PACKED COLLOIDAL SPHERES FOR THIN FILM STRUCTURATION; TOWARDS MODULATION AND TUNABILITY OF SURFACE PLASMON RESONANCE

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Abstract: This work is devoted to present developments of metallic triangular nano/micropatterns arrays based on self-assembly of closely packed colloidal polystyrene microspheres, using a combination of colloidal lithography and Pulsed Laser Deposition (PLD) process. Au and Ir metal triangular structures with thicknesses of 50 - 100 nm, directly fabricated on Al_2O_3 or embedded in a VO_2 matrix have been studied in order to tune the position and intensity of localized surface plasmon resonances (LSPR). The position of the LSPR depends strongly of the size and the shape of the metallic patterns, the spacing between them and the surrounding dielectric environment.

Keywords: LSPR, PLD, Colloidal lithography, Au and Ir LSPR, vanadium dioxide.

1. INTRODUCTION

Self-assembly of closely packed colloidal microspheres plays a major role in a plethora of applications such as localized surface plasmon resonances. In the last decades, localized surface plasmon resonances (LSPR) has become a rapidly developing subdiscipline of nanophotonics with various applications, particularly in waveguiding and sensing applications. 'Plasmons' are collective oscillations of free electrons in metals [1], that occur at a specific well-defined frequency. Excitation of plasmons by an electric field of electromagnetic radiation is not allowed in bulk matter, where plasmon and photon energy dispersion curves never cross each other [1]. The factors that influence the intensity and position of plasmon resonances are: dielectric and physical-chemical environment (such as: absorbing/ non-absorbing dielectric environment, temperature, pressure, surface chemical interactions), size, shape and structure periodicity (assembly) [2]. Specific Architectures, like metallic micro/nano-polygones (triangle, square ...) are the key of controlling the resonance response taking benefit of both "peak/size geometry effects" and the possibility to downsizing the same geometry. These architectures find interests in various applications such as wavelength-tunable optical absorbers [3], plasmonic circuits [4], surface-enhanced Raman scattering [5] [6], terahertz (THz) technology [7], bolometric photodetection [8], etc. The study presented here fits in this domain. To realize specific architecture, we employ a combination of colloidal lithography and Pulsed Laser Deposition (PLD) process in order to manufacture systems that can support localized surface plasmon resonances (LSPR). Furthermore, we study the link between the position of the LSPR to the nature, the size and the shape of the metallic patterns, the spacing between them and the surrounding dielectric environment.

2. EXPERIMENTAL PROCEDURES

Micro-patterns are defined by the assembly of microspheres into 2D lattice on a substrate based on a derivated-Langmuir Blodgett process coupling with deposition of metallic thin films. All the colloidal lithography experiments have been performed with a Langmuir Blodgett deposition system (KSV Nima << Langmuir-Blodgett Deposition Through Medium, KN 2002 >>). This method consists in the transfer onto a substrate of a one-molecule thick layer (Langmuir monolayer) spread at the air/water interface, process that can be repeated several times with the same substrate to form a multilayer film. Based on this classical process, the Langmuir-Blodgett technique has been adapted for nano/micro sphere lithography, where the role of the amphiphilic

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molecules is played by spheres of polystyrene, silica, etc. Our experiments have been carried out using polystyrene microspheres with sizes of 2 µm, 3 µm and 5 µm commercially available at Microparticles GmbH and Micro Partikeltechnologie GmbH and deposited on substrates. For the study presented here, Al_2O_3 substrates with polystyrene microspheres are covered by thin films using the pulsed laser deposition (PLD) process. Samples with thickness of 50-100 nm of Au and Ir are deposited using a KrF laser (TUI ThinFilmStar100) working at a wavelength of 248 nm and a fluence of 2-3 J/cm^2. After the PLD process, the polystyrene microspheres are removed with acetone, revealing periodic organized structures.

3. RESULTS AND DISCUSSION

In Langmuir-Blodgett system, the most common close packed microspheres arrangements look like to a 2D crystal with a hexagonally close packed structure and a packing density equal to 90.7% (see figure 1). On equation 2, τ_{max} defined as the maximum coverage rate for an ideal structure is independent of *D*, the colloidal sphere diameter. Consequently, a decrease or increase of the sphere diameter will never affect τ_{max} and optical transmission.

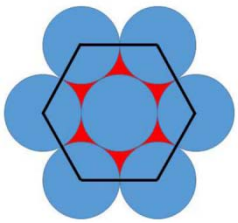


Fig. 1. 2D hexagonal close packed structure.

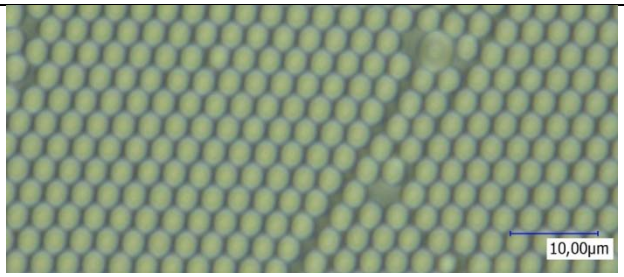


Fig. 2. Polystyrene microspheres with sizes of 3 µm on Al_2O_3substrate, (area specifically chosen to visualize defects).

$$\boldsymbol{\tau} = \frac{S_{sphere}}{S_{total}} \quad (1)\ ; \qquad \boldsymbol{\tau_{max}} = \frac{Area_{disk}}{Area_{hexagon}} = \frac{3\pi\frac{D^2}{4}}{\frac{3\sqrt{3}}{2}D^2} = \frac{\pi}{2\sqrt{2}} \approx 0.91 \quad (2);$$

where: τ= ration between the surface occupied by microspheres in report to the total available surface of the substrate, S_{total}= total surface available on the substrate, S_{sphere}= surface occupied by spheres on the substrate,

In practice, the monolayer still contains a small amount of "crystal" imperfections mainly consisting of grain boundaries, vacancy defects, and line defects with the gap of the grain boundary and line defects being around one period (= *D*) or less.

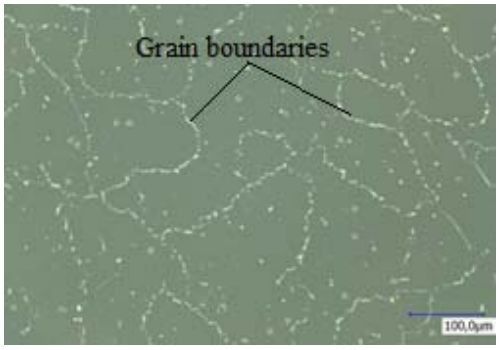


Fig. 3. Polystyrene microspheres with sizes of 3 µm on Al_2O_3 substrate (500x).

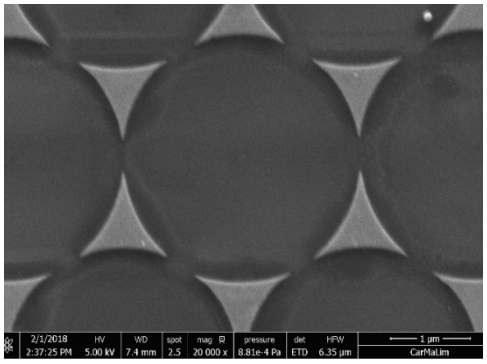
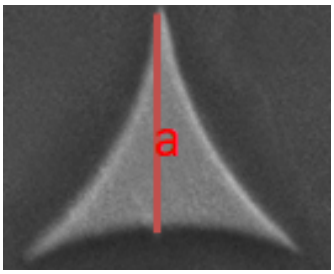


Fig. 4. Au micro-triangles made with 3 µm polystyrene microspheres on Al_2O_3 substrate.

The samples that made by Langmuir-Blodgett are used as substrates in the PLD setup. After the removal of the polystyrene microspheres, thin films deposited appear structured in well-defined metallic triangular array on the

Al_2O_3 substrate. Due to LB process, the single sketch illustrated figure n°4 presents the particularity to be downsizing. This "fractal" behavior is only dependent on the colloid size, *D*.
The specific size "a" of the triangular structures (perpendicular bisector of the triangles) is linked to the diameter of the polystyrene microspheres used for the manufacturing of arrays (see figure 4 and equation (3)).



$$\mathbf{a} = \frac{2}{3}(\sqrt{3} - 1 - \frac{1}{\sqrt{3}})D \qquad (3);$$

where: a= perpendicular bisector of the triangular structures and D= polystyrene microsphere diameter,

Fig. 4. Perpendicular bisector of the triangular structures ("a").

Calculation corresponding to array of polystyrene microspheres of 3µm, respectively 2 µm, give the specific size "a" of 0.70 µm, respectively 0.45 µm, for the triangular structures. For the metallic micro-triangular arrays, the intensity and wavelength position of LSPR is related to the coupling between the size of the micro-triangles (length, thickness), the distance between them and the nature of the material used for manufacturing them. 50 nm Au and Ir micro-triangles have been deposited on Al_2O_3 (C-sapphire) substrates. In the case of the chosen metals, the position of the LSPR is barely affected (4.33 µm for Au vs 4.25 µm for Ir) by the nature of the metal (see figure 5(a)). The intensity signal is only modulated by differences in the imaginary part of the permittivity for the two metals. Nevertheless, changing the size of the initial polystyrene microspheres leads to obtain self-similar patterns across different scales. As a consequence, a change of the LSPR position is observed (figure 5 (a)). Au layer in a combination with 3 µm polystyrene microspheres resulted in a LSPR maximum at 4.33 µm, while with 2 µm polystyrene microspheres the LSPR is localized around 2.90 µm. LSPR tunability vs polystyrene microspheres diameter appears evident (figure 5 (a)).

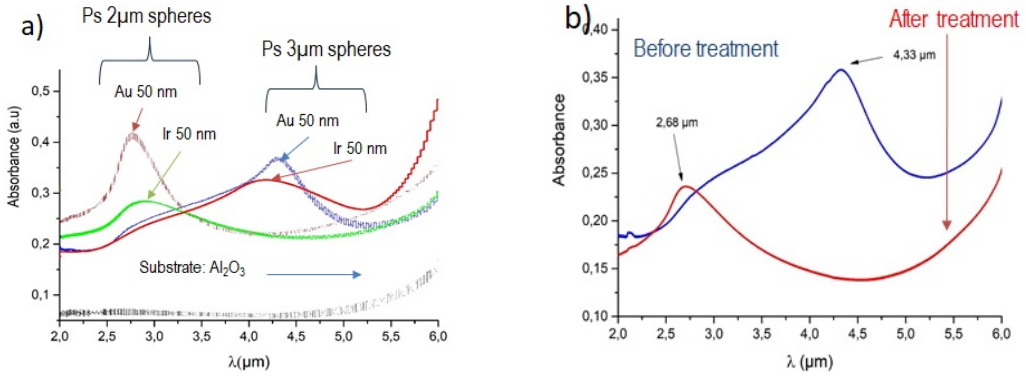


Fig. 5. a) Characterizations of LSPR for different sizes of micro-triangles of Au and Ir on Al_2O_3 substrates; b) Influence of thermal annealing at 700°C on LSPR of Au patterns (3 µm-spheres, 50 nm-Au thickness).

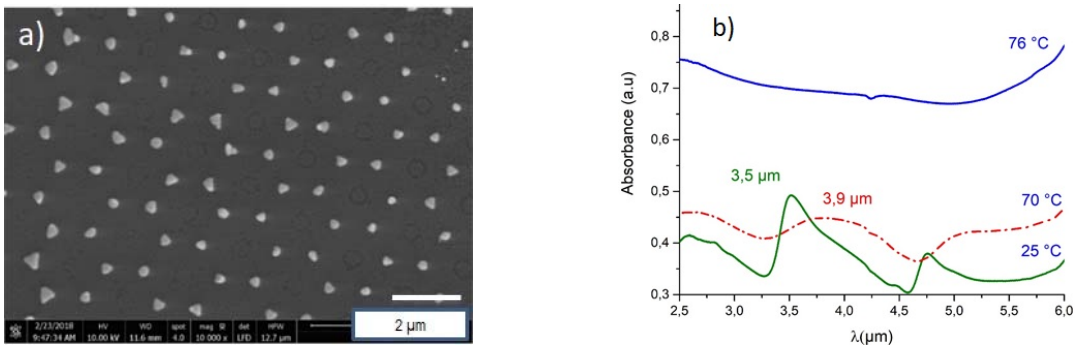


Fig. 6. a) Au micro-triangles embedded in a VO_2 matrix; b) LSPR maximum as a function of temperature of VO_2.

Taking benefit of the de-wettability of Au versus temperature, post-thermal treatment allows modifications of the initial micro-triangular shape. As a consequence, a post-annealing treatment at 700°C for 50 nm-Au patterns composed initially of micro-triangles defined by a=0.70 tends to change the geometry towards regular dispersed dots. The decrease of the size of micro-triangles is followed by the increase of the spacing between them (center to center) while their volume is preserved. The effect on the resulting LSPR is strong. A blue-shift of more than 1 μm for LSPR from 4.33 to 2.68 μm (see figure 5(b)) is obtained. Furthermore, the maximum of LSPR can be influenced by the environment. Vanadium dioxide (VO_2) is a promising candidate as a smart material. It undergoes an insulator to metal phase transition around 68°C with a simultaneous atomic rearrangement from monoclinic to tetragonal rutile structure and a change of refractive index. The VO_2, used as a matrix, through its transition, induces changes in the permittivity around the micro-triangles thus allowing the tuning of the resonance frequency, making the plasmons actively tunable (see figure 6 (a)). In this case, as the temperature of the samples is increased from 25°C to 90° C the maximum of LSPR redshifts, with a shift that is gradually proportional to the temperature (see figure 6 (b)). A LSPR position close to 3.5 μm at room temperature shifts to 3.9 μm at 70°C and disappears at 76°C, showing the extraordinary potential of these kinds of structures to tune and modulate the LSPR.

4. CONCLUSIONS

Through the combination of colloidal lithography and Pulsed Laser Deposition processes the development of systems with tunable localized surface plasmon resonances is shown. The position of the maximum of LSPR can be controlled via a specific architecture of the films deduced from the size of the LB polystyrene microspheres. The usage of 3 μm microspheres has yielded samples with the position of LSPR centred around 4.3 μm, while for 2 μm polystyrene spheres the LSPR is at 2.7 μm. The post-thermal treatment at 700°C performed on the 50 nm-Au patterns made with 3 μm polystyrene microspheres allows a blue-shift of more than 1 μm of the maximum of LSPR. Moreover, since the post-thermal treatment can be performed at different temperatures, in the future it is possible to blue-shift the position of LSPR to a very specific wavelength, procedure that can induce the enhancement of optical signals in the IR regime. Furthermore, by combining the metallic triangular nano/micro-patterns arrays with a smart material such as VO_2, we are able to actively tune and modulate the position of the maximum of LSPR. A relatively small change in the temperature (from 25°C to 70°C) of the VO_2 can induce a shift in the position of LSPR from 3.5 μm to 3.9 μm.

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