Granular metal films on the surfaces of transparent dielectric materials studied and modified via optical means

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ABSTRACT

Granular films of alkali and coinage metals are the most popular objects for exploring plasmonic effects. They are easy to obtain via physical vapor deposition and to study via optical means. In this contribution we show several ways not only to record but also to modify the granular metal films using thermal and nonthermal optical effects.

Keywords: metal nanoparticles, plasmon resonance, dephasing time, surface diffusion, surface morphology, laser assisted growth

INTRODUCTION

Granular metal films have found a number of applications. They are employed in surface enhanced Raman scattering, fast and sensitive photodetection, high performance photovoltaics, as well as in many other existing and emerging areas. Bright optical properties of granular metal films form the basis of these applications. On the other hand, optical means may be used to shape and to study granular metal films.

Granular metal films obtained via physical vapor deposition comprise nanoparticles with wide size and shape distributions. This property is detrimental in some applications. Selective reshaping of silver nanoparticles under the pulsed ruby laser illumination is shown to significantly change the shape distribution. On the other hand this process may be used to reveal the homogeneous width of the plasmon resonance in the particles of definite shape otherwise hidden under the inhomogeneous broadening of the whole ensemble.[1,2]

Much weaker cw diode laser illumination of sodium nanoparticles lead to the changes in the particle shape as well. This process is due to the non-thermal light-induced surface diffusion and detachment of the atoms from the metal nanoparticle surface.[3-5] Although only tiny changes in the inhomogeneously broadened plasmon band may be observed in this case clear evidence of the selective laser action was obtained.[6-7]

The photodesorption of metal atoms from the surface of transparent dielectric substrates may be used to obtain regular arrays of metal nanoparticles.[8] The general possibility was illustrated by the experiments with sodium on sapphire. A cw diode laser of moderate power was employed to avoid condensation of sodium vapor on illuminated parts of the substrate while the metal deposits grew in dark areas. This is a parallel one-step process that may compete with photolithography in some niche applications.

In this contribution we present a new observation of the light action on the morphology of the granular metals films. We found that the UV illumination of the granular silver film leads to latent changes in the surface structure of the nanoparticles comprising the granular. These changes are, then, revealed in the annealing process that stops at another stage as compared to the film kept in the dark.

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GRANULAR FILMS OF PLASMONIC METALS

In many cases, adsorption of metal elements on dielectric substrates goes via Volmer-Weber growth mode. This means that the atoms arrived onto the surface from the gas phase are, first, adsorbed in the surface potential well, then, diffuse over the surface of the substrate, and, finally, meat each other and form metal nanoparticles. This process depicted in the fig. 1 is easily implemented and may be stopped at any desirable surface mass density of the deposited material. Consequently, the exposition time as well as the temperatures of the substrate and the source is the parameter that may be used to control the size, the shape and the surface number density of the metal nanoparticles spread over the substrate. The shapes of the nanoparticles obtained in this way are metastable. Annealing leads to the considerable changes in morphology of the films that are mirrored in the optical extinction spectra.

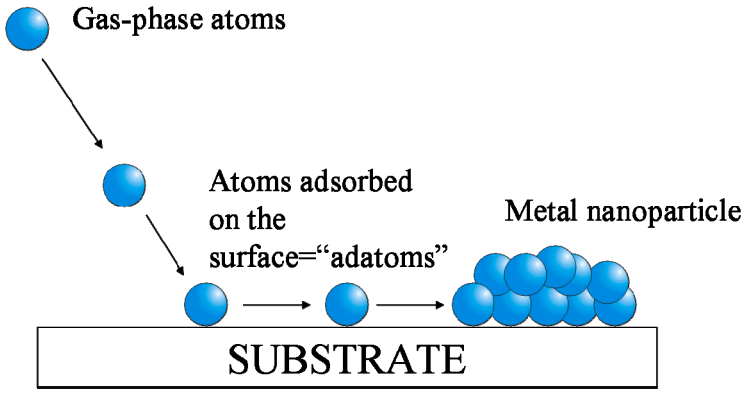

Figure 1. Schematics of the nanoparticle formation via Volmer-Weber growth mode. Blue spheres represent the atoms of a metallic element.

Imaging of nanostructures on the dielectric substrates via scanning electron microscopy (SEM) is difficult due the charging effect. Nevertheless, very small but nonzero conductivity of the granular metal films enables implementation of

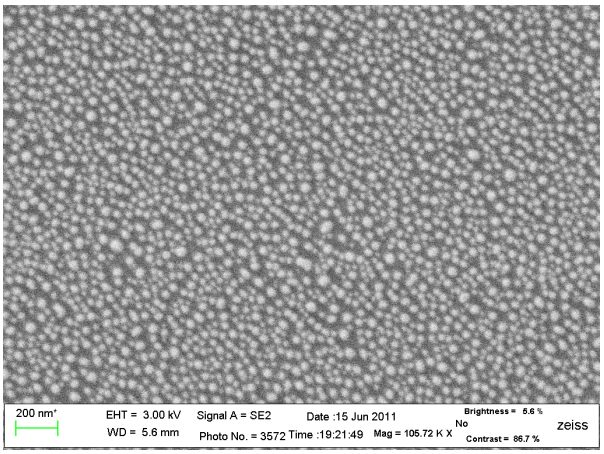

Figure 2. SEM image of the granular silver film on sapphire substrate.

SEM in this case. Fig.2 displays the SEM image of the granular silver film on sapphire taken after annealing at 200 C for 40 min in vacuum.

If the element is a good "plasmonic" material like alkali or coinage metals the granular metal films demonstrate a huge resonance in visible due to the excitation of the collective electronic motion in the individual particles.[9] Fig. 3 plots the extinction spectrum of the granular silver film on sapphire that was recorded on the same sample as the SEM image of fig. 2. The spectral width of the plasmonic band is much larger than the theoretical estimate based on the quasistatic approximation and the bulk optical properties of silver.[9] This discrepancy is corroborated by the observation of the

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variety of shapes of the nanoparticles in fig. 2. As the spectral position of the plasmon resonance depends on the particle shape, the width of the plasmon band in fig. 3 is due to the inhomogeneous broadening.

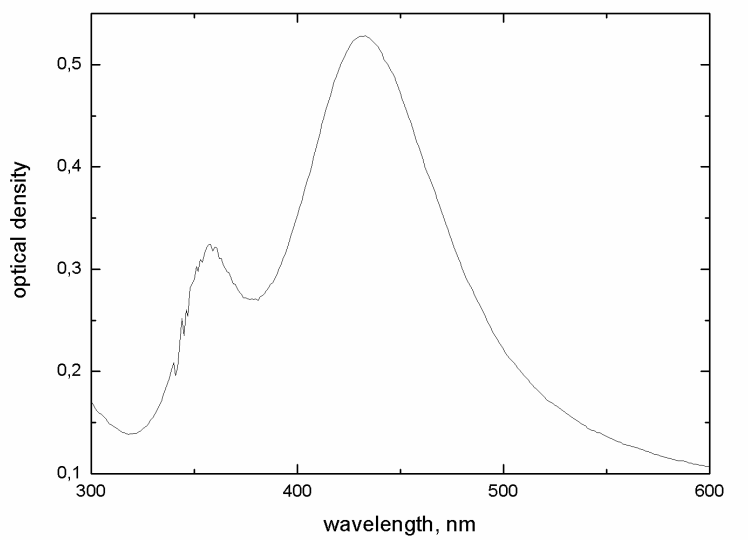

Figure 3. Optical extinction spectrum of the granular silver film on the sapphire substrate.

We are not aware of any example of direct imaging of alkali deposits on dielectric substrates. Nevertheless, optical measurements support the conclusion that sodium and potassium form granular films as well. Inhomogeneously broadened plasmon band of sodium granular film on sapphire is depicted in fig. 4.

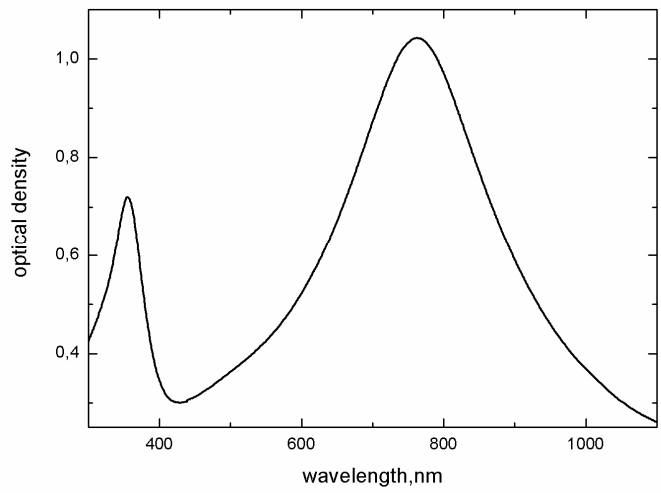

Figure 4. Extinction spectrum of the granular sodium film on the sapphire substrate

REVEALING OF THE HOMOGENEOUS WIDTH OF THE PLASMON RESONANCE HIDDEN IN THE INHOMOGENEOUSLY BROADENED PLASMON BAND

There are several well known methods to reveal the homogeneous width of the optical resonances hidden under the common structureless contour of an inhomogeneously broadened band in the arsenal of nonlinear optics. Due to the ultrafast dephasing of the collective electronic excitations in metal nanoparticles, most of them have never been applied to the granular metal films. The only successful exclusion is the persistent hole-burning technique.[1,2] In the case of silver nanoparticles hole burning relies on the selective heating and reshaping of those nanoparticles that are in resonance with

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the laser radiation.[10-12] In our experiments, the ruby laser operating at 694 nm was used. Three to thirteen pulses of 17 ns duration and fluences of 30 to 50 mJ cm^{-2} illuminated the sample. To get the stable granular silver film with the appreciable amount of nanoparticles of desired shape leading to the plasmon resonance on the laser wavelength, the film was treated with alcohol instead of annealing. Keeping the silver film in the alcohol bath overnight removes the nanoparticles loosely attached to the surface but preserve the broad shape distribution.

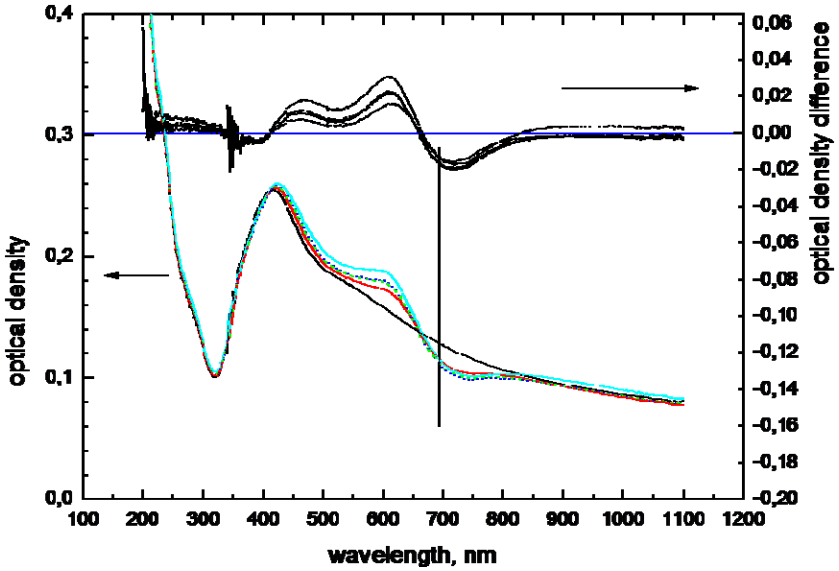

Figure 5.Persisten spectral hole burnt in the inhomogeneously broadened plasmon band of silver granular film on sapphire. Left axis shows the optical densities of the as prepared film (black solid line) and after successive exposition to ruby laser pulses (colored lines). Right axis shows the optical density differences between the as prepared and the laser treated films. Larger differences correspond to larger number of pulses applied to the sample. Vertical line marks the wavelength of the ruby laser.

The results of the laser treatment are shown in fig. 5. Those nanoparticles that are in resonance with the laser radiation are heated and change their shape. As the laser wavelength coincides with the long tail of the plasmon band that is due to oblate nanoparticles, after heating these particles obtain more spherical form. According to the quasistatic theory of plasmon excitations, this change in the form is followed by the shift of the plasmon resonance to shorter wavelengths.

This is indeed observed in fig. 5 as a dip in the extinction spectrum on the laser wavelength accompanied by the bump on the somewhat shorter wavelengths. The width of this structure, the distance between the minimum and the maximum in the difference spectrum is directly related to the homogeneous width of the plasmon resonance in those silver nanoparticles that are in resonance with the laser radiation.[10,12]

At larger laser intensities and longer treatment this process may used not only as an analytical tool to study the dephasing times of collective electronic excitations in the plasmonic nanoparticles but also to globally change the shape distribution of the nanoparticles in the desired direction.

LASER CONTROL OVER THE GRANULAR METAL FILM DEPOSITION

In many cases it is desirable to pattern the granular metal films. Photodesorption of metal atoms from the surface of transparent dielectric materials was suggested as an enabling tool to reach this goal.[8] Illumination of the substrate in the course of the physical vapor deposition reduces the number density of the atoms adsorbed on the surface, thus, precluding the nucleation and growth of the granular film in the illuminated areas.[3]

We report here on the results of two experiments performed with the sodium deposition on sapphire. The threshold intensity of a cw diode laser operated at the wavelength of 440 nm was found to be 1 W cm^{-2} for the deposition rate of 0.02 nm s^{-1}. First, the substrate was illuminated through a copper wire grid with a pitch of 100 μm. The microscopic

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images of the sodium deposits as well as the image of the wire grid are presented in fig. 6. It is seen that the grid pattern is reproduced in the sodium deposits.

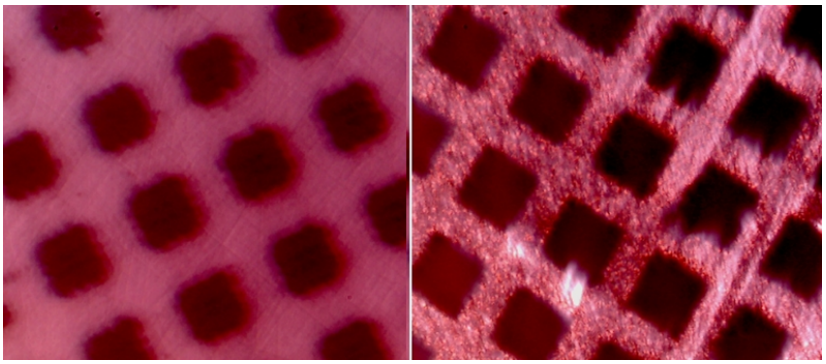

Figure 6. Left panel - microscopic image of the sodium deposits on sapphire substrate obtained via physical vapor deposition under simultaneous laser illumination trough the copper wire grid depicted in the right panel.

Finer patterns were obtained by illumination of the substrate through the mire with a pitch of 10 μm. The pattern was well reproduced in this case too. Father reduction of the pitch may be achieved with the interference technique.[8]

LIGHT-INDUCED CHANGES IN THE ANNEALING BEHAVIOR OF GRANULAR METAL FILMS

Annealing, just mentioned in section 2, may be studied in more details via optical means too. Fig.7 plots the kinetics of the annealing process at the temperature of 230 C followed up by recording extinction spectra of the silver granular film at different time intervals after deposition.

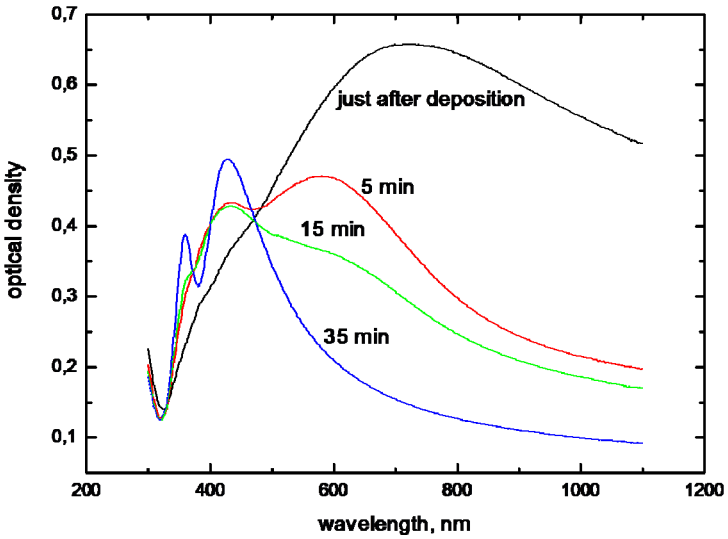

Figure 7. Annealing kinetics of the silver granular film on sapphire. The film was kept at the temperature of 230 C. The time elapsed after the deposition is written at the curves.

The temperature of annealing is too low to cause any significant loss of material through evaporation. Hence, the changes in the morphology of the film revealed by the optical extinction are due to diffusion. The general trend of the extinction spectra changes are rationalized in terms of the blue shift of the plasmon resonance due to the transformation of the nanoparticle shapes from oblate to more spherical form. Considerable reduction of the integral extinction in the

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course of annealing is due to the interband transitions in silver that lead to the deviations of the bulk silver optical properties from Drude model and damping of plasmon oscillation at shorter wavelengths.

A new and rather unexpected phenomenon was observed when the freshly prepared granular silver film was illuminated by UV light before annealing. We use the mercury lamp radiation with a filter that transmits radiation with wavelengths shorter than 350 nm. The intensity of the illumination in this spectral range was 20 mW cm^{-2}. The results are presented in fig. 8. There are no noticeable changes in the extinction spectra after 3 hours of illumination. Then, the illuminated sample was annealed at the temperature of 230 C for 40 min. The difference in the results of annealing for an ordinary film and the film subjected to UV illumination is drastic.

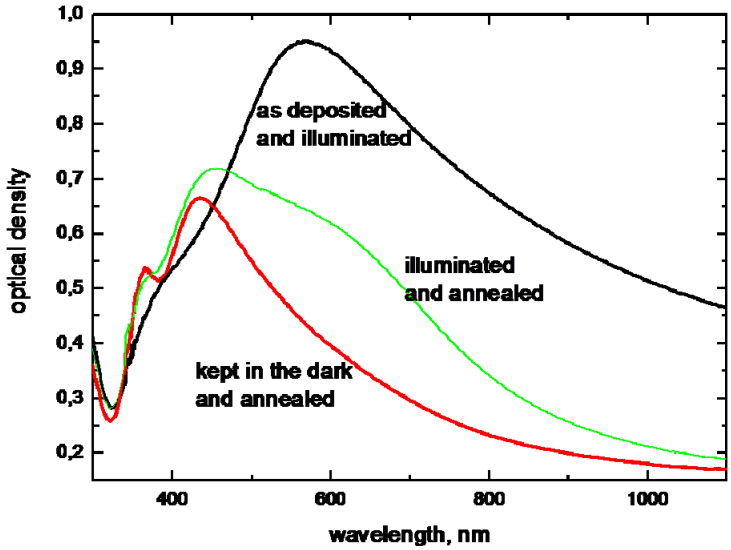

Figure 8. Influence of UV illumination on the annealing of granular silver films. Illumination itself does not cause noticeable changes in the extinction spectrum (black curve). After annealing for 40 min at the temperature of 230 C the difference in the extinction spectra of the illuminated film (green curve) and the film kept in the dark (red curve) becomes obvious.

Optical density of the illuminated film is lager than that of the film kept in the dark by more than 0.2 in the range from 560 to 680 nm. This leads to the difference in the appearance of the corresponding parts of the film easily seen by eye as the illuminated area is more than 50% darker.

Illumination of granular metal film with longer wavelengths even with higher intensities does not produce any measurable effect on the annealing process.

CONCLUSION

The results presented above show the ability of optical techniques to record and to change the morphology of the granular metal films. Of particular interest is the observation of the changes in the annealing behavior of the granular metal films subjected to UV illumination. As the annealing process is connected with the diffusion of the indigenous atoms over the surface of nanoparticles,[13] this observation leads to the conclusion that UV illumination changes the surface structure of metal nanoparticles and inhibits the surface diffusion.

We also demonstrated the possibility to obtain the patterned granular metal films in a one-step parallel process of physical vapor deposition accompanied by laser illumination.

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