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Full Length Article

# Decoration of silica nanowires with gold nanoparticles through ultra-short pulsed laser deposition

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ABSTRACT

The ablation of a metal target at laser energy densities in the range of 1–10 TW/cm$^2$ leads to the generation of nanoparticles (NP) of the ablated material. This aspect is of particular interest if the immobilization of NPs on three-dimensional (3D) substrates is necessary as for example in sensing applications. In this work the deposition of Au NP by irradiation of a Au bulk target with a sub-picosecond laser beam (500 fs; 248 nm; 10 Hz) on 2D (silica and Si(100)) and 3D substrates (silica nanowire forests) is reported for different number of laser pulses (500, 1000, 1500, 2000, 2500). A uniform coverage of small Au NPs (with a diameter of few nm) on both kinds of substrates has been obtained using a suitable number of laser pulses. The presence of spherical droplets, with a diameter ranging from tens of nm up to few μm was also detected on the substrate surface and their presence can be explained by the weak electron-phonon coupling of Au. The optical characterization of the samples on 2D and 3D substrates evidenced the surface plasmon resonance peak characteristic of the Au NPs although further improvements of the size-distribution are necessary for future applications in sensing devices.



## 1. Introduction

The development of accurate, robust and selective sensors, that can be able to provide a real time monitoring of analyte elements, is a key tool for the advancement in many research and technology fields. In particular, there is a lot of interest in biological sensing and in the fabrication of nanosensors for their use in several biomedical areas including proteomics, drug discovery, cancer diagnostics, and therapy [1–5]. Among the various optical sensing techniques available for these applications, surface plasmon resonance (SPR) spectroscopy is a well-known promising candidate. In this technique, which is based on the signal transducing principle that converts the chemical signal into a useful optical signal [6,7], the use of noble metal nanoparticles (NP) is crucial since they are the key of the optical phenomenon responsible for the transduction. Moreover, for this kind of sensors, the use of unconventional substrates like silica nanowire (NW) forests represents an interesting strategy to increase the sensitivity and selectivity of the sensor [8–11]. In fact, a high surface-to-volume ratio and curvature features guarantee more sites available for adsorption than conventional bulk substrates and high density of hot spots. At the same time the use of this kind of substrates provides withstanding high temperatures (up to ~1000 °C) and a macroporous support framework for three-dimensional (3D) NP assembly, easily accessible by analyte molecules [12–15]. Therefore, the strong light scattering typical in NW materials combined with the selective SPR absorption of Au NPs is a strategic tool to achieve efficient light absorption just at the SPR frequencies. Indeed, light passing through a NW forest undergoes multiple scattering events that fold the light path many times in a random walk inside the NW forest. This process causes light trapping i.e., an enhancement of light

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absorption with a consequent drastic reduction of the reflectivity at the frequencies absorbed by the NW material.

The decoration of NW forests with plasmonic NPs requires of growth/deposition methods of the metal nanostructures with control on their morphology, distribution, size and size-dispersion as well as density. To date, approaches allowing the deposition of plasmonic NPs on NW forests include wet chemical reduction methods [11,16,17], thermal evaporation [18], electron beam evaporation [19], ion implantation [20], electro-deposition [21], sputtering [22], atomic layer deposition [23], electrophoretic deposition [24] chemical vapor deposition or chemisorption of pre-synthesized or in situ synthesized NPs [10,12,25,26], dewetting of thin metal films evaporated on the NWs [27,28], galvanic deposition-annealing [10] and pulsed laser deposition (PLD) [29–31]. In general, non uniform coverage and size distribution as well as surface dispersion of the NPs result in the case of wet-chemical reduction or vapor phase deposition and dewetting of thin metal films. Moreover, thermal treatment is often required as a post-processing step to increase size and improve crystallinity of the NPs anchored over NWs. Instead, PLD could be advantageous for depositing substrate-immobilized plasmonic NPs because it is a clean method without need of surfactants or stabilizing agents in chemical synthesis and functionalization, presents a variety of experimental parameters that can be tuned and interplayed, and provides an enhanced adherence with reduced size dispersion and high growth rate. Indeed, the nature of the ablation process involves the production of very energetic particles [32] and supersaturated fluxes of ablated materials [33] that favor enhancement of the nucleation rate [34] and the production of highly dense and uniform NP layers on different kinds of substrates [35], even at room temperature [36]. By exploiting sub-picosecond time duration for the ablation of solid targets at laser intensities in the range of 1–10 TW/cm$^2$, the generation of the NPs is achieved directly within the ablation target [37,38], leading to a narrower size distribution of the NPs.

Moreover, the presence of different ablation regimes, such as photomechanical spallation, explosive boiling and fragmentation [37], should promote the arrival onto the substrate surface of NPs produced inside the target with a kinetic energy considerably higher than those involved in other approaches and capable of enhancing their adhesion to the silica NWs without the need of NP functionalization. Hence, energetic deposition flux combined with high curvature substrates (such as NWs) are expected to enhance the rate of surface redistribution and nucleation, improving the coverage of the substrates with NPs. For comparison, annealing process is effective for changing size and size distribution of the NPs by means of migration rate depending on the NW curvature changed by changing the diameter of the NW [11,28].

In this study we extend our previous investigation on the PLD deposition of Au NP deposited over NW forests [31] turning from nanosecond to sub-picosecond ablation in order to inspect changes in the deposit features (NP morphology, growth evolution and distribution) and test the potentiality of the sub-picosecond regime in applications such as optical sensitive transducers.

## 2. Experimental details

All the experiments were carried out in a typical PLD system, described in a previous work [39]. Different kinds of substrates were used for the analysis and characterization of the Au NP deposition: silica glass and silica NW forest for the investigation of their optical response on 2D and 3D substrates, respectively, and Si(100) for the morphological analysis. The substrates were placed in front and parallel to a high purity (99.99%) Au bulk target at a distance of 4 cm. Prior to every deposition, the PLD system was pumped down to a pressure of $10^{-5}$ Pa in order to minimize the contribution of possible contaminant gases to the NP growth. A dye laser, with a pulse duration of 500 fs and a wavelength of 248 nm, pumped by an excimer laser, was focused on the rotating gold target surface at an angle of 45° producing a spot with an area of 0.09 mm$^2$. The laser fluence was fixed at 3 J/cm$^2$ in all the experiments, while the number of laser shots was increased from 500 up to 2500 with a step of 500. For cleaning aims, the target surface was previously irradiated with 500 laser shots at the same laser fluence used for the deposition, the transfer of material from target to substrate being avoided by means of a retractile shield. The NP morphology was studied by Field Emission Scanning Electron Microscopy (FESEM, JEOL 7000) and the correspondent optical response in the range between 350 and 850 nm was analyzed with a PerkinElmer Lambda 900 and an Ocean optics USB2000 + UV–vis spectrophotometer equipped with an optical bifurcated fiber probe, for the 2D- and 3D-based samples, respectively.

## 3. Results and discussion

In Fig. 1, the high (a, b, c) and low magnification (d, e, f) FESEM images of the samples deposited with different number of laser pulses are presented. The most noticeable characteristic of the low magnification images is the appearance of a high density of large spherical droplets with diameters ranging from a few tens of nanometers to few microns; in the high magnification micrographs, on the image background, smaller NPs can be also observed whose density increases with the number of pulses. For 500 laser shots, the appearance of faint NPs can be observed in the micrograph, whereas in the sample deposited with 1500 pulses the surface is already completely covered by well developed NPs having a diameter of few nm. These results suggest that in our experimental conditions at least 1500 laser pulses have to be used to obtain a good Au NP coverage on 2D substrates. Instead, the coverage of 3D substrates, such as the silica NWs used in this work and previous dewetting experiments [15], requires a larger number of laser pulses to obtain similar morphologies because of the increased surface deposition area. In fact, in order to uniformly cover silica NWs by Au NPs, 2000 and 2500 laser shots were used (Fig. 2a and b, respectively). From these images, it can be observed a shadow effect of the top of silica wires for the deposition of Au NPs on deeper wires as well as the presence of the spherical droplets observed on the 2D substrates. However, the shadowed areas represent a small percentage of the overall exposed surface. In addition, the very energetic flux of ablated material promotes a better coverage of the NWs. The comparison between the Au coverage obtained at 2000 and 2500 pulses demonstrates that larger and more defined NPs form at higher number of pulses, having an average size of about 9 nm at 2000 pulses and 13 nm at 2500 pulses. Further increase of the NP size to about 21 nm and better NP separation are reached after thermal treatment at 500 °C for 10 min in $N_2$ flow, as demonstrated by the image in Fig. 2c that shows the morphology of the sample obtained with 2500 laser shots. This finding can be ascribed to increased rate of Au migration rate at high temperature that favors Ostwald ripening, i.e., growth of larger NP at the expense of the smaller ones.

The observed increase in the mean size of Au NPs for increasing number of ablation pulses is consistent with other reports in the literature [40] and relays on the enhanced absorbance of Au following femtosecond laser ablation at high fluences with a large number of pulses at high fluence. Under such experimental conditions, the increase in the mean size of Au NPs can be attributed not only to pure cumulative effects proper of multishot ablation, but also the change of the target morphology [41] that leads to an increase in the density of NPs generated within the target.

The presence of circular droplets with dimension from tens of nm up to few μm (Fig. 1) deserves a dedicated discussion and can

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