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Laser-induced patterning of silver thin films using interference effects

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Abstract Submicron patterning of the spatial arrangement of spherical silver nanoparticles on a substrate is reported. The patterned samples were obtained by irradiating a thin silver film in the quasipercolated state with short laser pulses. Light reached the sample through a slit on a highly reflecting silicon mask placed parallel to the surface of the sample and was reflected between the sample and the inner face of the mask. The incident and reflected light interfered on the sample's surface creating a complicated pattern of thin lines along which spherical-shaped silver nano-particles are concentrated. We provide a simple model to explain the observed patterns and briefly discuss how could one control the shape and thickness of the patterned lines of nanoparticles.

1 Introduction

Metallic nanoparticles (NPs) have been studied extensively due to their unique optical properties [1]. In particular, metallic NPs show size and shape dependent resonant light absorption and scattering [2, 3]. The optical properties of the medium surrounding the NPs also modifies the resonances of metallic NPs, offering the possibility to monitor with high-sensitivity physical and chemical variations of the medium around them by measuring the spectral position of the absorption peaks of an ensemble of metallic NPs. Patterning of material properties at a micron and submicron level is of interest in several applications such as memories [4], encryption of data, electric circuits and sensors for different medical, biological, and industrial applications. In recent years, it was shown that patterned arrays of NPs on a surface can be created by irradiating a metal thin film with a structured light pattern obtained by diffraction of short laser pulses [5]. This technique has been referred to as diffraction-aided laser-induced microstructuring and has been used to fabricate specific arrays of NPs [6]. In previous works, it was shown that the patterned samples had different sizes of NPs [7, 8] depending of the energy density used to transform the substrate into NPs. Laser interference lithography has also been investigated in recent years [9, 10]. As an example, two and up to five beam interference pattern models for nanostructuring have been developed for applications in self-cleaning surfaces [11].

The aim of this work is to report clear evidence that a two-wave interference pattern can be used to imprint submicron patterns in a quasipercolated silver thin film. We present a simple theoretical model that is in good agreement with the experimental results. This model allows us to explore the parameters we may control to modify the shape of the patterns and energy density that determine the optical properties of the NPs.

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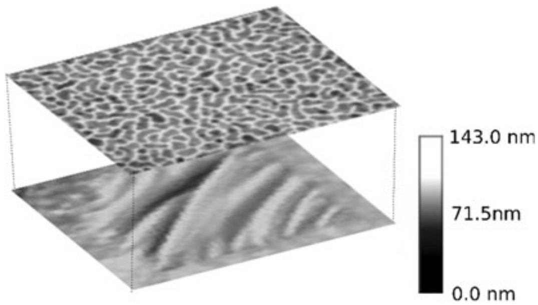

Fig. 1 Images of the quasipercolated silver layer and the substrate. The irregular surface of the substrate is shown separately below visualized by AFM. The high resolution AFM surface-profile image of the substrate shows height variations up to about 100 nm

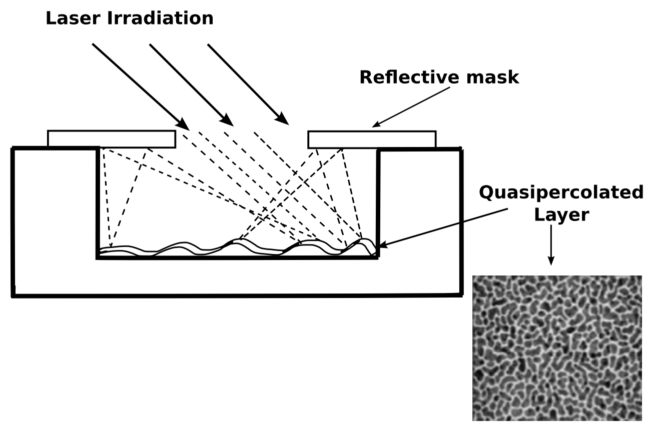

Fig. 2 Schematic illustration of the patterning experiment. A quasipercolated nanostructured silver thin film is shown on the *lower right side* of the figure. This sample was irradiated through a rectangular opening on a highly reflective mask

2 Experimental details

Quasipercolated Ag films were prepared by pulsed laser ablation (PLA) in a vacuum (1×10^{-5} Torr), using shots of a Q-switched Nd:YAG laser providing 5 mJ pulses of 10 ns duration with a repetition rate of 5 Hz, at a wavelength of $\lambda = 355$ nm, and at an average fluence of 0.64 $\mathrm{J\,cm^{-2}}$. The Ag layers were prepared directly on Cu transmission-electron-microscopy (TEM) support grids in order to analyze them after being irradiated with the electron microscope. The Cu grids consisted of a regular array of about two hundred 100 μm × 100 μm squares holes covered with a carbon film and separated from each other by about 30 μm.

For short deposition times, one obtains individual silver nanoparticles and as the deposition time increases different morphologies are obtained. From spherical to beanshape nanostructures. These bean shape nanostructures coalesce to form “fingered like structures” that generate a quasipercolated film. In the experiments described here, such a quasipercolated film was used as the starting morphology to be subsequently laser irradiated. For longer deposition times, a continuous thin film is obtained. The same laser used for the PLD deposition process is employed to irradiate the nanostructured samples. A focusing lens is placed in the laser beam to control the energy density.

A detailed description of the experimental conditions is given elsewhere [7, 8]. The surface of the Cu grid covered by a carbon film and Ag layer, previous to patterning the Ag layer, was imaged with an atomic force microscope to evidence the surface morphology. The image is shown in Fig. 1.

The experimental set-up used to irradiate the samples is schematically shown in Fig. 2. It consists of a silicon mask with a long slit placed parallel to the thin Ag film. The irradiation effects reported here were induced after a single laser pulse. The laser pulse was incident on the sample through the slit at an oblique angle of incidence. The angle of incidence was a few degrees. (For ease of understanding, in Fig. 2, we draw the incidence angle much larger). In a previous work, we have reported the diffraction pattern obtained using a sling slit at normal incidence [8]. As it is illustrated in Fig. 1, the substrate supporting the Ag layer (TEM grid) had an irregular surface. Due to the surface variable slopes, part of the light incident on the sample was reflected toward the inner surface of the mask and reflected back to the sample. The doubly reflected light interfered with the incident light over some portions of the sample, thus creating a fringe pattern of the irradiating light on the surface of it.

3 Results and analysis

A detailed characterization of the initial quasipercolated silver (shown in Fig. 1) thin film morphology by atomic force microscopy was reported previously [12]. The surface is found to be covered by the finger-shaped aggregates of silver nanoparticles. These aggregates of nanoparticles have different diameters. They can be divided mainly into two groups: first, particles with a diameter of 21 ± 1 nm (about 70 % of the total number of nanoparticles) and bigger ones with a diameter of 30 ± 1 nm. However, these two groups differ significantly in their height. The smaller ones have a height of only 7 ± 0.5 nm, and the height of the larger structures is 14 ± 1 nm. The (RMS)/Rq factor, as the measure of roughness, of the imaged surface is 2.07 nm.

The morphological changes on the Ag films after being irradiated with a single laser pulse were investigated by TEM microscopy. In Fig. 3(a), we show a TEM picture of one of the square sections of the TEM grid with a patterned Ag layer. The interference patterns in the top of the figure present uniformity in shape (wavy like) and present fringes of about 4 μm wide. Around the center of the picture, we can appreciate nearly parallel fringes about 0.8 μm wide; see

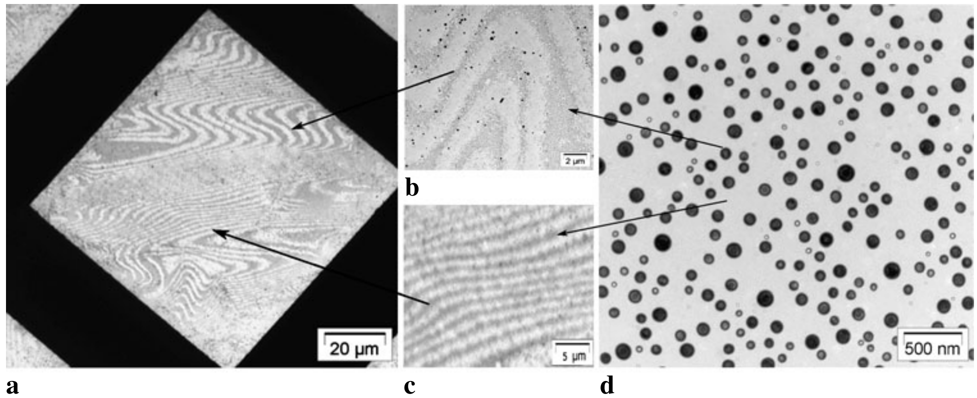

Fig. 3 (**a**) TEM microphotograph of the imprinted interference pattern in a square section of the sample grid, (**b**) a subsection of the TEM image showing *curved fringes* about 4 μm wide, and (**c**) a section of the image with *parallel fringes* about 0.8 μm wide. (**d**) NP's present in the fringes

Fig. 3(c). Finally, in the lower portion of the figure, we can appreciate curved fringes without specific shape. In Fig. 3(b) and Fig. 3(d), we show two enlargements of a small portion of the TEM picture where we can observe the NPs formed with sizes ranging from 20 to 70 nm. The black dots present in Fig. 3(b) are most probably debris particles.

The fringes where the NPs disappear almost completely correspond to the maxima of the interference pattern. At the minima of the interference pattern, we can find the highest number of NPs. In a previous work, we have found different energy density thresholds in order to convert fingered nanostructure into nanoparticles in one case and to evaporate them in the other [8]. In the present case, the energy density is such that when it is maximum, the threshold for evaporation is reached and the silver material disappears and in the minimum regions the energy density is enough to transform the fingered nanostructures into spherical-shaped nanoparticles as shown in Fig. 3(d). This patterning is quite different from the one obtained in a previously reported experiment by irradiating the sample through the slit normal to the surface; in that case, we obtained a diffraction pattern composed of definite bands of nanoparticles as predicted by a Fresnel diffraction model for a single slit [8].

The theoretically simulation of the interference fringes is relatively straightforward once we realize that the surface where the Ag layer is deposited (the amorphous carbon layer) is not flat as shown in Fig. 1 (bottom). Basically, the fringe patterns correspond to the intensity of a two-wave interference pattern with a phase-modulation term arising from the height variations of the substrate's surface.

The Ag layer is assumed to have a constant thickness, and thus, the surface of the Ag layer is a rough surface following the variations in height of the substrate's surface. Let us place our coordinate system with the z-axis normal to the plane corresponding to the average plane of the Ag layer's surface and pointing upward (see Fig. 4). Let us put the origin of the coordinate system on this average plane. Thus, the xy plane of our coordinate system coincides with the average plane of the layer's surface. Then the surface of the Ag layer can be described by a function $z = h(x, y)$ and the average of $h(x, y)$ is 0.

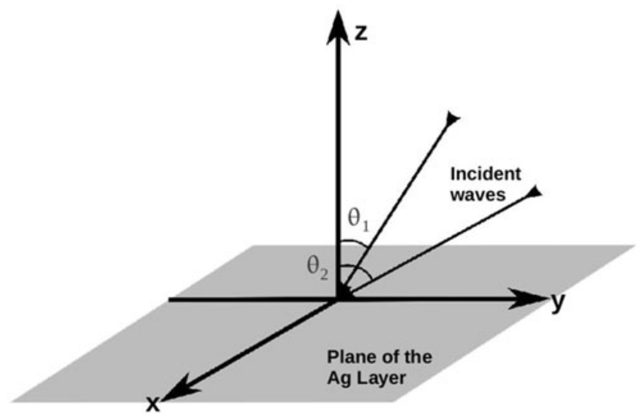

Fig. 4 Coordinate system placed in the Ag layer surface. The plane electromagnetic waves have incident angles θ_1 and θ_2

Let us consider two plane electromagnetic waves incident on the surface. The angles of incidence (with respect to the z-axis) are θ_1 and θ_2 for the first and second plane waves. The intensity of each plane wave, in the absence of the other one, will be denoted as I_1 and I_2, respectively. Note that for the case of plane waves, I_1 and I_2 are constant in space. When both waves are simultaneously incident to the Ag layer, they interfere and the intensity is given by

$$I(x, y, z) = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left[\delta(x, y, z)\right]. \quad (1)$$

The phase term, $\delta(x, y, z)$ is given by, $\delta = (\vec{k}_1 - \vec{k}_2)\cdot\vec{r}$ where $\vec{r} = (x, y, z)$ is the position vector, $\vec{k}_1$ and $\vec{k}_2$ are the wave-vectors of the incident plane electromagnetic waves. The wave-vectors can be written as, $\vec{k}_n = k_0 \sin\theta_n \cos\phi_n \hat{a}_x + k_0 \sin\theta_n \sin\phi_n \hat{a}_y + k_0 \cos\theta_n \hat{a}_z$ where ϕ_n is the angle of the projection of the wave vector on the xy plane and the x-axis, n is either 1 or 2, $\hat{a}_x$, $\hat{a}_y$, and $\hat{a}_z$ are unit vectors along the coordinate axes and $k_0 = 2\pi/\lambda$ is the wave-number in the incidence medium, where λ is the wavelength of light. The phase term evaluated on the surface of the Ag layer assuming $\phi_1 = \phi_2$ i.e., that the interfering waves are in the same

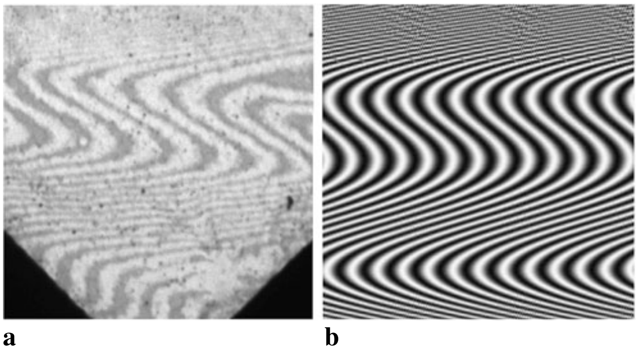

Fig. 5 Comparison of (**a**) experimental and (**b**) theoretical patterns. The theoretical pattern was generated using Eqs. (1) and (2) with $\theta_1 = 20°$, $\theta_2 = 4°$, $\phi = 45°$ and $h = 0.3[x \sin(0.3x)]\lambda/2$

plane of incidence reducing the number of parameters involved in the present calculation is given by

$$\delta = \frac{2\pi}{\lambda}(\sin\theta_1 - \sin\theta_2)[x\cos\phi + y\sin\phi] + \frac{2\pi}{\lambda}(\cos\theta_1 - \cos\theta_2)h(x, y). \quad (2)$$

Note that if $h = 0$ (a flat surface), the interference pattern obtained by substituting Eq. (2) in Eq. (1) consist of straight lines. That is, the maxima and minima on the surface (in this case the *xy* plane) lie along straight lines given by

$$\cos\phi(\sin\theta_1 - \sin\theta_2)x + \sin\phi(\sin\theta_1 - \sin\theta_2)y = p\pi,$$

where $p = (2m + 1)\pi$ for the minima and $p = 2m\pi$ for the maxima, m being an integer.

When h is a smooth function (in a wavelength scale), the interference pattern on the surface $z = h(x, y)$ consists of fringes which will in general be curved. Choosing simple functions for the surface height, $h(x, y)$, one obtains different patterns of curved fringes. For instance, in Fig. 5, we plot an example of an interference pattern over a smooth rough surface which clearly resembles the patterning lines obtained in the experiment. We assumed $\theta_1 = 20°$, $\theta_2 = 4°$, $\phi = 45°$ and $h = 0.3[x \sin(0.3x)]\lambda/2\pi$.

Equation (2) explicitly shows the parameters we can use to control and design different fringe patterns, which could be recorded on an Ag layer by pulsed laser irradiation. Clearly, the wavelength of light divided by $(\sin\theta_1 - \sin\theta_2)$ gives the length scale of the fringe patterns and we can use the height variations of the surface h to curve the fringes at will.

Thus, our experimental results together with our theoretical simulation, indicates that patterning a thin layer over a smoothly rough surface is a possible way to obtain in practice complicated pattern of curved fringes. If one aims to obtain a specific designed pattern, one must find a way to produce the required surface height variations roughness, which in some cases could be a difficult challenge. The angle of incidence between the two interfering waves, θ_1 and θ_2, could be used to control the width of the printed fringes. Of course, one would require assembling an appropriate interferometer to control the angles of incidence as desired. The two-wave interfering irradiation using optical pulsed lasers allows in principle to pattern at the micron and submicron scale relatively large areas (many wavelengths across). Our experimental results show that submicron patterning by this technique in the case of Ag layers is indeed possible.

4 Summary and conclusions

Laser-induced restructuring of a quasipercolated Ag thin film into a pattern of thin curved lines concentrating spherical Ag nanoparticles was achieved over an area of 10^4 μm^2. The patterning was obtained by a single laser pulse at an oblique incidence. The interference phenomena was formed by multiple reflections between the sample and a highly reflective silicon surface placed parallel to the sample's plane at a distance of about 300 μm. The obtained pattern is basically a two-wave interference pattern on a surface with height modulations. The interference fringes are curved and zigzags around regions where the surface supporting the Ag thin layer undulates. We obtained regions where the patterned lines of Ag nanoparticles had widths smaller than a micron. The experimental and the theoretical simulations suggest that we can use substrates with specific modulations of its surface to imprint complicated patterns of curved lines over relatively large areas, and by means of an appropriate control of the experimental parameters it should be possible to control the width and shape of printed microfringes as well as the size of the nanoparticles concentrated along the fringes. This is one more way we may engineer nanostructured silver thin films on a substrate.

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