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Mesoporous Silica Membranes By Self-Assembled Nanospheres And Mediated Laser Ablation

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Abstract. Monodisperse silica nanospheres with sizes ranging from 250 to 515 nm have been synthesized and self-assembled to produce laser hot spots at the surface of oxidized silicon substrates. Illumination with single UV nanosecond laser pulses produces direct local ablation of the silica membrane. By preparing self-assembled nanosphere monolayers, the resulting nanoholes take the form of two-dimensional arrays in hexagonal close packed (hcp) configuration. Periodicity of the arrays is determined by the size of the assembled spheres. While the local field enhancement is strongly dependent on the sphere size, the morphology of the produced features can be maintained for all tested situations by balancing the change in local fields with the laser pulse energy. This work demonstrates the fabrication of 100-nm thick porous membranes with pore size of about 100nm and periodicity ranging from 250 to 650 nm.

Keywords: Silica Nanoparticles, Supramolecular self-assembly, Nanosphere Lithography.

INTRODUCTION

Supramolecular self-assembly of colloidal nanoparticles allows today a variety of fabrication methods for periodic nanostructures on large area. These methods are commonly termed Colloidal Lithography (CL) or Nanosphere Lithography (NSL)[1,2,3]. Among these methods, hexagonal close packed (hcp) ordered nanospheres can be used as an optical masks for near-field lithography, each sphere behaving like a microlens, producing sub-wavelength light spot when illuminated by a planar wave.

The process works on optical photoresist, with conventional ultraviolet (UV) extended sources, like Hg lamps, allowing good selectivity with a very low dose of UV radiation and even cross-linking and inverting the resist. The same happens with irradiation of deep UV laser pulses, (DUV) in this way local writing or also ablation occurs on almost any type of solid substrate supporting the spheres[4]. In the last decade, this laser machining approach has yield to impressive two-dimensional nanostructured materials from dielectrics to metals.

In this work, laser structuring of silicon dioxide is performed, and pores can be optically drilled underneath each particle by the so-called optical nanojets produced by the spheres.

EXPERIMENTAL RESULTS AND DISCUSSION

Silica nanospheres with diameters ranging from 117 to 568 nm were synthesized according to the method of Stöber by hydrolysis and condensation of tetraethylorthosilicate (TEOS) with ammonia in presence of a controlled amount of water in an alcoholic medium.

Typically, in a 500 ml round-bottomed flask equipped with a reflux condenser, a thermometer and a mechanical stirrer, appropriate amounts of HPLC water, ammonium hydroxide (aqueous solution, 16 M) and absolute ethanol were introduced to a volume of 320 ml. The solution was heated to 30 ± 2 °C in an oil bath at a stirring rate of 200 rpm, then 20 ml of tetraethylorthosilicate (TEOS, 0,090 mol) were added and the reaction was carried out for 2,5

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hours. Particle size and size distribution were measured by scanning electron microscope and by dynamic light scattering (PCS; each value is the average of five measurements). Table 1 collects the details for samples' preparation, including the SEM and PCS diameters, uniformity ratio U and polydispersity index PdI.

TABLE 1. Synthetic details and diameters of the silica nanoparticles obtained.

Sample	TEOS[a] (M)	H_2O[a] (M)	NH_3[a] (M)	D / SEM (nm)	U[b]	d / PCS (nm)	PdI[c]
G1	0.265	6.122	0.200	117	1.021	146	0.015
G2	0.265	6.122	0.400	221	1.009	262	0.063
G3	0.265	6.122	0.654	261	1.008	294	0.030
G4	0.265	6.122	0.850	362	1.012	434	0.059
G5	0.265	6.122	1.059	416	1.005	497	0.089
G6	0.265	6.122	1.400	517	1.005	612	0.092
G7	0.265	6.122	1.855	558	1.006	637	0.015
G8	0.265	6.122	2.120	568	1.005	675	0.073

[a] Total reaction volume: 340 ml. [b] Uniformity ratio. [c] Polydispersity index, obtained from PCS.

Silica nanospheres self-assembly is achieved by depositing silica ethanolic suspensions either by spin-coating (900 rpm) or drop coating on an oxidized silicon substrates (oxide layer thickness: 90 nm). The substrates are then subjected to deep UV (DUV) laser exposure (λ = 193 nm). The process scheme is depicted in Figure 1.

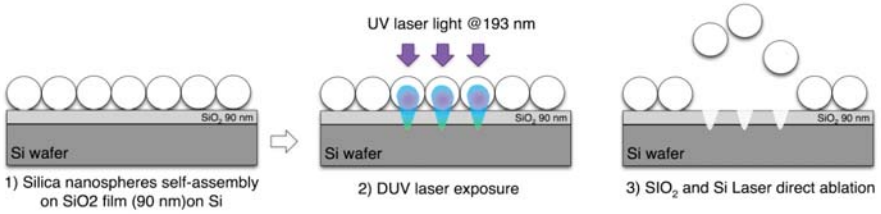

FIGURE 1. Schematic of the process to obtain arrays of nanoholes with DUV laser nanofocalization..

The different spheres have been dispersed onto the oxidized substrates after 1 hour of RCA SC1 treatment. Depending on the spheres-substrate surface functionalisation and hydrophilicity, different methods have been adopted for the self-assembly, drop coating and spin coating. Scanning Electron Microscopy analysis has been performed by a Field Emission Gun Inspect F FEI microscope, Micrographs in top view and cross sections along the exposed areas have been analyzed and measured by image analysis software. From the top views, three round areas have been recognized, the outer border of the crater in the SiO_2 top surface, a darker round area corresponding to silicon and to the lower interface between SiO_2 and silicon, and a smaller dark dot corresponding to the drilled pore in the silicon substrate. This pore morphology is confirmed by the cross section along the exposed stripes as shown in Figure 2.

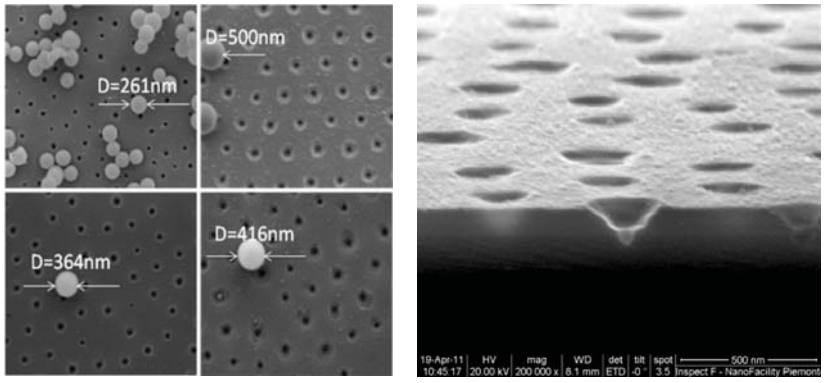

FIGURE 2. SEM characterisation of different membranes. Left, top view of different samples, depending from nanospheres size, different lattice spacing is achieved. Right, cross section of one sample, the SiO2-Si interface is clearly visible, and the typical pore profile due to ablation is shown.

Figure 3 illustrates the effect of the particle size on the hole lattice spacing. Changing the sphere size means changing the periodicity of the pore array. In contrast (Figure 2), sphere size does not change efficiently the size of the holes which can be tuned by varying the laser energy.

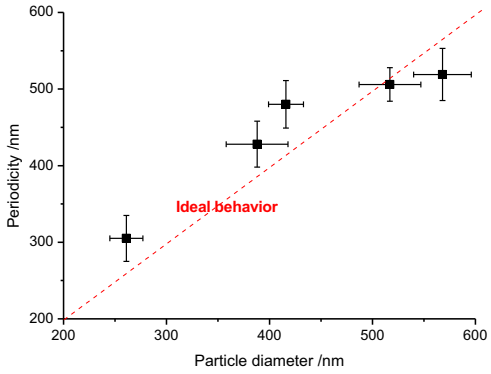

FIGURE 3. Trend of the pore array periodicity as a function of the particle size.

CONCLUSIONS

Nanoporous membrane can be prepared by a purely photonic approach without the usage of chemicals, being clean and contactless method. However appropriate laser and substrate preparation conditions must be chosen. Two main factors affect the morphology of the produced features: the sphere size and the laser energy. Playing with these two parameters allows a complete control of size and periodicity of the nanopores.

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