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Thin films of silver nanoparticles deposited in vacuum by pulsed laser ablation using a YAG:Nd laser

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ABSTRACT

We report the deposition of thin films of silver (Ag) nanoparticles by pulsed laser ablation in vacuum using the third line (355 nm) of a YAG:Nd laser. The nanostructure and/or morphology of the films was investigated as a function of the number of ablation pulses, by means of transmission electron microscopy and atomic force microscopy. Our results show that films deposited with a small number of ablation pulses (500 or less), are not continuous, but formed of isolated nearly spherical Ag nanoparticles with diameters in the range from 1 nm to 8 nm. The effect of increasing the number of pulses by one order of magnitude (5000) is to increase the mean diameter of the globular nanoparticles and also the Ag areal density. Further increase of the number of pulses, up to 10,000, produces the formation of larger and anisotropic nanoparticles, and for 15,000 pulses, quasi-percolated Ag films are obtained. The presence of Ag nanoparticles in the films was also evidenced from the appearance of a strong optical absorption band associated with surface plasmon resonance. This band was widened and its peak shifted from 425 nm to 700 nm as the number of laser pulses was increased from 500 to 15,000.

1. Introduction

Metal (Ag, Au, Cu, etc.) nanoparticles supported on solid substrates or embedded in solid thin films are of great interest owing to their unique physical and chemical properties [1,2], which enable applications such as single molecule detection using surface-enhanced Raman scattering (SERS) [3–7], synthesis of composite materials for nonlinear optical devices [8,9], and catalysts [10–12]. For the optical applications, the light-induced localized surface plasmon resonance (SPR) is the main optical property to control, which in turn depends on the size, filling factor, size distribution, shape, and dielectric properties of the metallic nanoparticles, as well as their surrounding dielectric medium [13–24]. With the purpose of studying and/or manipulating these aspects, thin solid films of silver nanoparticles have been prepared using diverse methods such as: Langmuir–Blodgett [6], nanoscale lithography [13,14], gas aggregation [15], chemical synthesis [16,17], d.c. and rf sputtering [18–21], electron-beam evaporation [23], and pulsed laser deposition (PLD) [12,25–27]. PLD presents some advantages over other methods for the fabrication of metal nanoparticles and the manipulation of their properties, since it is possible to change various parameters such as: laser wavelength, pulse duration, ambient gas pressure, energy per pulse, target-substrate distance, etc., to control the size and distribution of nanoparticles. In spite of this, only a few sets of deposition conditions have been investigated for depositing silver (Ag) nanoparticles, and there is still controversy on which are the best conditions for their efficient synthesis. Theoretical and experimental works have demonstrated that the use of ultrashort laser pulses, in the range of femtoseconds (fs), is the most viable route to the production of nanoparticles of different materials by laser ablation in vacuum, because in this regime the nanoparticle formation takes place in the first stage of the sudden expansion and

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cooling of the target material [28–30]. In consistency with this, Ag nanoparticles with mean diameters in the range from 24 nm to 30 nm have been deposited onto mica substrates by laser ablation in vacuum using a Ti:sapphire laser with 20 fs pulses at 780 nm [25]. The above mentioned studies also suggested that laser ablation with longer pulses, in the range of picoseconds (ps) or nanoseconds (ns), leads to laser absorption, heating, and evaporation of the ablated material, which suppress the formation of nanoparticles in the ablation plume. These studies claim that the only way to promote in this case the formation of nanoparticles is to introduce an inert gas pressure to confine the expansion of the plume to allow sufficient time for nucleation [29,31]. According to this, silver nanoparticles with mean diameter around 20 nm, have been prepared by laser ablation in an ambient pressure of 1333 Pa of helium (He), using a YAG:Nd laser with 10 ns pulses at 532 nm [12]. In spite of the prediction of the lack of nanoparticles in a nanosecond ablation plume, recently, ultrathin films with Ag nanoparticles with diameters less than 7 nm, and in the range from 4 nm to 8 nm, have been prepared by PLD in vacuum, i.e., without an inert gas pressure, using pulses of 300 ps from a Ti:sapphire laser ($\lambda = 793$ nm), and of 26 ns from a KrF excimer laser ($\lambda = 248$ nm), respectively [26,27]. On the other hand, YAG:Nd lasers with pulses of picoseconds and nanoseconds have been extensively used for the preparation of colloidal solutions of silver nanoparticles by laser ablation of Ag targets in liquids [32–39]. However, to our knowledge there are no report on the use of a YAG:Nd laser for the formation of Ag nanoparticles by PLD in vacuum, without introducing an ambient gas.

In this work, we report the deposition of thin films of silver (Ag) nanoparticles by PLD in vacuum using the third line (355 nm) of a YAG:Nd laser. The existence of Ag nanoparticles in the deposited films was evidenced by transmission electron microscopy (TEM), and atomic force microscopy (AFM), and an analysis of the sizes of the nanoparticles as a function of the number of laser shots was carried out. We have also explored how the absorption spectrum due to the SPR changes as a function of the number of pulses.

2. Experimental

The thin films of Ag nanoparticles were prepared by the pulsed laser ablation of a 1.00 in. diameter $\times$ 0.259 in. thick, 99.99% Ag target (Kurt J. Lesker), carried out in a vacuum chamber at a background pressure of 1×10^{-5} Torr, obtained with a turbomolecular pump. The second harmonic ($\lambda = 355$ nm) of a Q-switched Nd:YAG laser (Lumonics HY 1200), providing 5 mJ pulses of 10 ns duration with a repetition rate of 5 Hz or 10 Hz, was used for the pulsed laser ablation process. Float glass and Cu TEM support grids covered with formvar and/or carbon film were used as substrates placed at a distance of 2.5 cm directly in front of the target. The pulsed laser beam was imaged onto the target, at an incident angle of 45°, using a quartz lens of 50 cm of focal length, which produced a spot 1 mm in diameter aproximatly and an average fluence of 0.64 J/cm^2. In order to avoid crater formation, a set of two mirrors whose orientation is automatically controlled with rotating step motors, was used to move the ablation spot onto the target surface, over a square area of approximately 0.75 cm $\times$ 0.75 cm. Under this

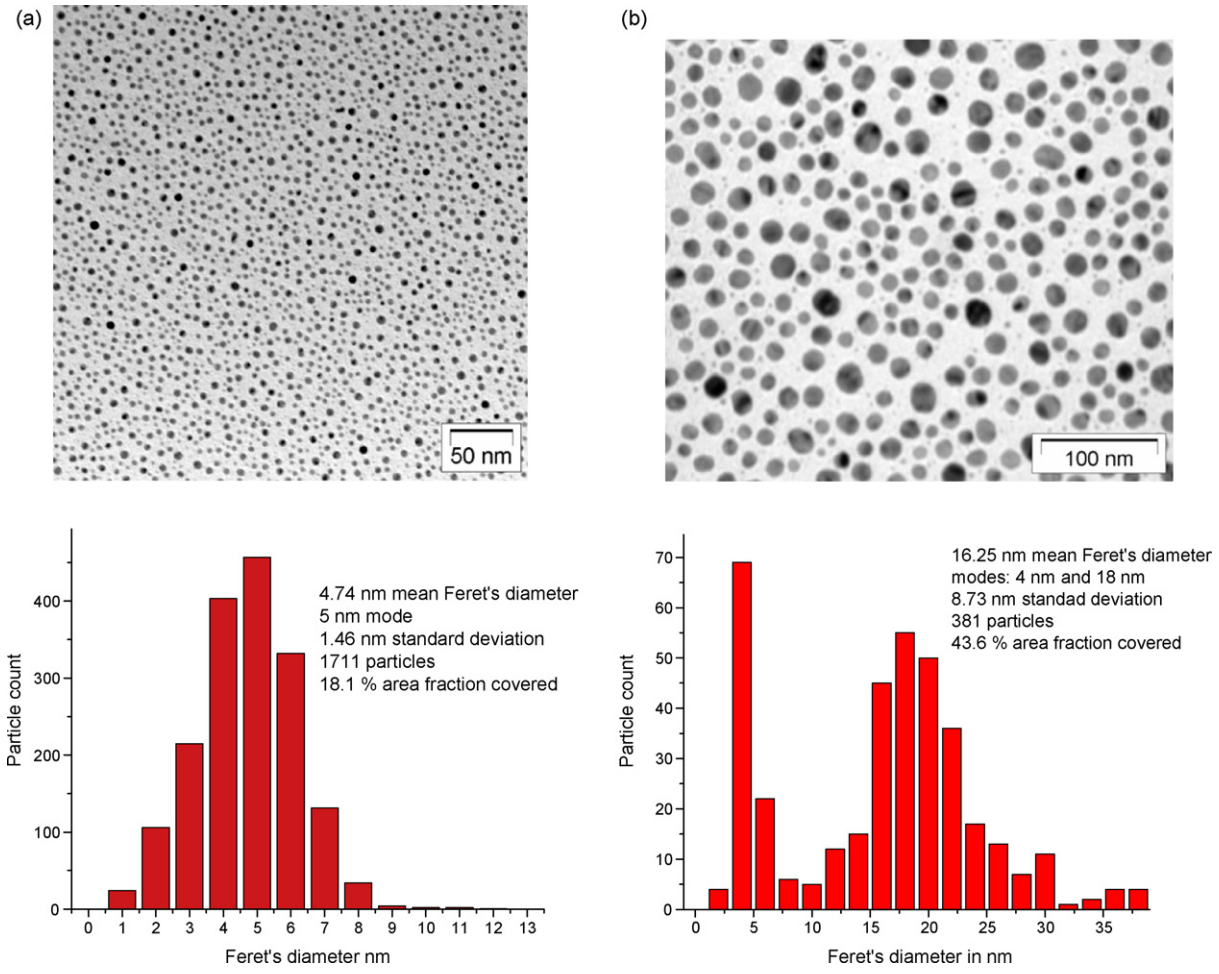

Fig. 1. TEM image and size histogram of as-grown films of Ag nanoparticles deposited in vacuum by: (a) 500, (b) 5000, (c) 10,000 and (d) 15,000 laser pulses.