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Plasmonic response and transformation mechanism upon single laser exposure of metal discontinuous films

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ABSTRACT

Ag and Au discontinuous films were exposed to single nanosecond pulses of a homogenized beam of an excimer laser operating at 193 nm. For low fluences, the films convert into big, almost spherical and isolated nanoparticles (NPs) due to laser-induced dewetting. Their optical response exhibits a sharp surface plasmon resonance (SPR) consistent with that of spherical and non-interacting NPs. For higher fluences, the formation of many small NPs and almost no big NPs is observed instead. The SPR features change and the plasmonic response becomes influenced by multipolar interactions among neighbouring NPs. Low and high fluence regimes are respectively related to melting and boiling threshold of the metal, and additionally, craters appear in the latter regime.

1. Introduction

Thin films based on metallic nanoparticles (NPs) are attracting attention as platforms for chemical or bio sensing [1], as well as optical devices [2]. Their optical response is dominated by the surface plasmon resonance (SPR) and silver and gold NPs have extensively been studied because their SPR is in the visible part of the spectrum. The features of the SPR typically depend on the NPs diameter, shape and separation [3]. When separations become small enough compared to diameter, the NPs are no longer isolated and contribution of dipole–dipole interactions becomes significant [4,5]. Development of cost-efficient tools for producing nanostructures with controlled features is thus a subject of current research interest. Laser irradiation of thin metal films on non-wetting substrates is a way to produce a variety of nanomorphologies with a high potential for nanofabrication [6]. It produces heat instabilities and melting that eventually lead to the breakup of the films into nanoislands, beads or NPs and even to self-organised patterns [6–9]. However, a range of results are reported most likely related to the different irradiation conditions used making unclear if the nanomorphologies can be controlled through the laser irradiation parameters. On the one hand, much of the work reported use multipulse irradiation [6,9,10]. However, the fact that the first pulse already modifies the material makes the material exposed to next pulses different from the initial one [7,8,11–13]. Furthermore, the edges and vertices of the nanomorphologies produced in the first pulse have been reported to act as programmable instabilities for next pulses [14]. On the other hand, the beam profile is either described as Gaussian or a Gaussian-like profile as can be deduced from the experimental approach [6–12]. However, non-homogeneous beam intensity produces in-plane thermal gradients that are in many cases responsible for the mass flow observed. In a recent work, it was shown that the number of pulses should be limited to 1–3 in order to achieve sharp interfaces when nanostructuring and that the thermal gradient should be kept low in order to prevent mass flow [13]. Overall, most of the reported works aim either to understand the dewetting/mass flow mechanism or its dependence on the metal layer thickness [6,7,9,10,13]. By contrast, there are very few works relating the nanomorphologies to their plasmonic response [8,11,13].

The aim of this work is to investigate the use of single nanosecond laser pulses to irradiate metal layers on glass substrates to produce NPs with controlled features and/or tailored optical response. The metal samples are discontinuous silver and gold layers and we explore the use of laser fluence as a control parameter. In

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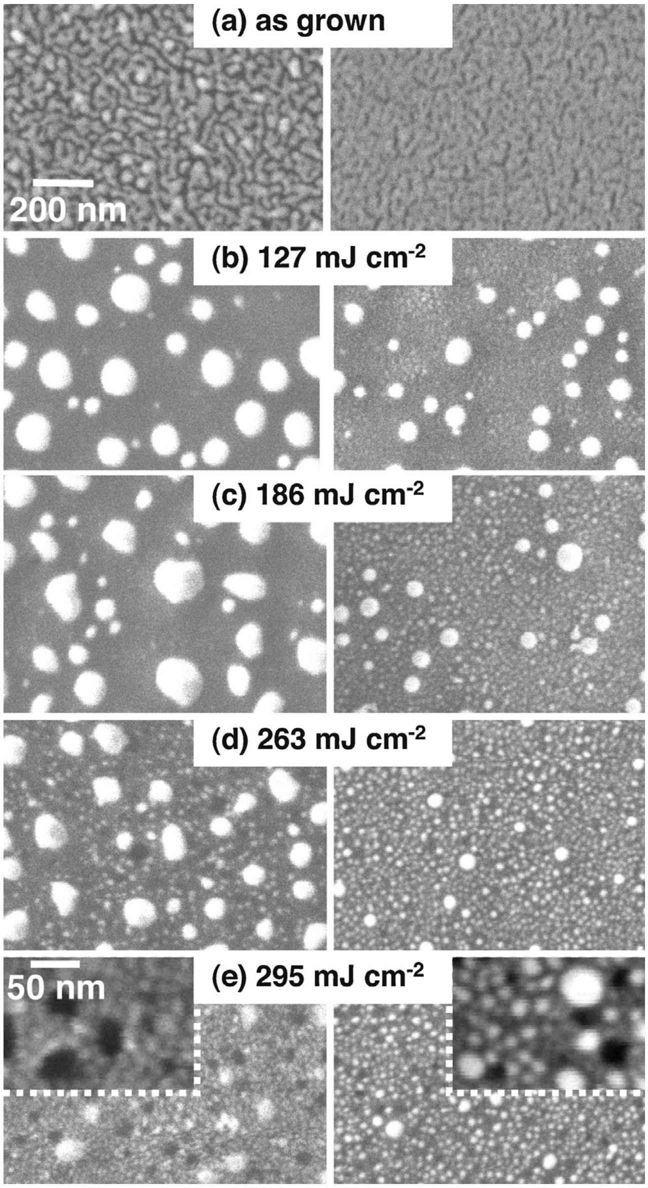

Fig. 1. SEM images from (a) as-grown samples and (b–e) laser irradiated areas where numbers correspond to fluences in mJ cm^{-2}. The insets in (e) show magnified images. The images were obtained in the Ag (left column) and Au (right column) samples.

order to make conditions compatible with manufacturing, we will in addition use a beam with homogeneous intensity over relatively large areas and thus in conditions in which thermal gradients can be ruled out.

2. Experimental

The metal samples were prepared by pulsed laser deposition (PLD) in vacuum (<5×10^{-6} mbar) by means of an ArF laser (193 nm wavelength and 20 ns full width half-maximum pulse duration). The laser beam incidence angle was 45° and the beam was focused on the targets leading with energy of ≈38 mJ or fluence of ≈2.7 J cm^{-2} per pulse. The repetition rate was fixed at 5 Hz. The substrates were glass slides held at room temperature, positioned at ∼38 mm away from the target and rotated along an axis parallel to the plasma expansion axis and shifted a few mm in order to produce a homogenous deposit over an area >1 cm^2. The number of pulses in each target (2750 and 2500 for Ag and Au, respectively) was selected in order to produce almost continuous layers but still exhibiting a plasmonic response.

The samples were exposed in air to single nanosecond pulses from the same excimer laser using a fly's eye lens homogenizing system manufactured by Laser- Laboratorium Göttingen. The beam intensity was constant (within 5%, mainly related to laser intensity fluctuations) over ≈4×4 mm^2 square regions and we have used four irradiation fluences up to 295 mJ cm^{-2} that was the highest achievable fluence. Both, as-grown and irradiated areas were analyzed by scanning electron microscopy (SEM) using a Zeiss Cross Beam 1540 XB microscope. The images were processed using the standard threshold criterion of the *Image J* software and taking into account a 10 nm diameter as the minimum resolvable diameter for the magnification that could be used in the SEM without significant distortion due to charge effects. The mean Feret diameter (Φ) of the metal NPs was determined through a statistical analysis performed on 1.0×0.6 μm^2 areas. From now on we will refer to it as the diameter of the NPs.

The amount of metal [M] in atoms per cm^2 of both as-grown areas and a selection of irradiated areas was obtained by Rutherford backscattering spectrometry (RBS) using a 2 MeV Li beam with the CMAM 5 MeV tandetron electrostatic accelerator [15]. The incident beam was normal to the sample surface and the surface barrier energy detector was allocated at a scattering angle of 170.5°. The RBS spectra have been simulated using the SIMNRA software [16]. Finally, the extinction spectra were determined as $\ln(1/T)$ from transmittance spectra (T) measured at 0° of incidence angle in the range of 300–800 nm with a UV–Vis Cary 5000 dual beam spectrometer.

3. Results

Fig. 1 shows SEM images of Ag and Au samples both as-grown (a) and upon irradiation (b–e) for increasing fluences. It is seen that the as-grown samples are discontinuous but close to the percolation limit as intended. Upon laser irradiation with low fluence (Fig. 1b), the metal samples convert into big and almost round NPs. As fluence is increased, the number of big NPs decreases and smaller NPs start appearing. For the highest fluence used (Fig. 1e), there are many small NPs and almost no big NPs. In addition, some black areas appear as seen better in the magnified images of the insets in Fig. 1e that will be referred to from now on as craters.

The different morphological features described have also been sequentially imaged by SEM in the neighbourhood to the edge of the areas exposed to the highest fluence when moving from the as grown layer towards the center of the exposed area. The images make evident that the conversion of the discontinuous layer into NPs is a threshold process and above threshold, NPs features are those shown in Fig. 1b. For lower fluence, a coarsening of the almost percolated layer is the only feature that could be observed. Therefore, the lowest studied fluence, 127 mJ cm^{-2}, will be referred to from now on as fluence close to the transformation threshold.

Fig. 2 shows the histograms obtained upon the analysis of images such as those shown in Fig. 1 for the lowest (a) and highest (b) fluences studied. It is clearly seen that the NPs mean diameter and the number density of NPs, respectively, decreases and increases strongly as fluence is increased. While for the lowest fluence, the mean diameter of Ag is almost twice of that of Au, it becomes very similar for the highest fluence.

Fig. 3 shows the RBS spectra of samples in the range of energies corresponding to the metal and for both as-grown areas and the areas irradiated with the lowest and highest fluences. A single, sharp and isolated peak is observed in all cases. In the as-grown areas, the amount of metal is [Ag] = 3.9×10^{16} at cm^{-2} and [Au] = 2.6×10^{15} at cm^{-2}. Assuming the metals were forming a