the approximation curve. c – The transmission spectra of the silver nanoparticles and the spectral position of the plasmon absorption peak with its FWHM (insert) depending on the thickness d of the initial Ag film produced on the c-sapphire substrate. d – A photo of Ag nanoparticles step structure.

4. Conclusion

It has been demonstrated, that the variation of the thickness of as-grown gold and silver films permits controlling the plasmon nanoparticles size. It gives a possibility to retune the plasmon oscillation frequency that will allow fabricating highly effective optoelectronics devices based on surface plasmon resonance.

This research was supported by the Russian Foundation for Basic Research projects № 15-07-03331, № 15-29-01171-ofi-m, № 15-38-20369-mol-a-ved.

References

[1] Berini. Surface plasmon-polariton amplifiers and lasers / I. De Leon // Nature Photonics – 2011. – Vol. 6. - P. 16-24.

[2] Jin, R. Controlling anisotropic nanoparticle growth through plasmon excitation / Y.C. Cao, E. Hao, G.S. Métraux, G.C. Schatz, C.A. Mirkin // Nature – 2003. – Vol. 425. – P. 487.

[3] Yong, K.T. Preparation of gold nanoparticles and their applications in anisotropic nanoparticle synthesis and bioimaging / M.T. Swihart, H. Ding, P.N. Prasad // Plasmonics – 2009. – Vol. 4. – P. 79.
[4] Amendola, V. Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles / M. Meneghetti // Phys. Chem. Chem. Phys. – 2009. – Vol. 11. – P. 3805-3821.
[5] Simakin, A.V. Nanoparticles produced by laser ablation of solids in liquid environment / V.V. Voronov, N.A. Kirichenko, G.A. Shafeev // Appl. Phys. A – 2004. – Vol. 79. – P. 1127.
[6] Shim, J.-Ph. A self-assembled Ag nanoparticle agglomeration process on graphene for enhanced light output in GaN-based LEDs / DoH. Kim, M. Choe, T. Lee, S.-J. Park and D.-S. Lee // Nanotechnology – 2012. – Vol. 23. – P. 255201.
[7] Lotin, A.A. Device for pulsed laser deposition of nanostructural materials / O.A. Novodvorsky, D.A. Zuev // Pat. RF № 135638; 20.12.2013.
[8] Lotin, A.A. Dimensional effects in exciton and defect-related luminescence of ZnO-based step quantum wells / O.A. Novodvorsky // Las. Phys. Lett. – 2015. – Vol. 12(9). – P. 095901.
[9] Cherebilo, E.A. Optical properties of Au and Ag nanoparticles produced by PLD / A.A. Lotin, D.A. Zuev, A.V. Shorokhova, O.A. Novodvorsky, O.D. Khramova // ICONO/LAT, Technical Digest. 2013. – P. 59.