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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

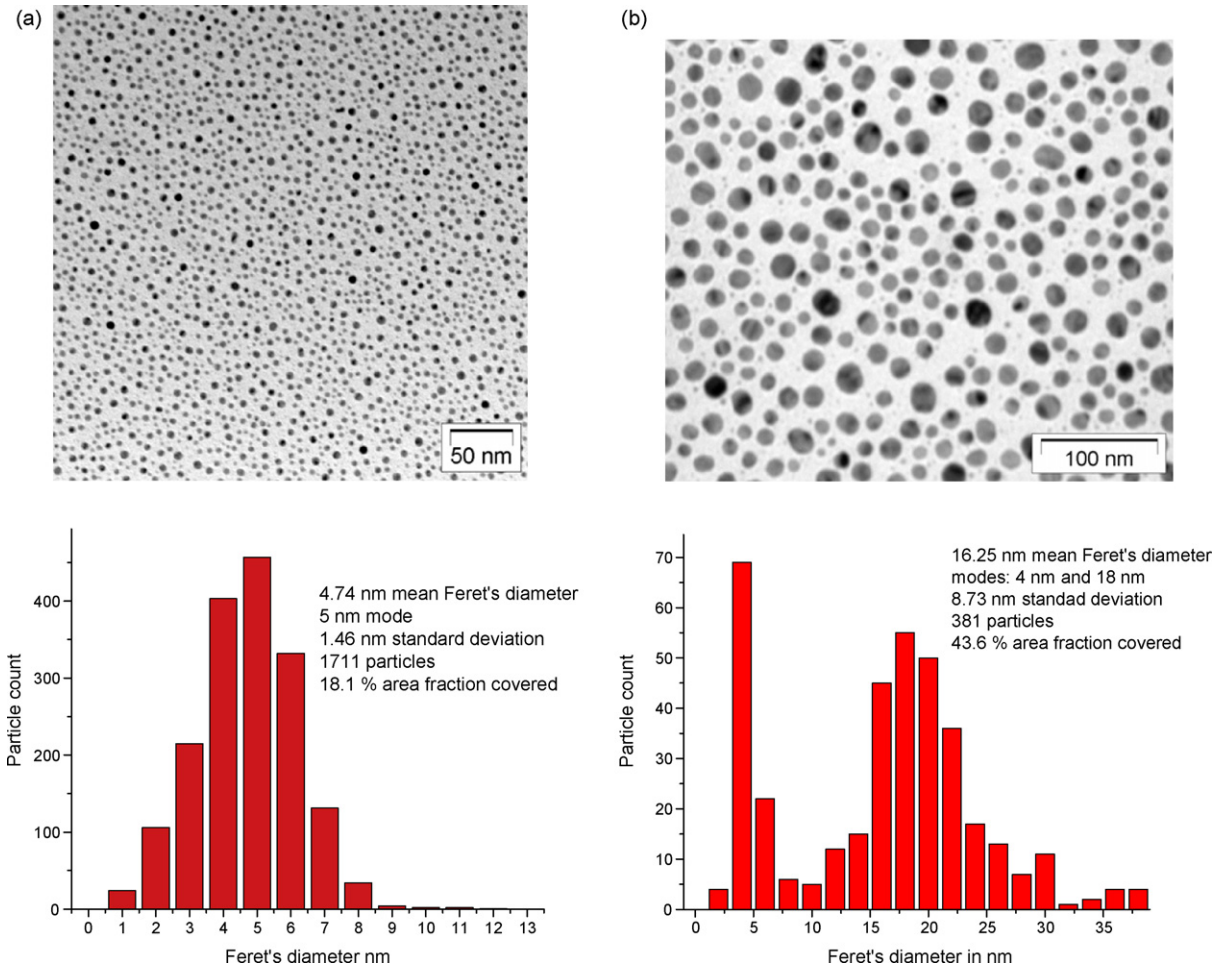

Fig. 1. TEM image and size histogram of as-grown films of Ag nanoparticles deposited in vacuum by: (a) 500, (b) 5000, (c) 10,000 and (d) 15,000 laser pulses.

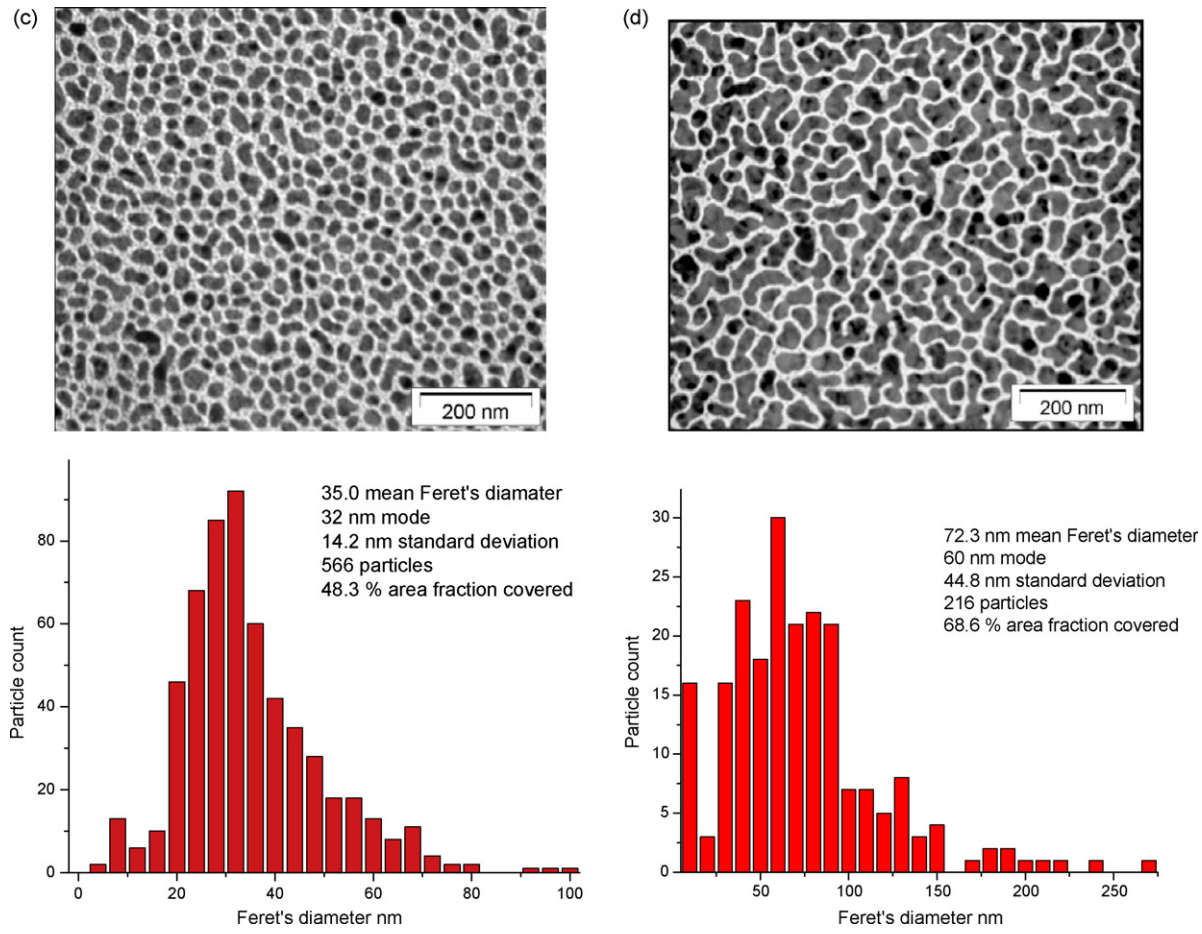

Fig. 1. (*Continued*).

configuration uniform thin films of Ag nanoparticles were deposited over glass substrates with an area of approximately 1.5 cm × 2 cm. A set of films were deposited using different number of laser pulses, varying between 150 and 15,000. The morphology of the films deposited on the TEM grids and the mean sizes of the Ag nanoparticles were examined by TEM, using a CARL ZEISS microscope of 120 kV, model EM910. Some of the films analyzed by TEM were also analyzed by AFM using a Nanoscope III, Digital Instruments, USA, equipment. The absorption spectra of the films deposited on glass substrates were analyzed using a UNICAM UV 300—dual beam UV–vis spectrophotometer.

3. Results and discussion

Fig. 1a–d shows TEM images of nanostructured silver films deposited with 500 and 5000, 10,000 and 15,000 laser pulses. The corresponding nanoparticles size distribution for the TEM images is also shown in these figures. As can be seen, the film deposited with 500 pulses is formed by well-separated nearly spherical silver nanoparticles with sizes in the range from 1 nm to 8 nm, with a mean diameter of around 5 nm. As the number of laser pulses is increased to 5000, the shape of the Ag nanoparticles starts changing to ellipsoidal and bean-like shapes. The corresponding size distribution is bimodal with modes of 4 nm and 18 nm, and a mean Feret's diameter of 16.2 nm. The film deposited with 10,000 pulses shows clearly the presence of larger Ag nanoparticles with a broad distribution of size and shape, including many bean-like particles indicating coalescence between small islands. The film deposited with 15,000 laser shots shows a quasi-percolated state, in which larger islands have grown together, leaving channels of uncovered substrate. Fig. 2 shows the plot of the Feret's diameter (defined as the measured distance between parallel lines that are tangent to the particle's profile and perpendicular to the ocular scale) of the Ag nanoparticles in the deposited films, as a function of the number of laser pulses. As this plot shows, the mean Feret's diameter increases non-linearly with the number of laser shots, and a percolation threshold, where the Feret's diameter would be diverging or infinite, is indicated by a meshed bar for a number of pulses just above 15,000. In Fig. 3 the absorption spectra of films deposited with different

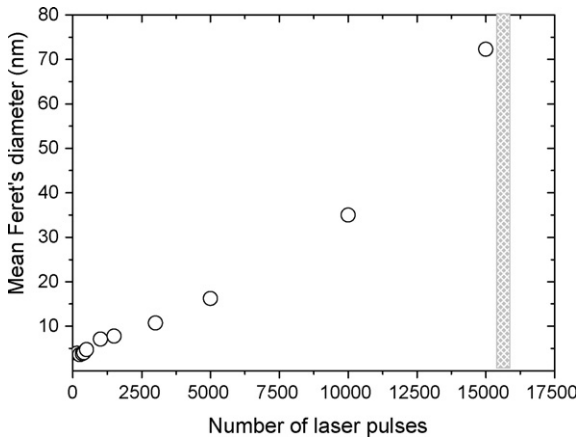

Fig. 2. Plot of the mean Feret's diameter (in nm) of the Ag nanoparticles as a function of the number of laser pulses used for film deposition. The grey bar suggests that there is a threshold pulse number, above 15,000 pulses, for which the film is percolated and therefore the Feret's diameter diverges.

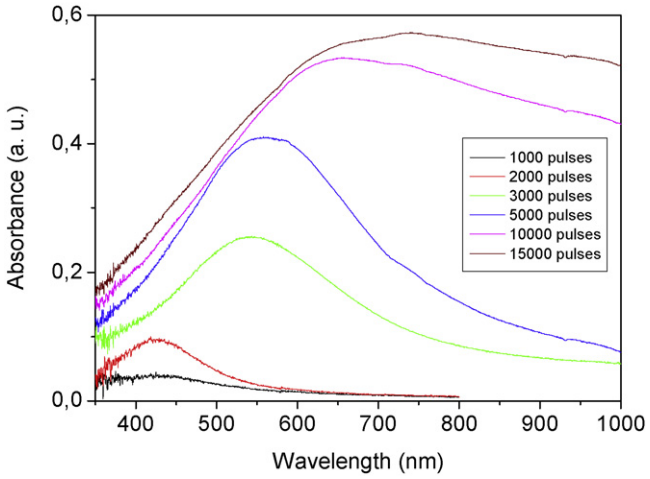

Fig. 3. Absorption spectra of Ag films deposited on glass using different number of pulses.

number of pulses, from 1000 to 15,000 are presented. The absorption peak due to surface plasmon resonance (SPR) is clearly observed in all the spectra. Table 1 summarises the mean Feret's diameter and the wavelength of the SPR peak for nanostructured Ag films deposited with different number of ablation pulses. As Fig. 3 and Table 1 show, the SPR peak has a red shift from 425 nm to 737 nm as the number of pulses increase from 1000 to 15,000. In addition to the wavelength redshift, one can note that the resonance band becomes broader as the number of pulses increases. The correlation of the peak position, red shift and widening of the SPR with the increase of the mean diameter of nanoparticles and widening of size distribution, is in good agreement with the red shift and widening of the SPR peak with the increase in the thickness of nanostructured Ag films prepared by PLD and/or sputtering [18,21,26].

In order to have a three dimensional view of the Ag nanoparticles and to measure their height, some of the films deposited on the TEM grids of Cu covered with carbon, were analyzed by AFM using the tapping mode. To avoid the damage of the carbon film with the AFM tip, the force between this and the sample surface was minimized. Fig. 4a–c shows the typical AFM images for the films deposited with 5000, 10,000 and 15,000 pulses, respectively. The morphology of the films displayed in these AFM images is very similar to the corresponding one obtained by TEM, i.e., the film deposited with 5000 is basically formed by spherical and ellipsoidal or bean-like Ag nanoparticles, meanwhile that deposited with 10,000 shows larger Ag nanoparticles with worm-like shape and that deposited with 15,000 appears quasi-percolated. It is interesting to note from the information displayed in Table 1 that while the Feret's diameter of the nanoparticles doubles with the number of pulses from 5000 to 15,000 pulses, their corresponding height increases by a factor close to 10. This indicates that the nanostructures have a columnar like growth.

Table 1
Mean Feretś diameter and SPR peak position for Ag nanoparticles deposited with different number pulses. The average height of those Ag nanoparticles films observed by AFM images is also shown.

# of ablation pulses	Mean Feret's diameter (nm)	Peak of SPR (nm)	Average height of nanoparticles (nm)
1,000	7.12	425	–
2,000	–	426	–
3,000	10.7	542	–
5,000	16.35	560	6.28
7,000	–	624	–
10,000	35	656	61.84
15,000	72.3	700	53.8

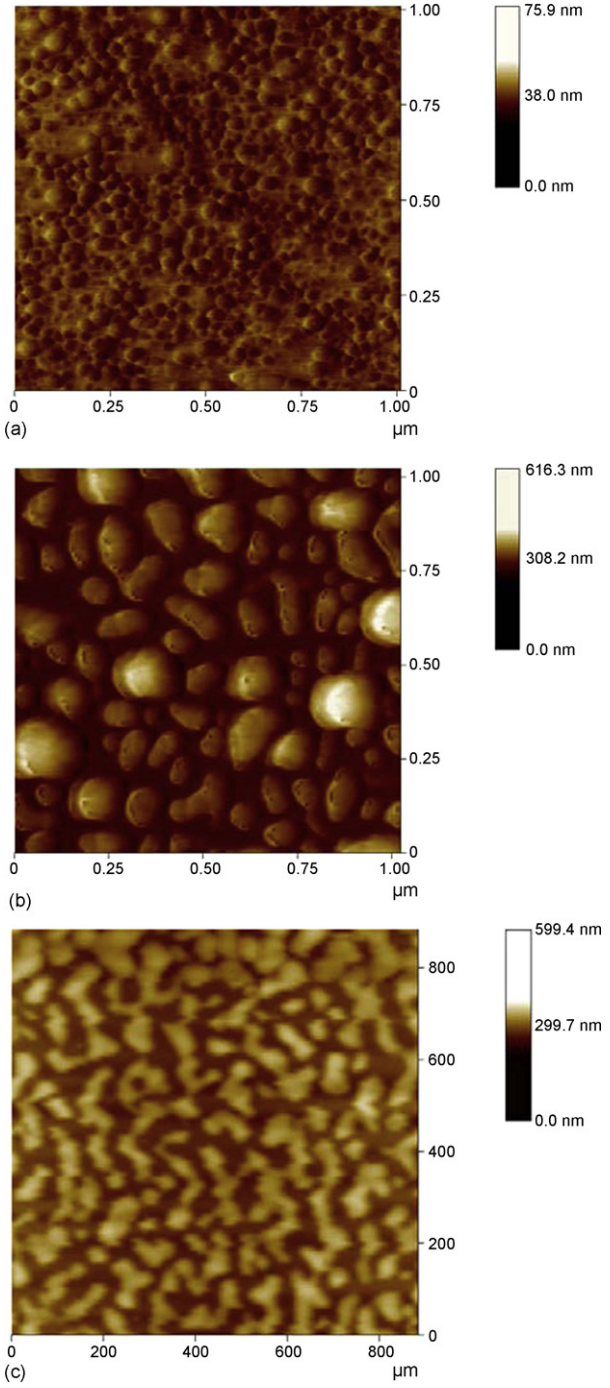

Fig. 4. AFM images of the Ag nanoparticle films deposited after: (a) 5000, (b) 10,000 and (c) 15,000 pulses. The vertical bar on the right side of each image indicates height.

In order to investigate if the nanoparticle deposit is accompanied by the formation of a uniform thin film of silver we analyzed and compared the TEM and AFM images of the grids (originally covered with a carbon film) with and without Ag nanoparticle deposit. The TEM images did not show significant difference in the bottom surface texture, however, one could notice a slight difference in the surface roughness measured by AFM. Namely, the RMS (R_q) value for the pure carbon surface was 0.199 nm, and for the bottom surface of samples with silver nanoparticles was 0.264 nm. This difference is rather small, however, the possibility that one or two thin layers of silver are formed underneath silver nanoparticles cannot be excluded.

Further measurements need to be performed in order to elucidate this particular point.

Since the pulsed laser ablation is a complex process, which involves the interaction between the laser and the solid target, plasma formation and transport of material (ablation plume) across the vacuum or ambient gas to the substrate, the mechanisms of formation of the Ag nanoparticles are not easily elucidated. It is generally accepted that the absorption of a high energy laser pulse focused on a small target surface area can produce the ejection of clusters (nanoparticles), along with ions, electrons, atoms, or radicals, in the form of the ablation plume, however, the nanoparticles can also be formed in the gas phase by condensation of ions, atoms or radicals during plume expansion or they can be formed by nucleation of atomic or molecular species at the substrate surface. Which of these three mechanisms predominate depends on the experimental conditions used in the pulsed laser ablation process. Based in previous works on PLD which have reported that a gas ambient is necessary to promote the nanoparticles formation in the gas phase [29,31,40–42], and the fact that our laser ablation process is performed in vacuum, we can ruled out condensation in the gas phase during plume expansion as an important mechanism to the Ag nanoparticles formation. Although, it is possible that the nucleation and growth of our Ag nanoparticles occur at the substrate surface, as has been assumed that happens for PLD of Cu nanoparticles [43,44], the fact that nanoparticles of approximately 1 nm appear in the TEM images and size distributions of all our deposited films, independently of the number of laser pulses and substrate (TEM grids covered with carbon or formvar film), suggests that these small nanoparticles form part of the ablation plume generated during each pulse. Since a focused laser pulse usually produces a crater in the target material with transient velocity fields and molten pool contours in which solidification and/or crystallization processes occur [45–47], it is possible that the nanoparticles be formed in the low energy density portion of the Gaussian profile of the laser beam, by thermal processes in the periphery of the transient liquid pool. This would indicate that the small Ag nanoparticles are ejected from the Ag target during the first stage of the pulsed laser ablation process. However, in order to support this hypothesis, detailed studies of optical emission of the plasma plume are necessary.

4. Conclusion

Nanostructured Ag thin films have been prepared by pulsed laser ablation in vacuum using pulses of 20 ns at 355 nm of a YAG:Nd laser, and the nanostructure and surface plasmon resonance of the films as a function of the number of ablation laser pulses was studied. TEM analysis evidenced that films deposited with 500 ablation pulses are formed by nearly spherical Ag nanoparticles with diameters in the range from 1 nm to 8 nm, with a size distribution centred around 5 nm. The effect of increasing the number of pulses was to increase the mean diameter of the Ag nanoparticles. Above 5000 pulses, the Ag nanoparticles, besides growing in size, start changing their shape to ellipsoidal and bean-like shapes. For 10,000 pulses fingered shapes are formed in the films, and for 15,000 pulses, quasi-percolated Ag films are obtained. The three dimensional analysis of the films, made by AFM, showed similar trends in the morphology of the films to that observed in the two dimensional analysis made by TEM. In addition a columnar like growth is observed. We can conclude that under the ablation approach used in this work, it is possible to control, with the number of ablation pulses, the nanostructure of the Ag films.

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