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Optical properties of gold nanostructures obtained with laser methods

E.B. Kaganovich, I.M. Kizyak, A.A. Kudryavtsev, E.G. Manoilov, Ye.V. Begun
V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prospect Nauky, 03028 Kyiv, Ukraine
E -mail: dept_5@isp.kiev.ua

Abstract. Adduced in this paper are the visible range transmission spectra of thin gold films as well as those for films of aluminum and silicon oxides containing gold nanoparticles prepared by pulse laser deposition in vacuum. Besides, shown here are the spectra of colloidal gold particles obtained by laser ablation in liquids. Ascertained are the conditions providing creation of gold nanostructures, in extinction spectra of which one can observe a resonance band related with local surface plasmons.

Keywords: gold nanostructures, laser ablation, extinction spectra, surface plasmons.

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1. Introduction

One of characteristic features inherent to optical properties of noble metals is resonant bands in extinction spectra that are related with local surface plasmons – collective oscillations of conduction electrons. On the one hand, interest to these nanostructures is based on studying the effects caused by diminishing these objects down to nanosizes on their optical properties; on the other hand, it is related with variety of their practical applications in non-linear optics, sensorics, in enhancing the Raman scattering, IR absorption, photoluminescence of radiators, *etc.* Optical properties of gold and silver nanostructures depend on sizes of nanoparticles (NP) (clusters), their shape and dielectric surrounding, which provides opportunities to control these properties. To study the surface plasmon resonance (SPR) in gold nanostructures, investigators prepared free clusters, island (granular) films, composite films containing Au NP in dielectric matrix, rough films with developed microrelief [1-9].

As compared to various methods providing creation of nanostructures, namely: chemical, plasmochemical, magnetron sputtering, ion implantation, the method of pulse laser deposition (PLD) in vacuum was paid poor attention to. But it has a set of advantages related with congruence of the process aimed at creation of composite films, flexibility of controlling the deposition parameters, illumination of a target, its composition, pressure of operation gas in a chamber. The PLD method provides obtaining the films containing nanocrystals, clusters, their aggregates with specified parameters, shape, concentration in various dielectric matrixes. Moreover, the lack of this method related with formation of drops on condensate surfaces or formation of rough surfaces can be used when studying the influence of morphology and developed microrelief on features of surface plasmons. As an example, the method of laser ablation in liquids was successfully used to obtain colloid gold particles [10-12].

The aim of this work is to study the influence of conditions providing preparation of gold nanostructures by using the laser methods on extinction spectra with SPR bands.

2. Experiment

The gold nanostructures were formed as films with the PLD method in vacuum as well as colloidal particles with the method of laser ablation in liquids. The PLD method allowed preparation of thin rough gold films by deposition using a forward high-energy flow of particles from the erosion torch and composite films containing gold nanoparticles in dielectric matrixes of aluminum and silicon oxides by deposition from the backward low-energy particle flow. We used glass and silica substrates. YAG:Nd^{3+} laser beam (wavelength 1.06 μm, pulse energy 0.2 J, pulse duration 10 ns and pulse frequency 25 Hz) scanned the target in a vacuum chamber with the argon pressure 10 to 20 Pa. When obtaining the gold

films, the substrate was located normally to the torch axis at the distance 20 to 25 mm from the Au target. When forming the composite films, the substrate was located in the target plane, and target contained gold and aluminum or silicon pieces. The gold volume fraction in the target was changed within the range of 1 up to 100 %. The energy density for illumination of the target was varied from 5 up to 20 J/cm^2. Some films were subjected to thermal treatment in air at the temperature 400 °C for 10 min.

When the laser beam irradiates the target, there arises plasma consisting of atoms, ions and clusters of target material. The following adiabatic expansion of plasma in the form of an erosion torch results in interaction of the torch particles with atoms of operating gas and dissipation of their energy. Energy losses are rather weak during deposition from forward particle flow but essentially stronger in braking processes with reverse motion of particles to the substrate when depositing them from backward particle flow. In the latter case, one deals with separation of gold particles by their sizes: larger particles are deposited closer to the erosion torch axis, and the smaller ones are located further. The thickness of films was reached within the range 5 – 500 nm. The thickness profile of the films prepared on the substrate lying in the target plane was of a wedge shape.

Using the method of scanning atomic-force microscopy in the tapping mode, we have ascertained that the surface of gold films deposited from the forward particle flow is rough, sizes of grains lie within the range 10 to 100 nm, the size distribution is rather wide. The surface of films deposited from the backward flow is homogeneous, one can observe a large number of pores. Grain sizes are 10 to 20 nm. In accord with the data of X-ray phase analysis, there are present the amorphous phase of aluminum or silicon oxides along with X-ray amorphous and cubic phases of gold NP.

Colloidal gold nanoparticles were prepared using the method of laser ablation with the Au target and laser used in the PLD method in a silica cell filled with distilled water, ethanol, water solutions of citric acid and sodium citrate. The typical volume of liquid was 2 ml, gold concentration was close to 0.4 mg/cm^3. The rate of gold sputtering was 1.2 and 3.2 mg per hour for the energy density used to irradiate the target 5 and 20 J/cm^2, respectively.

When using laser ablation of solids in liquids, the free path of molecules is several orders less than that in vacuum. Nanoparticles experience collisions with vapors of surrounding liquid being at pressures of hundred atmospheres. Size distribution of nanoparticles and their shape are determined by their convective motion as well as possibilities of repeated action of radiation on them. The shape of particles is spherical, as a rule.

Transmission spectra of the obtained films and colloidal nanoparticles were measured using the spectrophotometer СФ-26 within the wavelength range 350 to 1200 nm.

3. Results and discussion

Shown in Fig. 1 are the transmission spectra of gold films prepared with the forward particle flow. The films differ by their thickness and energy density used to irradiate the target in the deposition process. One can see typical wide extinction bands related with surface plasmons. The transmission curve minima are located within the range 620 to 700 nm. With decreasing the film thickness and energy for target irradiation, band minimum positions are shifted to the blue side of the spectrum. The observed features correspond to the expected ones, as the investigated object is some rough gold surface and not a spherical nanoparticle, and the film roughness and cluster sizes on the surface decrease with the film thickness and energy of target irradiation. It is known (see, for instance [1-6]) that with decreasing the Au cluster sizes the minimum of transmission bands related with local SPR shifts to the blue side of spectrum and becomes wider. Some part of this widening is also determined by dispersion of cluster sizes at the film surface. The said above is well confirmed by the results of an additional experiment when the transmission spectrum minimum of the annealed gold film shifted to the shortwave range (550 nm), and its extinction band became more narrow (Fig. 1, curve 4′). Indeed, we have ascertained that annealing results in re-crystallization of clusters (de-aggregation in this regime), in decreasing of cluster sizes and smoothing the film surface relief.

Fig. 2 shows the transmission spectra of gold films obtained using the backward flow of particles from the erosion torch. Here, the films differ by their thickness, cluster sizes and energy density for target irradiation. These films are characterized with considerable porosity but more uniform surface and possess spectra typical for local surface plasmons. As seen from Fig. 2, decrease in cluster sizes (as a consequence of moving the substrate

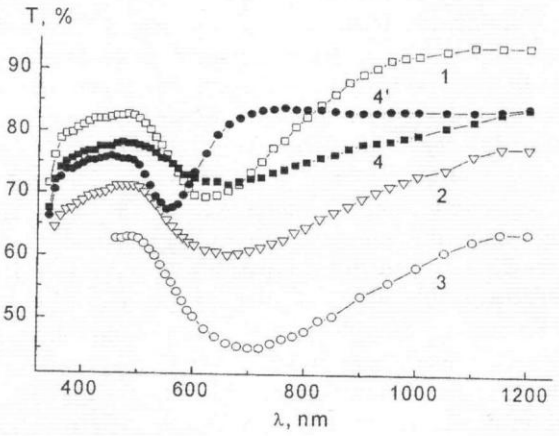

Fig. 1. Transmission spectra of gold films prepared using the forward particle flow from the erosion torch for different values of the film thickness d, nm: *1*, *4* – 5; *2* – 10; *3* – 20, and two values of the density for target irradiation energy j, J/cm^2: *1*, *2*, *3* – 5; *4* – 20. The curve *4′* describes the annealed film 4.

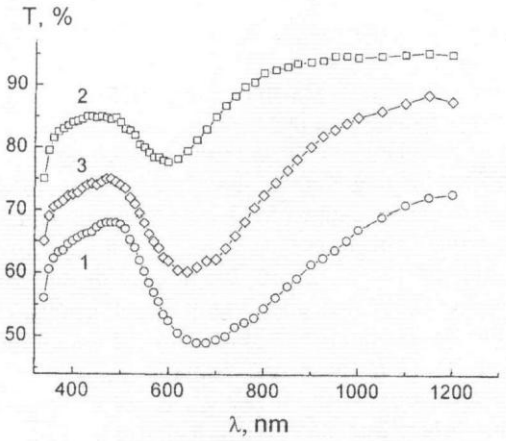

Fig. 2. Transmission spectra of gold films prepared using the backward particle flow from the erosion torch and differing by the conditions of their deposition (j, J/cm^2: *1*, *2* – 5; *3* – 20, and the distance of the substrate from the torch axis l, mm: *1* – 5; *2*, *3* – 15). P_{Ar} = 13.5 Pa.

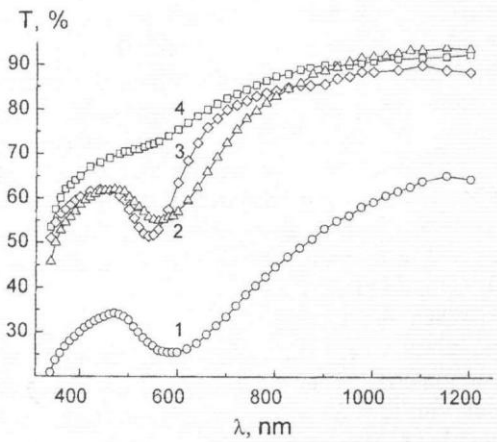

Fig. 3. Transmission spectra of Al_2O_3 films containing gold nanoparticles prepared at j = 20 J/cm^2 and the gold concentration in the target C_{Au} = 25 %, which differ by the value l, mm: *1* – 5; *2* – 15. The curves *4* and *3* correspond to the films obtained at j = 5 J/cm^2, C_{Au} = 50 %, l = 15 mm before and after annealing, respectively.

away from the torch axis) and in target irradiation energy results in a blue shift of transmission band minima. The films with higher thickness, larger cluster sizes and wider their dispersion are characterized with wider transmission bands. Thus, the gold films prepared in above conditions of PLD show local SPR. It can be explained that the obtained films are characterized either by highly developed surface microrelief or structure similar to granular films owing to their considerable porosity.

At the next stage, we investigated composite films of the following composition: aluminum or silicon oxides with Au NP obtained by deposition using the backward flow of particles from the erosion torch. In the films of Al_2O_3 with Au NP obtained using the irradiation energy density 20 J/cm^2, plasma resonance was observed only for the gold concentration in the target higher than 20 % (Fig. 3). As seen from this figure (curves 1 and 2), the transmission band minima are located within the range 550 – 580 nm, that is in more shortwave range than those in pure gold films. As it was expected, with decreasing the Au NP sizes the transmission minimum shifts to the shortwave side. When the gold concentration in the target was less than 20 %, sizes of Au NP were too small to observe SPR. They were also small when the energy density for irradiation of the target was less than 20 J/cm^2 (see Fig. 3, curve 4). But in the latter case the bands of plasmon resonance appeared after annealing. And the position of the band minimum was no longer than 540 nm, while the band was symmetric and narrow (see Fig. 3, curve 3). It is related with coalescence, increase of Au NP in their sizes and tendency of their shape to be close to spherical.

Adduced in Fig. 4 are the transmission spectra of SiO_x films containing Au NP. Plasmon resonance was observed in transmission spectra of these films only after exposing them for more than two days in ambient atmosphere. It is explained by the fact that dielectric properties of the matrix change with time not only due to supplementary oxidizing the non-stoichiometric phase SiO_x up to SiO_2, but mainly owing to decrease in film porosity when pores are filled with oxide in the course of oxidation observed for silicon nanocrystals. With increasing the exposure time up to one month, local surface plasmons became more pronounced. That confirms the influence of dielectric surrounding on the extinction bands inherent to Au NP. With increasing time of keeping the films in air, transmission band minima shifted to the longwave spectral range (just compare curves 4, 5 with 4′, 5′ in Fig. 4). These data correlate well with results of other authors (see, e.g. [8]),

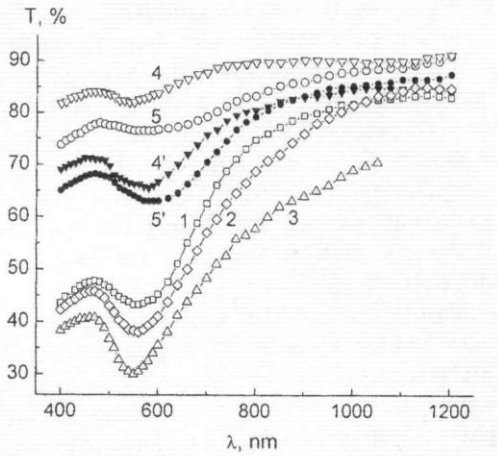

Fig. 4. Transmission spectra of SiO_2 films containing Au NP prepared at j = 20 J/cm^2, l = 5 mm, which differ by the value C_{Au}, %: *1* – 10; *2* – 20; *3* – 50. The curves *4* and *5* correspond to the films obtained at j = 20 J/cm^2, C_{Au} = 5 %, which differ by the value l: l = 18 mm (curves *4*, *4′*) and l = 10 mm (curves *5*, *5′*) after exposing them in air for time t, days: 2 (curves *4*, *5*) and 30 (curves *4′*, *5′*). d = 200 nm.

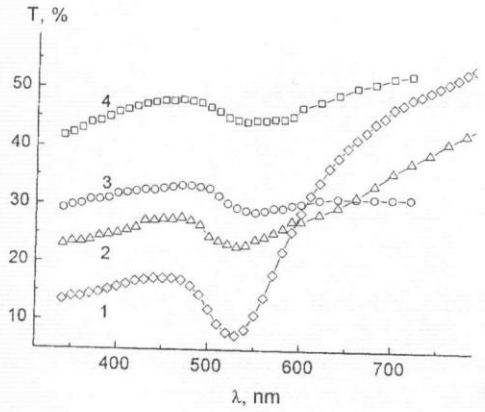

Fig. 5. Transmission spectra of colloidal Au NP prepared in distilled water (*1*), ethanol (*2*), 30 % water solutions of sodium citrate (*3*) and citric acid (*4*). j = 20 J/cm^2.

who showed that growth of the dielectric constant value for the medium surrounding the Au NP causes a shift of their extinction peak into the longwave spectral range. When the gold fraction in the target increases from 1 up to 10 %, the amplitude of the resonance peak is enhanced, band minima are shifted from 650 down to 550 nm, and the bands become narrower.

Gold colloidal nanoparticles prepared using laser ablation in water, ethanol, 30 % water solutions of citric acid and sodium citrate possess typical transmission spectra with extinction bands caused by local SPR (Fig. 5, curves 1 to 4). Transmission band minima are located within the range 520 – 550 nm and depend on dielectric properties of liquids. These spectra contain no longwave bands related to the particle shape that decline from the spherical one. The colloidal particles were formed under action of various irradiation energy densities within the range of 5 to 20 J/cm^2. In this set of densities, the position of transmission band minima changed insignificantly, but with decreasing the irradiation energy one could observe increased interaction of radiation with local surface plasmons.

4. Conclusions

Laser methods provide preparation of gold nanostructures, in optical transmission spectra of which one can observe the bands caused by local surface plasmon resonance. It has been shown that availability of local plasmons is related with roughness and porosity of gold films formed by pulse laser deposition by using, respectively, forward and backward particle flows from the erosion torch. We have determined the conditions for pulse laser deposition to obtain composite films of aluminum and silicon oxides with gold nanoparticles, plasmons of which are pronounced in optical transmission spectra. Laser ablation in liquids provides preparation of gold colloidal nanoparticles that cause the resonant extinction bands.

References

1. V. Kreibig, Optics of nanosized metals, Chapter 7, In: Handbook of Optical Properties, v. 2 // *Optics of Small Particles, Interfaces, and Surfaces*, Ed. by R.E. Hummel, P. Wißmann. CRC Press, 1997.
2. B. Palpant, B. Prevel, J. Lerme et al., Optical properties of gold clusters in the range 2-4 nm // *Phys. Rev. B* **57** (3), p. 1963-1970 (1998).
3. H. Hövel, S. Fritz, A. Hilger et al., Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping // *Phys. Rev. B* **48** (24), p. 18178-18188 (1993).
4. D. Dalacu, L. Martinu, Optical properties of discontinuous gold films: finite size effects // *JOSA* **18** (1), p. 85-92 (2001).
5. S. Link, M.A. El-Sayed, Shape and size dependence of radiative, non-radiative and photothermal properties of gold nanocrystals // *Int. Reviews in Phys. Chemistry* **19** (3), p. 409-453.
6. G. Fu, W. Cai, C. Kan et al, Controllable optical properties of Au/SiO_2 nanocomposite induced by ultrasonic irradiation and thermal annealing // *Appl. Phys. Lett.* **83** (1), p. 36-38 (2003).
7. Z. Liu, H. Wang, A. Li et al., Red shift of plasmon resonance frequency due to the interacting Ag nanoparticles embedded in single crystal SiO_2 by implantation // *Appl. Phys. Lett.* **72** (15), p. 1823-1825 (1998).
8. H. Liao, W. Wen, K.L. Wong, Photoluminescence from Au nanoparticles embedded in Au:oxide composite films // *JOSA B* **23** (12), p. 2518-2521 (2006).
9. E. Hutter, J.H. Fendler, Exploitation of localized surface plasmon resonance // *Adv. Matter* **16** (19), p. 1685-1706 (2004).
10. A.V. Kabashin, M. Meunier, Laser ablation-based synthesis of nanomaterials, In: *Recent Advances in Laser Processing of Materials*, Ed. by J. Perriere, E. Millon and E. Fogarassy. Elseveir Ltd, 2006.
11. E. Dulkeith, T. Niedereichholz, T.A. Klar, Plasmon emission in photoexcited gold nanoparticles // *Phys. Rev. B* **70**, p. 205424(4) (2004).
12. G. Zhu, V.I. Gavrilenko, M.A. Noginov, Emission of Au nanoparticles with and without rhodamine 6G dye // *J. Chem. Phys.* **127**, p. 104503-104511 (2007).