



Effect of technological parameters on properties of Ag plasmonic structures prepared on garnet substrates

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Abstract

In this work technological aspects of preparation of silver nanostructures and their plasmonic properties are studied. The plasmonic structures were prepared on single-crystalline YAG and GGG garnets as well as amorphous glass substrates by the magnetron sputtering technique. Nucleation and growth of Ag nanoparticles (NP) was controlled by a thermal annealing process. Two broad absorption bands peaked at 350-370 nm and 440-650 nm were observed due to quadrupole and dipole modes, respectively, of surface plasmon resonance (SPR) of Ag nanoparticles. Changes of the positions, intensities, and widths of these absorption bands related to the nanoparticle sizes, densities, and shapes are presented. Degradation of the plasmonic structures at ambient conditions, which is revealed as diminishing of the plasmonic absorption bands and associated with sulphidation of Ag nanoparticles in the natural environment, was studied in details. Theoretical simulations of the sulphidation process modelled as coating of Ag nanoparticles with silver sulphide (Ag₂S) film confirm the experimentally observed diminishing of SPR.

Motivation

The gadolinium gallium Gd₃Ga₅O₁₂ (GGG) and yttrium aluminium Y₃Al₅O₁₂ (YAG) garnets are well-known optical host materials with a wide range of applications, such as luminescent materials, phosphorescent coatings for LEDs, solid-state lasers, scintillators, etc. [1]. In recent years, several reports announced that similar phosphorescent materials have high photoluminescence (PL) enhancement (ratio from 3 to 100) due to silver nanostructures with plasmonic properties [2-4].

The present work is devoted to a detailed study of the effects of density, shape, and size of silver nanoparticles deposited on garnet substrates as well as the effects of thermal treatment on the plasmonic absorption of the structures. We also focused on a detailed study of the silver corrosion processes on SPR in the near ultraviolet and visible regions.

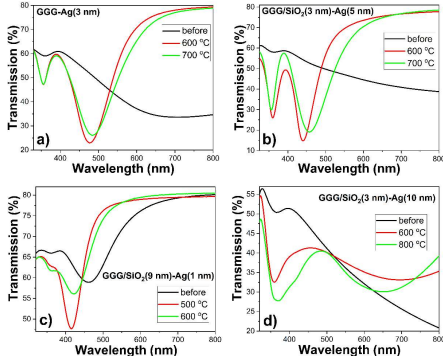
Methodology

Ag NPs as well as SiO₂ spacer layer on the garnet substrates were deposited (0.05 nm/s) by the vacuum magnetron sputtering method using a COM-TH2-SP2-ION combined sputtering equipment. Thus, the following samples were obtained:

Sample structure (mass thickness of the material)	Thermal annealing parameters
GGG – Ag (0.5 nm); GGG – Ag (1 nm); GGG – Ag (2 nm)	No thermal treatment
GGG/SiO ₂ (3 nm) – Ag (1 nm); GGG/SiO ₂ (6 nm) – Ag (1 nm); GGG/SiO ₂ (9 nm) – Ag (1 nm)	No thermal treatment
GGG – Ag (3 nm)	
GGG/SiO ₂ (3 nm) – Ag (5 nm)	T=600 °C, N ₂ atmosphere, time: 5 min
GGG/SiO ₂ (3 nm) – Ag (10 nm)	
GGG/SiO ₂ (9 nm) – Ag (1 nm)	
GGG – Ag (3 nm); GGG/SiO ₂ (3 nm) – Ag (5 nm)	T=700 °C, N ₂ atmosphere, time: 5 min
GGG/SiO ₂ (3 nm) – Ag (10 nm)	T=800 °C, N ₂ atmosphere, time: 5 min
GGG/SiO ₂ (9 nm) – Ag (1 nm)	T=300 °C, N ₂ atmosphere, time: 5–20 min
GGG/SiO ₂ (9 nm) – Ag (1 nm)	T=500 °C, N ₂ atmosphere, time: 5 min
GGG, YAG or Glass substrate/ SiO ₂ (10 nm) – Ag (10 nm)	T=500 °C, N ₂ atmosphere, time: 40 min

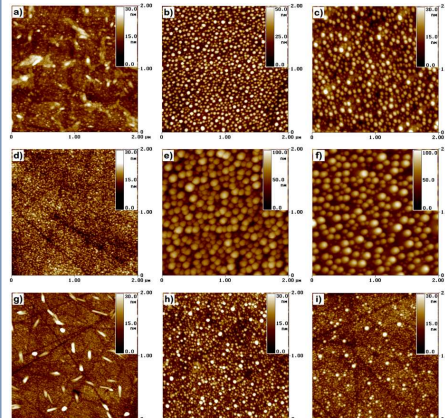
Impact of thermal annealing on Ag NPs structure

Direct transmission spectra before and after annealing.



Impact of thermal annealing on Ag NPs structure

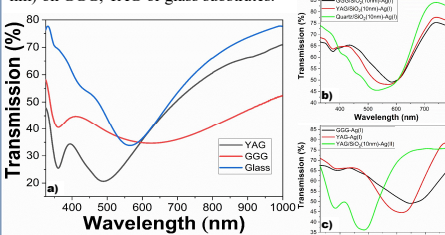
Corresponding AFM (2x2 μm) images of Ag NP morphology.



On this image: GGG – Ag (3 nm) (first row): a) – before annealing; b) – after annealing at 600 °C; c) – after annealing at 700 °C; GGG/SiO₂ (3 nm) – Ag (5 nm) (second row): d) – before annealing; e) – after annealing at 600 °C; f) – after annealing at 700 °C; GGG/SiO₂ (9 nm) – Ag (1 nm) (third row): g) – before annealing; h) – after annealing at 500 °C; i) – after annealing at 600 °C.

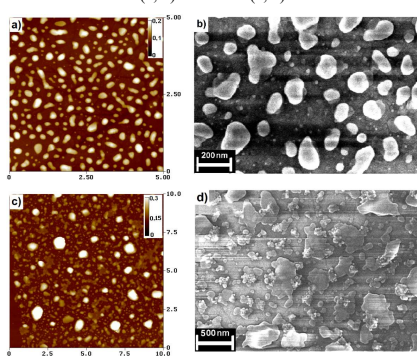
Effect of substrate on silver LSPR

Experimental (a) and simulation (b, c) results of transmission spectra of silver plasmonic structures (Ag mass thickness is 10 nm) on GGG, YAG or glass substrates.



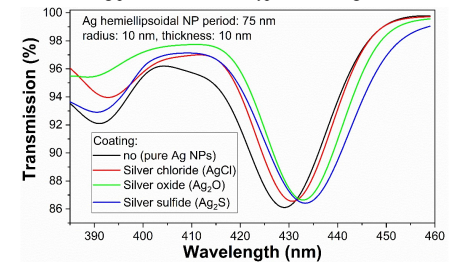
Ag(I) – NPs with average size 120x250 nm and height 75 nm; Ag(II) – NPs with average size 100x120 nm and height 50 nm.

AFM and SEM images of Ag NPs (Ag mass thickness is 10 nm) on YAG (a, b) and GGG (c, d) substrates

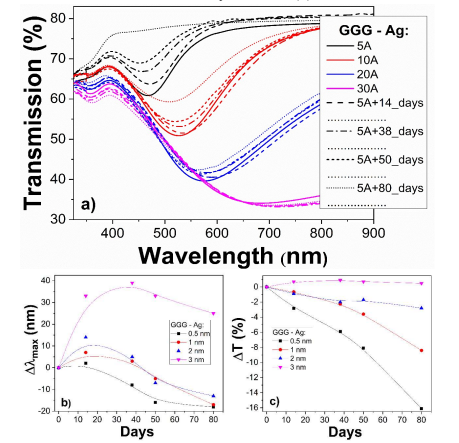


Conclusions

Transmission spectra simulation of an array of hemiellipsoidal Ag particles with three types of coatings



Time-dependent transmission spectra changes (a), spectral shift of the dipole mode plasmon resonance band maximum (b), and its intensity decrease (c)



Conclusions

Thermal annealing of the nanostructure in nitrogen atmosphere was shown to cause amplification and narrowing of the plasmon resonance bands for both dipole and quadrupole modes. The effective annealing temperature rises as the mass thickness of silver increases. Thus, for samples GGG/SiO₂ (9 nm) – Ag (1 nm) the optimum temperature of treatment is 400 – 500 °C, while for GGG/SiO₂ (3 nm) – Ag (5 nm) or GGG – Ag (3 nm) samples it rises up to 600 °C.

The differences in the optical properties of plasmon structures on the surface of GGG and YAG are shown, which are associated with the formation of the different structure of the SiO₂ spacer on the substrate surface, during its deposition and annealing of samples.

It was demonstrated that the degradation process of plasmonic structures was caused by step-by-step formation of several layers of Ag₂S and Ag₂O. The average speed of 0.02 nm/day. This process results in a significant reduction of the LSPR band intensities for small-sized NPs. However, the deviation of the maximum wavelength position of the plasmon resonance is near 30-40 nm and does not stabilize even after 80 days. Therefore, for applications of silver-based nanostructures an additional passivation layer is required.

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