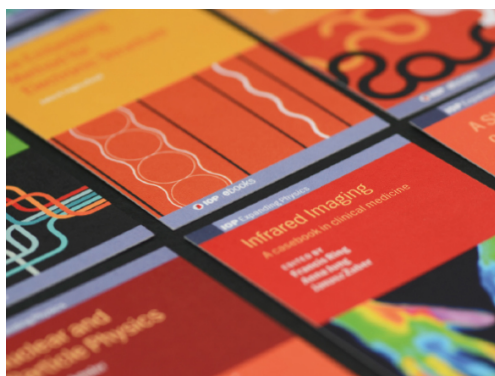


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The plasmonic nanoparticles with controlled optical properties

N N Eliseev¹, A S Kuz'mina², A G Putilov¹, A E Shepelev¹, S M Arakelian³, A A Lotin¹

¹ILIT RAS – Branch of the FSRC «Crystallography and Photonics» RAS, Svyatoozerskaya 1, 140700, Shatura, Moscow Region, Russia

²Irkutsk National Research Technical University, 664074, Irkutsk, Russia

³Vladimir State University, Gorkii St 87, Vladimir, 600000, Russia

lotin_82@mail.ru

Abstract. The gold and silver plasmon nanoparticles have been synthesized on the *c*-sapphire and *p*-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.

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 this 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) epitaxial substrates by the pulsed laser deposition method. The step variation of metal film thickness was carried out with the special device [7] developed by our team. The details of the synthesis of step structures are given in work [8]. The step films were further heated to the temperature of $(700 \pm 2)^\circ \text{C}$; 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 $T(\lambda)$ of the gold and silver nanoparticles were investigated by the UV-visible spectrophotometer Cary-



50 (200–1100 nm, $\Delta\lambda=1.5$ 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.

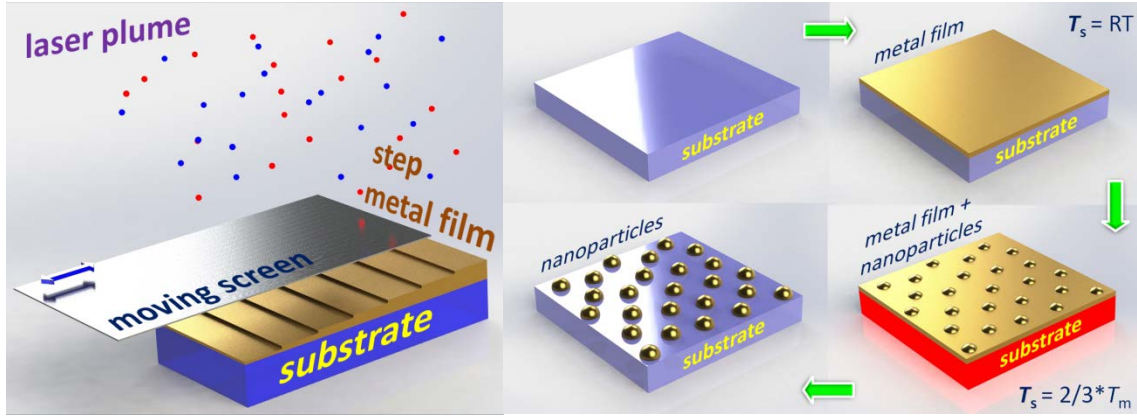


Fig.1. The schematic representation of the nanoparticles formation stages.

3. Results and discussion

Formation of nanoparticles on a substrate surface by post-growth annealing can be described qualitatively in terms of a tension of a metal surface and interface [9]. The surface tension γ is defined as force operating per length unit of interface. Let consider a contact point between a metal drop and a substrate (fig. 2). If the angle of wetting is equal φ , then balance of forces can be written as following ratio:

$$\gamma_S = \gamma_{S/F} + \gamma_F \cos \varphi, \quad (1)$$

where γ_S – the tension of substrate surface, γ_F – the tension of metal droplet surface, a $\gamma_{S/F}$ – the tension of interface “droplet/substrate”, and φ – the wetting angle. Expression (1) gives balance of forces operating along a substrate surface.

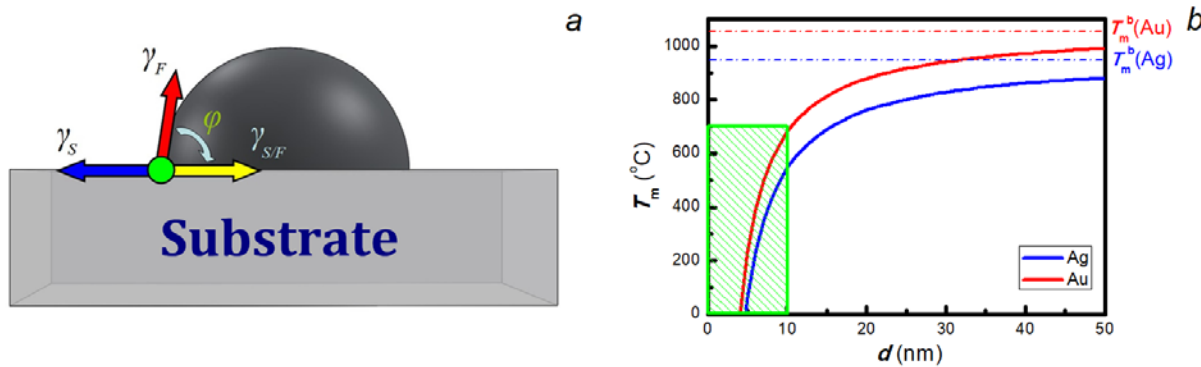


Fig. 2. *a* - The schematic image of metal droplet on substrate and surface tension vectors: γ_S – the tension of substrate surface, γ_F – the tension of metal droplet surface, a $\gamma_{S/F}$ – the tension of interface “droplet/substrate”, φ – the wetting angle. *b* – The calculated dependence of melting temperature T_m of thin Au and Ag films on their thickness d . The green zone is film thickness area suitable for formation plasmonic nanoparticles.

In the case:

$$\gamma_S \geq \gamma_{S/F} + \gamma_F \quad (\text{the condition of thin film formation}), \quad (2)$$

the droplet spreads in a thin film. The condition $\varphi < 0$ is necessary to shape the droplet and, therefore, the corresponding in equation has the appearance:

$$\gamma_S \leq \gamma_{S/F} + \gamma_F \quad (\text{the condition of droplet formation}). \quad (3)$$

In this case liquid doesn't wet a substrate surface.

The melting temperature T_m of nanoscale thin metal films is much lower than melting temperature of the volume materials T_b and its dependence on film thickness d can be defined by the following expression [10]:

$$T_m(d) = T_b \left[1 - \frac{4}{\rho_s \lambda} \left(\eta_s - \eta_l \left(\frac{\rho_s}{\rho_l} \right)^{2/3} \right) \frac{1}{d} \right] \quad (4)$$

where λ – the warmth of melting, ρ and η – the density and free energy of a solid state (s) and liquid (l). For platinum these constants are following: $T_b=960.7$ °C; $\lambda=1.06 \times 10^2$ J/g; $\rho_s=10.49$ g/cm³; $\rho_l=9.35$ g/cm³; $\eta_s=1.84 \times 10^{-3}$ N/cm; $\eta_l=9.1 \times 10^{-3}$ N/cm. For gold are following: $T_b=1064$ °C; $\lambda=6.6 \times 10^2$ J/g; $\rho_s=19.3$ g/cm³; $\rho_l=17.1$ g/cm³; $\eta_s=2.34 \times 10^{-3}$ N/cm; $\eta_l=1.1 \times 10^{-2}$ N/cm. The figure 2b represents the theoretical dependences of the melting temperature T_m of thin Au and Ag films on their thickness d calculated by equation (4).

The series of gold and silver thin films in the range of thicknesses from 1 nm to 12 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 fig. 3.

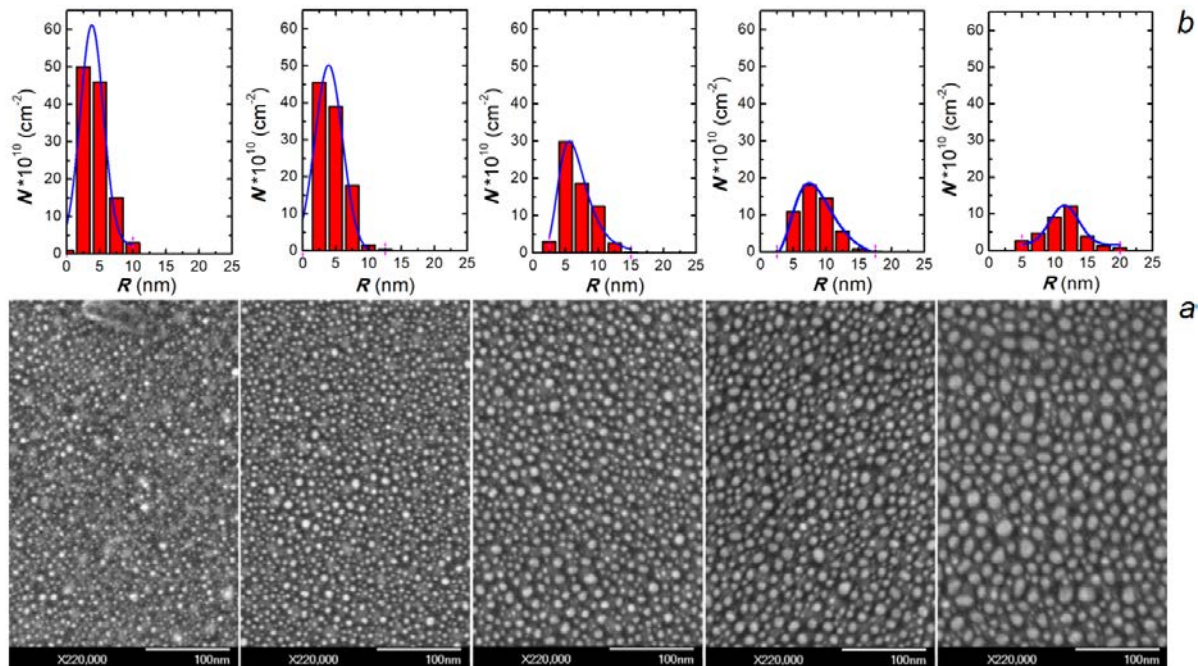


Fig. 3. The SEM images (a) and the histograms of the size distribution (b) of the gold nanoparticles on a *p*-Si surface (100).

The distribution maximum R , i.e. the average size of nanoparticles, and its dispersion w have been defined by approximation of the histogram by Gaussian function. The average size of Au nanoparticles is increased from 3.7 nm to 11.6 nm while the initial film thickness grew up from 1 nm to 12 nm (fig.4a). From fig. 4b and 4c 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 $\omega_p=2.28$ eV for nanoparticles with average size $R=3.7$ nm to $\omega_p=1.9$ eV for $R=11.6$ nm.

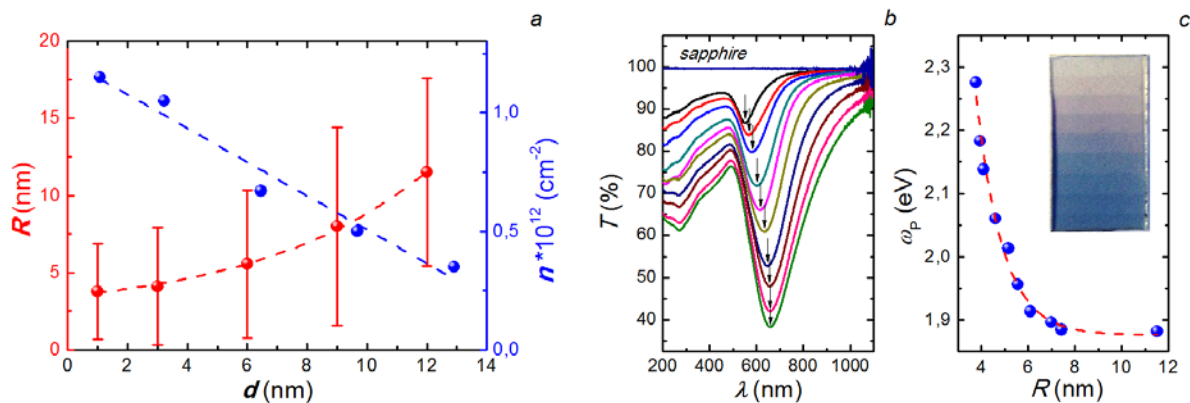


Fig. 4. *a* – The dependences of average size R and density n of Au nanoparticles on the initial d film thickness. *b* – The transmission spectra of Au nanoparticles synthesized on a c -Al₂O₃ substrate. *c* – The dependence of the spectral position ω_p of the plasmon peak on the average size of Au nanoparticles (an insert - the photo of the Au nanoparticles step structure).

The SEM-images of the silver nanoparticles synthesized on p -Si substrate are presented in fig. 5a. 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. For the silver nanoparticles the SPR band position shifted to the red area from $\omega_p=2.82$ eV to $\omega_p=2.36$ eV with increasing of the average size R of Ag nanoparticles from 3.7 nm to 13.5 nm (fig. 5c). The insert of fig. 5c shows the photo of the Ag nanoparticles step structure. The plasmonic spectral band in the transmission spectra is increased while the average size of Ag nanoparticles grew up from 1 nm to 12 nm. It is apparently caused by the growing of dispersion w of nanoparticles density on the substrate surface.

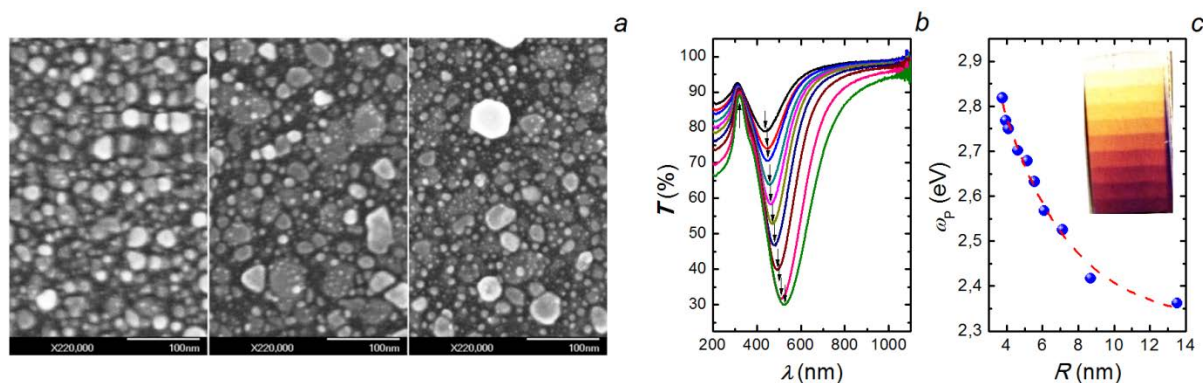


Fig. 5. The typical SEM-images of the Ag nanoparticles on a p -Si substrate (100). *b* – The transmission spectra of the silver nanoparticles (*b*) and the spectral position of the plasmon absorption peak (*c*) depending on the average size of Ag nanoparticles produced on the c -sapphire substrate (an insert - the photo of the 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.

5. Acknowledgment

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