

SYNTHESIS BY PULSED LASER ABLATION IN Ar AND SERS ACTIVITY OF SILVER THIN FILMS WITH CONTROLLED NANOSTRUCURE

C. D'ANDREA

*Dipartimento di Fisica della Materia e Tecnologie Fisiche Avanzate, Università di Messina,
Salita Sperone 31, 98166 Messina, Italy*

P.M. OSSI

*Dipartimento di Energia & Centre for NanoEngineered MAterials and Surface & NEMAS Politecnico di Milano Via Ponzio,
34-3, 20133 Milano, Italy*

N. SANTO

*Centro Interdipartimentale di Microscopia Avanzata, Università degli Studi di Milano,
Via Celoria 26, 20133 Milano Italy*

S. TRUSSO

*Istituto per i Processi Chimico-Fisici del CNR, S.ta Sperone, C.da Papardo,
Faro Superiore, 98158, Messina, Italy.*

Thin silver films were deposited by pulsed laser ablation in a controlled Ar atmosphere and their SERS activity was investigated. The samples were grown at Ar pressures between 10 and 70 Pa and at different laser pulse number. Other deposition parameters such as laser fluence, target to substrate distance and substrate temperature were kept fixed at 2.0 J/cm², 35 mm and 297 K. Film morphologies were investigated by scanning and transmission electron microscopies (SEM, TEM). Surface features range from isolated nearly spherical nanoparticles to larger islands with smoothed edges. Cluster growth is favored by plume confinement induced by background gas. After landing on the substrate clusters start to aggregate giving rise to larger structures as long as the deposition goes on. Such a path of film growth allows controlling the surface morphology as a function of laser pulse number and Ar pressure. These two easy-to-manage process parameters control the number density and the average size of the as-deposited nanoparticles. Surface enhanced Raman scattering measurements were performed by soaking the samples in rhodamine 6G aqueous solutions over the concentration range between 1.0x10⁻⁴ M and 5.0x10⁻⁸ M. The dependence of the film SERS activity on their surface morphology is discussed.

1. INTRODUCTION

There is a growing interest toward metal nanoparticles (NPs), owing to their peculiar optical, structural and electronic properties, which depend on their size, shape and their mutual aggregation properties [1]. As a consequence metal nanoparticles have been the object of intensive theoretical and experimental research. In particular the search for production methods able to control their structural properties was extended to physical deposition methods usually adopted for the growth of bulk materials. This is the case of the pulsed laser ablation (PLA) technique. PLA is nowadays widely employed to grow a large class of materials, especially when such materials cannot be produced by alternative methods, or when PLA gives superior results in terms of material quality [2]. In conventional PLA the use of an ambient gas during the deposition process is usually required to correct an incongruent stoichiometry transfer from the target to the deposited films, as in the case of superconductor oxides [3]; or when a foreign specie, not included in the target material, is desired in the resulting material, as, for example, in the case of carbon nitride thin films produced by ablating graphite in a nitrogen atmosphere [4]. The pressure values at which deposition takes place are determined by the need to incorporate in the growing films the desired quantity of the gaseous specie, yet avoiding to lower excessively the kinetic energies of the ablated species. Concerning this it was observed that the properties of the PLA deposited materials depend in a non trivial way on the pressure of an ambient gas. The presence of a ambient gas, in fact, leads to a radical modification of the laser generated plasma expansion dynamics. In vacuum a plasma free expansion is observed while in presence of an ambient gas

plasma slowing down, plasma confinement and shock wave formation can be observed, depending on the adopted deposition conditions [5-7]. As a consequence, increasing the pressure of the ambient gas do not lead simply to a compositional change but strongly influences the film morphological properties. From this point of view inert gases can be used to control the energies of the plasma species in order to modify the morphological properties of the films without altering their stoichiometry with respect to the target one. In this work we exploit the presence of an Ar gas atmosphere to grow silver thin films by means of PLA with controlled morphology, and hence controlled optical properties. We found that controlling two experimental parameters, namely the Ar gas pressure and the number of laser shots, markedly different morphologies are obtained. In this work Ag thin films were used as active layer in surface enhanced Raman spectroscopy experiments to detect the presence of a dye molecule in aqueous solutions at concentration levels so low as 2.0x10⁻⁷ M. The morphology influence on the observed SERS activity is presented and discussed.

2. EXPERIMENT

Silver thin films were grown by means of pulsed laser ablation using a KrF excimer laser ($\lambda=248$ nm, pulse width 25 ns). The laser pulse is focused onto the target surface using a quartz lens, a pure silver target is positioned inside a vacuum chamber on a rotating holder in order to avoid craterization phenomena. In front of the target is positioned the substrate holder. The system is equipped with a mass flow controller which allows for the controlled introduction of gaseous species into the chamber. Different substrates

were used depending on the characterization technique used to study the samples: c-Si for scanning electron microscopy (SEM), 7059 Corning glass for Raman and UV-vis absorption spectroscopy and a-C covered copper grids for transmission electron microscopy analysis. A set of samples was grown at the Ar gas pressure between 10 and 70 Pa using 15000 laser shots. All the other relevant deposition parameters were kept fixed: the laser fluence to 2.0 Jcm^{-2} , the target to substrates distance to 35 mm and the substrate temperature at room temperature (RT). TEM images were acquired with a Zeiss Leo 912AB microscope while SEM imaging was performed using a Zeiss Supra 40 field ion scanning microscope. In order to test the SERS activity of the samples they were soaked into rhodamine 6G aqueous (R6G) solutions at different concentrations for 1 h and then rinsed with deionized water. Four different R6G concentrations were tested in the range between 0.1 mM and 50 nM. Raman characterization was performed using a HR-800 Jobin-Yvon micro-Raman apparatus, using the 632.8 nm line of a He-Ne laser as the exciting source. The laser power at the samples surface was kept low, about $100 \mu\text{W}$, in order to avoid R6G degradation. Raman spectra were acquired using a 10x microscope objective resulting in a probed area of about $3.2 \mu\text{m}^2$, while integration times were varied between 1 s up to 240 s depending on the signal to noise ratio. UV-vis spectra were acquired using a Lambda 900 Perkin Elmer spectrophotometer.

3. RESULTS AND DISCUSSION

In Fig.1 are reported the SEM images of the surface of the samples grown at the Ar pressures of 10 and 100 Pa. The surfaces are characterized by the presence of silver nanoparticles whose size and shape depend on the adopted Ar pressure. In particular in Fig.1 the surface of the sample deposited at 10 Pa of Ar is shown. Large nanoparticles with size larger than 35 nm are surrounded by a *depletion region* where the presence of smaller NPs can be observed. The scenario is quite different for the samples deposited at 40 and 70 Pa of Ar (Fig.2 and Fig.3). For those samples the surface is characterized by the presence of the nearly spherical NPs with typical dimensions of 10 nm at 40 Pa and of 5 nm at 70 Pa. In previous works [7,8] we studied the growth mechanism of silver thin films at deposition conditions similar to the ones adopted in this study. In particular we investigated the Ar range pressure between 10 and 100 Pa and we used different laser shot numbers in order to follow the thin film formation mechanism. Our experiments gave evidence for a two step mechanism of film formation: in the first step the presence of the Ar atmosphere induces the aggregation between the silver atoms during the plasma expansion leading to the formation of NPs; in the second step NPs landing on the substrates and having very low kinetic energies start to aggregate giving rise to larger NPs and finally to a coalesced structure characterized by the presence of an interconnected network of silver island with smooth rounded edges. The dimensions of the NPs, which form *in flight*, are determined by the Ar pressure: the higher the Ar pressure the higher the collisional rate inside the plasma which results in larger NPs [9]. The laser shot number, on the other side, drives the aggregation process *on the substrates* (at a fixed Ar pressure). At low laser shot number, isolated NPs are observed on the sample surface, at increasing laser

shot number the NP number density on the surface increases and NPs start to aggregate, initially giving rise to bigger NPs, then to even larger islands with rounded edges, until, for high enough laser shot number, a totally covered surface is achieved. The morphologies observed for the samples grown at different Ar pressures, as shown in Figs.1-3, thus refer to different stages of film formation. The sample grown at 10 Pa of Ar shows the initial stage of aggregation among several NPs which result in the large NPs observed in Fig.1. The process produces the depletion area where are evident smaller NPs: the latter formed at a later time with respect to the bigger ones that underwent a more extended aggregation process. Also the surface of the sample grown at 40 Pa of Ar shows evidence for an aggregation process; in this case all the NPs seem to have nearly the same size. A different scenario is showed by the surface of the sample grown at 70 Pa of Ar. In this case a random distribution of nearly spherical NPs is observed on the surface, without any evidence of aggregation processes.

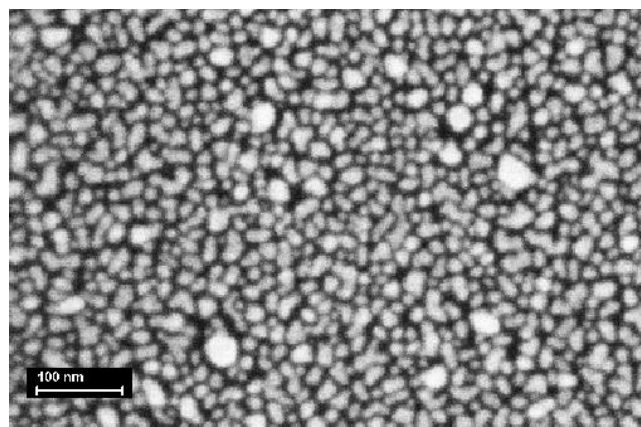


Fig.1. SEM picture of the surface of the sample grown in Ar at 10 Pa using 15000 laser shots. A magnified portion of the original SEM image is shown for a better comparison with the other images.

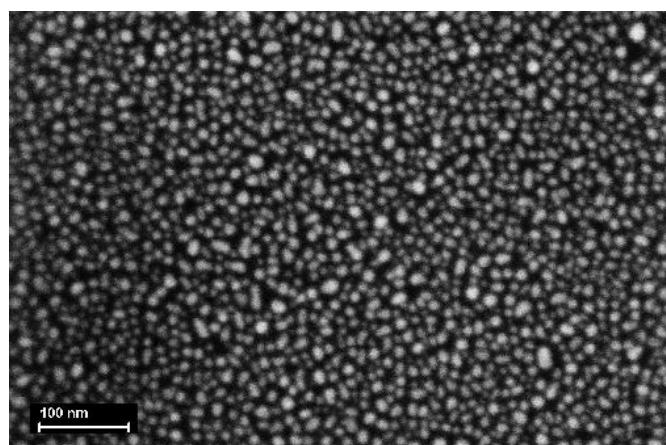


Fig.2. SEM picture of the surface of the sample grown in Ar at 40 Pa using 15000 laser shots.

The different observed morphologies lead to different optical properties. Bulk silver shows an absorption peak in the near-UV, due to the coherent oscillations of surface

electrons interacting with an external electromagnetic radiation, called surface plasmon resonance (SPR).

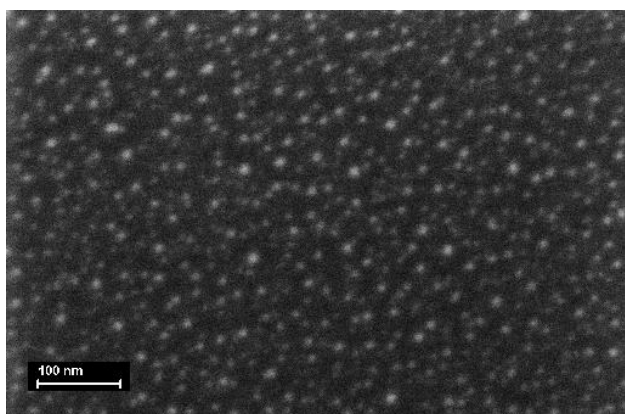


Fig.3. SEM picture of the surface of the sample grown in Ar at 70 Pa using 15000 laser shots.

When typical sizes are reduced to the nanoscale range, the SPR peak shifts to the visible region of the spectrum at about 390 nm. The position and shape of the SPR peak depend on size, shape and mutual aggregation properties of the nanostructures. In Fig.4 are shown the UV-vis absorption spectra of the samples grown at the Ar pressures of 10, 40 and 70 Pa. It can be observed that, keeping fixed the number of laser shots at 15000 and decreasing the Ar pressure from 70 Pa down to 10 Pa, the SPR position red-shifts from 482 to 558 nm while its width progressively increases from 280 nm up to more than 350 nm. As reported above, silver NPs of few nm in size show the SPR peak position near 390 nm and increasing NP size a red shift of the SPR is expected. However the shift is smaller than the observed one; on the contrary the peak position and its width markedly depend on the deviations of NP shape from spherical and on the interaction among closely spaced or aggregated NPs [1]. The SERS activity of the deposited films was tested soaking the samples in aqueous rhodamine 6G solutions at different concentrations for 1 h. In Fig.5 are reported the Raman spectra of the samples soaked in the 2.0×10^{-6} M R6G solution. The spectra are normalized to their own integration times. R6G dye Raman features can be observed at 615, 777, 1189, 1314, 1366 1513 and 1651 cm^{-1} in the spectrum of the samples deposited at 10 Pa of Ar. The 615 cm^{-1} Raman peak is due to the C–C in plane bending mode, the peak at 777 cm^{-1} is attributed to the C–H out of plane bending mode, the remaining peaks refer to aromatic stretching vibrations of C atoms. Less evident, but still visible, are the R6G Raman features in the spectra of the samples deposited at higher Ar pressures. Moreover in Fig. 5 these spectra are multiplied by a factor of 2 for the sake of clarity. Similar results were obtained from the samples soaked in the other R6G concentration solutions, with the exception of the 5×10^{-8} M one, for which no Raman activity could be detected even increasing the integration times up to 240 s.

It must be mentioned that no Raman signal can be detected from uncovered substrates, even if soaked in R6G solution at concentration of 0.1 mM.

We can compare the different SERS activity of the samples looking at the intensity of the 615 cm^{-1} peak which is discernible in all Raman spectra. The peak intensities, reported in the inset of Fig.5, are the higher, the lower the

adopted Ar pressure. In SERS experiments the observed enhancement of Raman signals depends on the excitation wavelength, the nanoparticle size and the interparticle spacing.

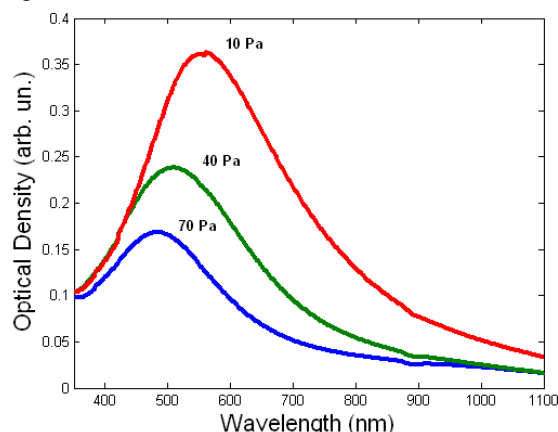


Fig.4. Absorption spectra of the samples deposited at different Ar pressures and with 15000 laser shots.

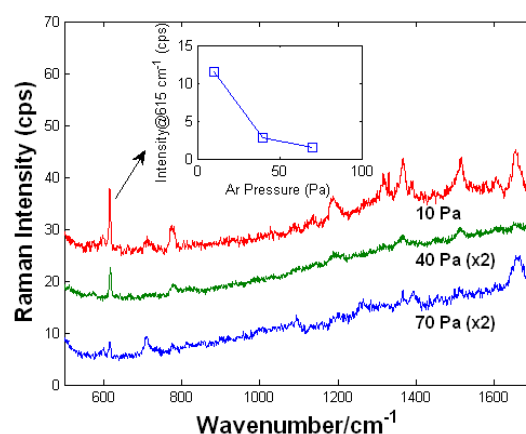


Fig.5. Raman spectra of the samples deposited at different Ar pressures with 15000 laser shots. Spectra collected from the 70 and 40 Pa deposited samples are multiplied by a factor of 2. In the inset the intensity of the Raman peak at 615 cm^{-1} vs the Ar pressure.

The increase of the average NP number density and size observed as the Ar pressure is decreased from 70 Pa down to 10 Pa corresponds to a decrease of the mean interparticle distance and can lead to mutual contact of adjacent NPs. The formation of ‘hot spots’ at the junction site between NPs [10-11] can result in very high enhancement factors. Alternatively, coupling of the excitation wavelength to the surface plasmon resonance of the two samples can explain their different activity. The SPR peak position, in fact, shifts from 482 to 558 nm so that a higher enhancement factor is expected for the samples showing a stronger absorption at the laser excitation wavelength of 633.8 nm .

4. CONCLUSIONS

In conclusion we described a method to grow arrays of silver NPs whose optical properties can be controlled through an easily accessible deposition parameter such as the Ar gas pressure. The deposited thin films present a clear SERS activity that depends on their optical and morphological properties: the detection of R6G molecules can be performed

in aqueous solution at concentration level as low as 5.0×10^{-7} M. The growth method is attractive because the deposition takes place at room temperature without imposing any restriction to the chemical nature of the substrates.

Noticeably, it can be further improved owing to the fact that only a limited range of deposition parameters was explored till now.

-
- [1]. *K. L. Kelly, T. A. Jensen, A. A. Lazarides, G. C. Schatz* in *Metal Nanoparticles: Synthesis, Characterization and Applications*, D. L. Feldheim, C. A. Foss Jr. eds., 2002, (Dekker, New York).
- [2]. *G.K. Hubler* in *Pulsed laser deposition of thin films*, chapt. 13, D.B. Chrisey, H.K. Hubler eds., 1994 (Wiley, New York).
- [3]. *A. Gupta*, *J. Appl. Phys.*, 73, 7877 (1993).
- [4]. *S. Trusso, C. Vasi, F. Neri*, *Thin Solid Films*, 355, 219 (1999).
- [5]. *D. B. Geohegan*, *Appl. Phys. Lett.* 60, 2732 (1992).
- [6]. *J. Gonzalo, C. N. Afonso, I. Madariaga*, *J. Appl. Phys.*, 81, 951 (1997).
- [7]. *E. Fazio, F. Neri, P. M. Ossi, N. Santo, S. Trusso*, *Laser Part. Beams*, 27, 281, (2009).
- [8]. *E. Fazio, F. Neri, P. M. Ossi, N. Santo, S. Trusso*, *Appl. Surf. Sci.*, 255, 9676 (2009).
- [9]. *A. Bailini, P.M. Ossi*, *Europhys. Lett.* 79, 35002-1 (2007).
- [10]. *H. Xu, J. Aizpurua, M. Kall, P. Apell*, *Phys. Rev. E*, 62, 4318 (2002).
- [11]. *A. M. Michels, J. Jiang, L. E. Brus*, *J. Phys. Chem. B*, 104, 11965 (2000).
- [12]. *E. C. Le Ru, P. G. Etchegoin*, *Chem. Phys. Lett.*, 396, 393 (2004).