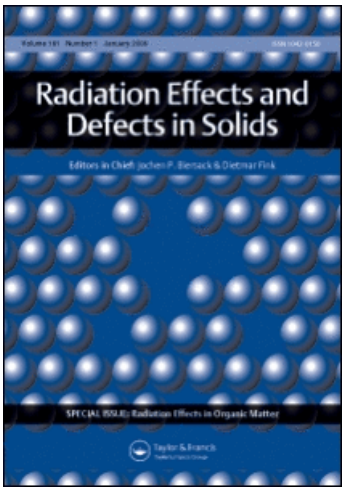

Radiation Effects and Defects in Solids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713648881

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Online Publication Date: 01 July 2009

To cite this Article Alonso-Huitrón, J. C., Acosta-Zepeda, C., Batina, N., Acosta-García, M. C., Castillo-Ocampo, P. and Haro-Poniatowski, E.(2009)'UV-laser-induced modifications through a single slit on quasi-percolated silver nanostructured films',Radiation Effects and Defects in Solids,164:7,438 — 442
To link to this Article: DOI: 10.1080/10420150902949753
URL: http://dx.doi.org/10.1080/10420150902949753

Radiation Effects & Defects in Solids
Vol. 164, Nos. 7–8, July–August 2009, 438–442

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(*Received 12 September 2008; final version received 20 January 2009*)

In this work, we report the synthesis of quasi-percolated Ag thin films by pulsed laser deposition. These Ag nanostructures are the starting material for obtaining spatially ordered silver nanoparticles by ultraviolet laser irradiation. The laser transformations are investigated by transmission electron microscopy. We have previously demonstrated that the arrangement of these silver nanoparticle assemblies can be controlled by irradiating the samples through suitable masks, such as razor edge or a phase grating among others, taking advantage of their respective diffractive properties. In this work, the effect of the irradiation through a single slit is discussed. A simple optical model based on Fresnel diffraction is presented in order to explain the obtained results.

Keywords: laser ablation; silver nanoparticles; laser irradiation; patterning; Fresnel diffraction; TEM

1. Introduction

Ultraviolet (UV) laser irradiation effects on noble metal nanoparticles have been studied extensively. It has been demonstrated that it is possible to control their size and shape by laser irradiation, (*1*, *2*). For these purposes, lasers of different characteristics such as pulse duration and wavelength have been used. The irradiated samples are of a wide variety, from supported nanoparticles in different substrates, nanoparticles in solution, or embedded nanoparticles in particular matrices. Depending on the laser parameters and on the type of samples, the irradiation effect can be to increase or to reduce the size of the nanoparticles (*3–9*). The motivation of these investigations is that noble metal nanoparticles have particular optical properties that can be used in a

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ISSN 1042-0150 print/ISSN 1029-4953 online

DOI: 10.1080/10420150902949753
http://www.informaworld.com

variety of applications. In particular, their plasmon resonance depends strongly on the size, the environment and on the shape of the nanoparticles (*10–12*). This has important consequences in surface-enhanced Raman spectroscopy (SERS), which is a widely used technique to study vibrational properties of biological systems. In the case of gold and silver nanoparticles, the plasmon resonance is in/near the visible region of the spectrum, which is convenient for SERS investigations (*13*). Another very important issue, besides the control of their size and morphology, is the ability to order them in regular patterns involving many nanoparticles (*6*, *7*). This has been achieved employing different techniques, such as nanolithography and bottom-up techniques. The interest of having the nanoparticles ordered on the surface or in the volume of a substrate or solid matrix is multiple. These composite materials can be used as sensors among other applications (*14*).

Recently, we have shown that it is possible to change the morphology of silver nanostructures and create designed patterns of nanoparticles within the same process by laser irradiation (*6*, *7*). The key points to realize are, first, to use a quasi-percolated silver thin film and, second, to use a diffractive mask. This method has been called diffraction-assisted method (DAM) (*15*).

Using this technique, we have generated different ordered patterns. If no diffraction mask is used, the irradiation process results only in a change of morphology but not in an ordered pattern (*6*, *7*). Typically, the nanostructures change from complex "fingered" structures to almost spherical nanoparticles. In the present work, we show how the morphology of the nanostructured films changes when irradiated through a single slit. Furthermore, using a simple Fresnel model, we can explain the observed results.

2. Preparation and characterization of the samples

The quasi-percolated Ag thin films were prepared by pulsed laser deposition (PLD). The second harmonic ($\lambda = 355$ nm) of a Q-switched Nd:YAG laser, providing 5 mJ pulses of 10 ns duration with a repetition rate of 5 or 10 Hz, was used for the pulsed laser ablation process of a 2.54 cm diameter $\times$ 0.66 cm thick 99.99% Ag target. The target and substrate were placed in a vacuum chamber at a background pressure of 1×10^{-5} torr, obtained with a turbo-molecular pump. Cu TEM (transmission electron microscopy) support grids covered with a carbon film were used as substrates, placed at a distance of 2.5 cm directly in front of the target. The pulsed laser fluence was 0.64 J/cm^2, on average. In order to calibrate the sample morphology, a set of samples with different numbers of laser pulses were prepared. The samples were systematically analyzed by TEM microscopy (Carl Zeiss model EM10 conventional TEM with 0.4 nm resolution at 120 kV). Approximately 15,000 pulses were needed to obtain quasi-percolated surfaces. Details are given elsewhere (*16*). It is important to point out that the Cu TEM microscopy grids covered with carbon films are not flat but have non-uniform topography with irregular ripples (*7*), which introduces differences of distances between the diffracting mask and the sample surface, and strongly influences the interference effects.

The same laser was used to irradiate the quasi-percolated Ag nanostructures deposited by PLD on the TEM grids. However, in this process a significant lower laser fluence was used (0.025 J/cm^2) in a single laser shot. This fluence is determined by irradiating several samples at different fluences and by systematically observing the laser-induced transformations on the TEM grid which can go from nothing to severe damage of the film. The experimental set-up is shown in Figure 1. In this figure, a TEM microphotograph of the starting quasi-percolated nanostructured silver thin film is presented. In order to pattern the impinging light field, we have used a variable slit; the width of the slit was set at $50 \pm 5\,\mu$m and the sample was placed at approximately $300 \pm 50\,\mu$m behind it. The morphological changes were investigated by TEM microscopy.

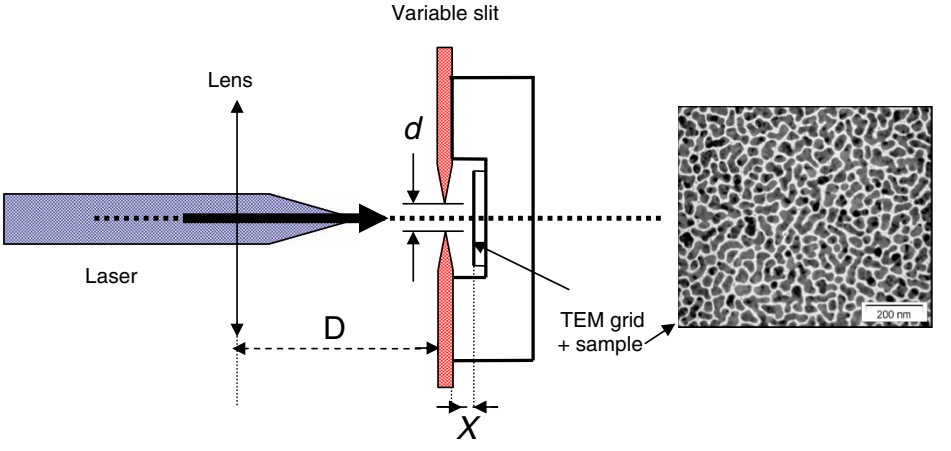

Figure 1. Experimental set-up for inducing the transformations on quasi-percolated Ag thin films deposited on TEM grids. Typical distances are $X = 300\,\mu$m, D = 15 cm, $d = 50\,\mu$m. On the right-hand side, the TEM photograph of the quasi-percolated Ag film is presented.

3. Results and discussion

After a single laser shot through a slit having a width of 50 μm at a laser fluence of 0.025 J/cm^2, the sample is analyzed by TEM. The corresponding microphotograph is presented in Figure 2. The transformations are evident, since two parallel bands of nanoparticles are clearly distinguishable. Outside these bands, the film is composed of the original quasi-percolated silver thin film shown in Figure 1. The Ag nanoparticles are almost spherical, with size ranging from 10 to 200 nm. However, a complementary analysis by atomic force microscopy has revealed in similar experiments that the particles are non-spherical, having bigger diameters (about two times) than heights (*7*).

In order to analyze the obtained results, we have used a Fresnel model for a single slit. The intensity in the case of a slit of width d in the y direction that is at a distance X from the plane of observation is given by (*17*):

$$\hat{I}(Y) = (C_p(Y) - C_q(Y))^2 + (S_p(Y) - S_q(Y))^2, \tag{1}$$

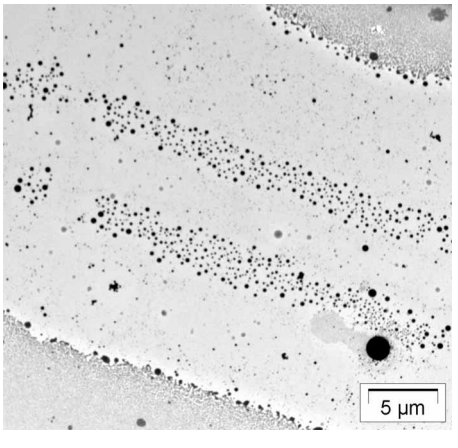

Figure 2. TEM photograph of the quasi-percolated Ag film after UV (355 nm) irradiation through 50 μm wide slit. Two bands, where the nanostructures have been transformed to nanoparticles, are clearly observable.

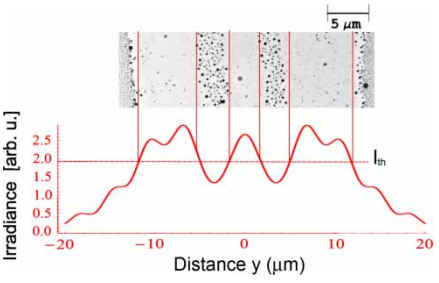

Figure 3. TEM photograph of the quasi-percolated Ag film with the transformed bands. The solid line is the result of the intensity spatial distribution in the plane of the sample using Fresnel diffraction theory as described in the text.

where Y is the horizontal coordinate in the plane of observation and

$$C_q(Y) = \int_0^{q(Y)} \cos\left(\frac{\pi}{2}\eta^2\right) \mathrm{d}\eta \quad C_p(Y) = \int_0^{p(Y)} \cos\left(\frac{\pi}{2}\eta^2\right) \mathrm{d}\eta,$$

$$S_q(Y) = \int_0^{q(Y)} \sin\left(\frac{\pi}{2}\eta^2\right) \mathrm{d}\eta \quad S_p(Y) = \int_0^{p(Y)} \sin\left(\frac{\pi}{2}\eta^2\right) \mathrm{d}\eta,$$

are the Fresnel integrals with

$$\eta = (Y - y)\sqrt{\frac{2}{\lambda X}}.$$

The dependence on y of the integral upper limits is given by

$$q(Y) = \left(Y + \frac{d}{2}\right)\sqrt{\frac{2}{\lambda X}} \quad \text{and} \quad p(Y) = \left(Y - \frac{d}{2}\right)\sqrt{\frac{2}{\lambda X}}.$$

In Figure 3, the transformed bands are presented together with the intensity profile obtained from Equation (1). For this calculation, we have used the following parameters: laser wavelength $\lambda = 355$ nm, distance from the slit to the sample $X = 320$ μm and the width of the slit d is 35 μm. The parameters d and X are certainly close to the experimental ones (50 μm and 300 μm); however, our experimental set-up has to be improved in order to refine the comparison between theory and experiment. Furthermore, as mentioned before, the irregularities of the surface of the samples introduce additional experimental uncertainties. The dotted horizontal line shown in Figure 3 has been determined using the imprinted pattern in the surface of the sample and is related to the energy density needed to produce the corresponding changes in the morphology of the nanostructures. In the regions having an energy density above this irradiance threshold, the silver nanostructures are completely removed. In the low irradiance regions just below this threshold, the nanostructures are transformed into nanoparticles. Further experiments are in progress in order to explore the capabilities of this lithographic technique.

4. Conclusions

In this work, we have shown that it is possible to induce by laser irradiation transformations and ordering effects through the DAM on nanostructured quasi-percolated silver thin films. For this purpose we have used a variable slit. The imprinted pattern matches closely the spatial intensity distribution obtained by Fresnel diffraction theory.

Acknowledgements

This work was supported by a multidisciplinary grant from the División de División de Ciencias Básicas e Ingeniería CBI-UAM-Iztapalapa and by a grant from the Consejo Nacional de Ciencia y Tecnología (CONACYT) of México.

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