Plasmonic substrates elaborated by plasma process: optimization of the plasma parameters according to the optical response of the structures

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Abstract: Elaboration in a controlled way of large-area plasmonic substrates is achieved by combining sputtering of silver nanoparticles and plasma polymerization in an axially-asymmetric capacitively-coupled RF discharge maintained at low pressure. The plasma parameters and deposition conditions were optimized according to the optical response of these substrates. Structural characterization of the samples confirms the process efficiency.

Keywords: silver nanoparticles, plasma silica, PECVD, PVD, plasmonic substrates

1. Introduction

The properties of nanocomposite materials are nowadays widely studied aiming at a large spectrum of applications. Nanocomposite materials consisting of noble nanoparticles embedded in dielectric matrix represent a huge interest for plasmonic devices to guide the electromagnetic energy [1]. The main advantage of these structures is the possibility to manipulate, localize and enhance the electromagnetic field at nanoscale level. The plasmonic coupling with light enhances the range of useful optical phenomena having potential applications in areas such as ultra-sensitive chemical and biomolecular detection and analysis, photocatalysis, etc.

It is generally acknowledged that the silver nanoparticles (Ag-NPs) realize the best nanoscale antenna for amplifying local electronic and vibrational signals in the visible range, providing unique molecular information in the optical far-field regime. In the field of scientific research, two main spectroscopy techniques have emerged based on Localized Surface Plasmon Resonance (LSPR) and Surface-Enhanced Raman Scattering (SERS). Advances in micro and nano-fabrication technology have made available integration of sensitive LSPR to lab-on-a-chip platforms. They are increasingly popular in fundamental biological studies, health science research and environmental monitoring [2]. Since its discovery in 1974 on pyridine molecules adsorbed on rough silver surfaces [3], SERS has received a great deal of attention as powerful analytical technique for molecular spectroscopy, biomolecular recognition and ultra-sensitive detection (down to a single molecule). However, the limits imposed by the fabrication of SERS substrates remain a major drawback for their large application. It is due to the drastic requirements for controlling on large areas, and in a reproducible way, a well-defined spacing between the metallic nanostructures and the probing molecules. Generally, the enhancement of the scattering cross-section for SERS substrates is attributed to an electromagnetic mechanism (EM based on surface “plasmon resonance”) and/or to a chemical one (CM based on “charge transfer”). Whatever the mechanism, the requirement for an efficient SERS substrate, is the control on the nanometer scale of either size and shape of the metallic particles but mainly of the distance between their surface and the probed molecules. As a consequence, another challenge to overcome is the control of thickness and porosity of the overlayer. The thickness of the overlayer must be selected at nanoscale level as a compromise between the preservation of SERS enhancement and the protection of Ag-NPs against oxidation, for example [4], and against direct interaction of the Ag-NPs with the probing molecules.

This work presents results on plasma elaboration in a controlled way of large-area plasmonic substrates consisted of a single layer of Ag-NPs covered and embedded in SiO2 matrix close to the free surface. The plasma process and details on the operation conditions are given in the next section. Diagnostic methods applied for the structural and optical characterisation (TEM, FTIR, ellipsometry and reflectometry) of the elaborated substrates and results from their analysis along with the discussion are presented in Section 3. The functionality of the elaborated plasmonic substrates is demonstrated on the basis of their optical response in ellipsometry and reflectometry measurements. Finally, Section 4 summarizes the main conclusions and gives the perspectives.

2. Plasma deposition process

The nanocomposite structures were elaborated by using the plasma of an axially-asymmetric capacitively-coupled RF (13.56 MHz) discharge combing Physical Vapor Deposition (PVD), as a first step, and Plasma Enhanced Chemical Vapor Deposition (PECVD) as a second step in the applied deposition procedure shown in Fig. 1. The discharge powered electrode (smaller electrode) was an
Ag-made target to bear the Ag-NPs sputtering. The axially-asymmetric design of this RF discharge induces a self-bias voltage \( V_{dc} \) on the powered electrode, controlling in that way the metal sputtering. The deposition of plasma silica overlayer was performed in the same reactor. The plasma reactor is described in details elsewhere [5]. The plasma behaviour during deposition was controlled by Optical Emission Spectroscopy (OES) and electrical measurements [5].

Fig. 1. Pathway for fabrication of large-area plasmonic substrates (Ag-NPs delta-layer embedded in SiO\(_2\) matrix).

The used plasma process is fully compatible with the standard microelectronic technologies. It is versatile in terms of experimental conditions which enlarges the possibility to probe and, consequently, to optimize the optical response of the elaborated plasmonic structures. To realize the plasmonic structures a single layer of Ag-NPs was deposited by Ag-sputtering on the surface of thermally grown SiO\(_2\)-layer (thickness of 80 nm) on Si-substrate (2” in diameter) in Ar-discharge maintained at low pressure \( p_{Ar} = 5.2 \text{ Pa} \). The substrate was fixed to the grounded electrode. The Ag-NPs size, density and shape were controlled through tuning the sputtering operating conditions. The sputtering time was varied between 5 s and 30 s for different input powers (\( P = 10 – 80 \text{ W} \)), corresponding to a self-bias voltage variation in the range \( V_{dc} = -400 – -1000 \text{ V} \). The plasma silica (SiO\(_2\)plasma) overlayer embedding the Ag-NPs was deposited in the plasma sustained in a gas mixture of argon (Ar flow - 2.8 sccm) - hexamethyldisiloxane (HMDSO - [CH\(_3\)]\(_6\)Si\(_2\)O) - oxygen (O\(_2\) flow – 1.25 sccm) at total gas pressure \( p_{tot} = 7.68 \text{ Pa} \). The HDMSO amount was introduced in the discharge by pulses with period \( T = 5 \text{ s} \) (\( T = t_{on} + t_{off} \)) and injection time \( t_{on} = 3.1 \text{ s} \) which corresponds to an average HDMSO flow of 0.248 sccm. The injected RF power for the SiO\(_2\)plasma deposition was fixed to 120 W assuring high degree of HMDSO decompositon in the plasma. The deposition time was varied during the study, controlling in that way the thickness of SiO\(_2\)plasma overlayer.

3. Diagnostic methods, results and discussion

Structural analysis of the elaborated plasmonic substrates was performed by Transmission Electron Microscopy (TEM) in plan and cross-section view, Fourier Transform InfraRed spectroscopy (FTIR) and ellipsometry. Cross-section and plan view specimens were prepared for TEM analyses by standard procedure using mechanical polishing followed by Ar\(^+\) ion milling. The observations were performed using a field emission Transmission Electron Microscope, FEI Tecnai\(^{\text{TM}}\) F20 microscope operating at 200 kV, equipped with a spherical aberration corrector. The FTIR spectra were acquired with a Bruker Vertex 70 spectrometer in the range 400 – 4000 cm\(^{-1}\) to obtain information about the composition of SiO\(_2\)plasma deposited layer. The refractive index and thickness of the film were determined by spectroscopic ellipsometry using a SOPRA GES-5 ellipsometer in the range 250 – 850 nm with an incident angle of 75\(^\circ\). The optical response of elaborated plasmonic substrates was analysed on the basis of ellipsometry and reflectivity measurements. The reflectivity spectra were recorded by using a Varian Cary 5000 spectrophotometer in the range 200 – 800 nm in quasi normal incidence.

Figure 2 represents a TEM image in cross-section view of typical elaborated sample. It corresponds to the following structure: Ag-NPs delta-layer deposited at \( P = 40 \text{ W} \) for \( t_s = 5 \text{ s} \) and covered by a SiO\(_2\)plasma layer of thickness \( d_{\text{SiO}_2\text{plasma}} = 13 \text{ nm} \) (deposition time, \( t_d = 60 \text{ s} \)). One can clearly notice the planarity in the Ag-NPs delta-layer (the Ag-NPs layer average thickness is of 9 nm). The total thickness of the structure is 105 nm which fulfills the conditions for anti-reflectivity of optical waves in the middle of visible range [6, 7].

Fig. 2. TEM cross-section image of a sample elaborated by combining silver sputtering and PECVD. Conditions for the Ag-NPs single layer deposition \( t_s = 5 \text{ s}, P = 40 \text{W} \) (\( V_{dc} = -750 \text{ V} \)). The SiO\(_2\)plasma deposition time \( t_d = 60 \text{ s} \).

The evolution of the Ag-NPs size, density and shape with the injected power for Ag-sputtering is shown in Fig. 3 for a fixed sputtering time \( t_s = 5 \text{ s} \) and two different powers 40W (Fig. 3a) and 80W (Fig. 3b) covered by a SiO\(_2\)plasma overlayer of thickness \( d_{\text{SiO}_2\text{plasma}} = 13 \text{ nm} \) (deposition time, \( t_d = 60 \text{ s} \)). The size of Ag-NPs increases from 11.1 \pm 2.4 nm to 19.6 \pm 7.8 nm. Their density is reduced from 4.6 \times 10^{11} \text{ NPs/cm}^2 to 1.7 \times 10^{11} \text{ NPs/cm}^2, covering an area of 45.8% and 42.6%, respectively. The same trend is observed when the injected power is fixed and the sputtering time is increased. For \( P = 10 \text{ W} \), increasing the sputtering time from 10 to 30 s leads to an increase of the mean diameter of the Ag-NPs from 6.2 \pm
2.6 nm to 10.4 ± 4.5 nm corresponding to a coverage area of 24% and 34%, respectively. The density of Ag-NPs however decreases from $7.6 \times 10^{11}$ NPs/cm$^2$ to $3.9 \times 10^{11}$ NPs/cm$^2$, for the two sputtering times, respectively.

For a fixed sputtering time by scaling up the injected power the shape of Ag-NPs changes from quasi-spherical ($P = 10$ W) to prolate spheroid ($P > 60$ W). Increasing the sputtering time from 5 s up to 30 s does not influence the Ag-NPs shape for low injected power ($P = 10$ W), while it leads to overtaking the percolation threshold for high injected power ($P = 80$ W). Consequently, to obtain a delta-layer of large Ag-NPs, high injected power and small sputtering times must be privileged.

As mentioned above, another challenge in the plasma elaboration of plasmonic substrates is the SiO$_2$ overlayer. To achieve a SiO$_2$$_{\text{plasma}}$ layer with properties close to thermal silica layer the plasma composition was adjusted by varying the gas mixture. The pulsed injection of HMDSO permits a fine control of the plasma parameters. The suitable HMDSO injection time was determined in relation with the O$_2$ flow rate in order to ensure both complete plasma organosilicon covering of the Ag-made electrode to prevent from Ag-sputtering and a plasma deposition of SiO$_2$ layer with properties close to a thermal silica layer. The oxygen injection into the plasma maintained in Ar-HMDSO mixture introduces reactive species that promote oxidation of the methyl groups and the volatile species, such as water and carbon dioxide. To improve the oxidation efficiency in the plasma reactor used for this study, the oxygen flow was introduced grazing the surface of the samples by means of an appropriate port. The parameters for plasma polymerization phase, like applied power, HMDSO injection time and O$_2$ flow rate were optimized and the composition of deposited SiO$_2$ layer was determined by FTIR and ellipsometry. The real-time monitoring of the plasma process by OES [5] is indispensable for obtaining plasma silica layers of high quality.

The ellipsometric spectrum of SiO$_2$$_{\text{plasma}}$ layer (Fig. 5) was used to determine the refractive index and the thickness of the layer by applying the Forouhi-Bloomer dispersion low [9] and the obtained values are $n = 1.45$ (at $\lambda = 632.8$ nm) and $d_{\text{SiO}_2\text{plasma}} = 96$ nm, respectively. The ellipsometric spectrum of SiO$_2$$_{\text{plasma}}$ layer is identical to the thermal SiO$_2$ layer for the same thickness. It means that the
Fig. 5. Ellipsometry spectra of elaborated samples: SiO$_2$$_{\text{plasma}}$ layer (black line) and two plasmonic substrates $P = 40$ and $80$ W, $t_s = 5$ s, and deposition time for the SiO$_2$$_{\text{plasma}}$ overlayer $t_d = 60$ s. Composition is close to thermal silica and there is no silver contamination in the structure. In fact, due to the electric field polarization, the ellipsometric measurements are extremely sensitive to changes in the refractive index and the extinction coefficient due to the presence of Ag-NPs inside the SiO$_2$ matrix. Even a very small fraction of Ag-atoms in the layer leads to a departure in the cos$\Delta$ variation, that gives the phase difference, induced by the reflection, between the perpendicular and parallel components of the polarized electric field. When Ag-NPs are embedded in the SiO$_2$ layer, the ellipsometric spectra indicate their presence by shift to higher energies in the tan$\Psi$ variation, the latter closely related to changes in the amplitudes of the polarized electric field after reflection, and by appearance of a peak in the cos$\Delta$ variation at the same wavelength as for the tan$\Psi$ variation, as shown in Fig. 5 for the two substrates presented on the TEM plan-view images in Fig. 3. Larger the size of Ag-NPs, larger the energy shift of their peak on the ellipsometric spectra is.

To guarantee the performance of plasmonic substrates when integrated in devices one needs to characterize their dielectric response. A good way is to use reliable non-destructive diagnostic methods like ellipsometry and reflectometry. Visible-UV reflectance spectra are particularly easy to obtain and they display a notable sensitivity to the incorporation of Ag-NPs in the dielectric matrix, as shown in Figs. 6 and 7.

Fig. 6. Reflectance spectra of plasmonic substrates: the Ag-NPs delta-layers were deposited with $P = 10$ W for increasing sputtering times $t_s = 10, 20, 30$ s. The SiO$_2$$_{\text{plasma}}$ deposition time $t_d = 30$ s ($d_{\text{SiO$_2$$_{\text{plasma}}}} = 4$ nm).

By changing either the sputtering time (Fig. 6) or the injected power (Fig. 7) one drastically affects the reflectance in the visible range (400 – 750 nm) where most of the potential applications of plasmonic substrates are expected. This enhanced sensitivity is a direct consequence of the design of our specific substrates which allows to simultaneously combine strong absorption at the LSPR (near 410 nm) and antireflective effect of the multilayer structure (near 600 nm) [6]. On Figs. 6 or 7, one clearly observes that higher the embedded Ag amount, by increasing the deposition time or the injected power respectively, higher the reflectance in the middle of the visible range is (near 500 nm). One thus expects a high sensitivity in the elastic scattering response for LSPR-sensitive devices or inelastic scattering response for SERS substrates.

Fig. 7. Reflectance spectra of plasmonic substrates: the Ag-NPs delta-layers were deposited with $P = 40, 60$ and $80$ W for fixed sputtering time $t_s = 5$ s. The SiO$_2$$_{\text{plasma}}$ deposition time $t_d = 60$ s ($d_{\text{SiO$_2$$_{\text{plasma}}}} = 13$ nm).

4. Conclusions
We have shown how the key parameters of the plasmonic nanostructures (size, density, distance to the surface) can be controlled by tuning the elaboration conditions combining sputtering of silver nanoparticles and plasma polymerization. The optical response of the composite substrates has shown to be very sensitive to any stimuli that affect the dielectric response at the vicinity of their surface. They thus appear as promising for enhanced spectroscopies based on LSPR or SERS, and for surface-plasmon mediated photocatalytic devices.

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References