Management of polymeric spheres diameter in colloidal lithography by low and atmospheric pressure plasma treatments

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This paper refers to the reduction of polystyrene bead diameter in colloidal lithography by low and atmospheric pressure plasma treatment.. A single layered PS spheres was spin-coated on Si substrates and O_2, Ar or O_2/Ar plasmas generated at low or atmospheric pressure were applied afterwards in order to control the size of PS beads. The effects of plasma etching on the surface morphology were evaluated by means of Scanning Electron Microscopy (SEM).

1. Introduction

Colloidal lithography, also known as natural lithography or nanosphere lithography [1], is a method to produce periodic nanostructures on various substrates [2-5]. The combination of colloidal lithography with low pressure plasma processing proved its efficiency in various fields. Ref. [6] reported on controllable PS spheres diameter by combining of preheating and oxygen RIE (reactive ion etching) techniques. Using air plasma treatment the shape of PS beads can be significantly modified [7].

On the other hand, atmospheric pressure plasma techniques have appeared as an interesting alternative to material processing. For example, an important application of atmospheric pressure plasmas is the modification of polymeric surfaces in order to change their surface energy, improve wettability, getting a good adhesion or in obtaining biocompatible surfaces [8-10].

In this context, the present paper investigates the efficiency of plasma processing both at low and atmospheric pressure for controlling the PS beads diameter in combination with nanosphere lithography. Moreover, it proposes two approaches for working with atmospheric pressure plasma, in open and controlled atmosphere, while oxygen is either injected through the plasma source or into the chamber.

The PS monolayered colloidal particles were exposed to argon, oxygen, or oxygen/argon plasma to control the diameter size and interparticle spacing. The effects of plasma etching on the surface morphology were evaluated by Scanning Electron Microscopy (SEM).

2. Materials and method used

A monolayer of polystyrene nanospheres of 520 nm diameter was spin-coated on 3" silicon wafers according to the method described in [11, 12]. The typical size of the samples used for treatment was 10x10 mm.

2.1. Low pressure plasma

The experimental system used for the surface treatment of PS spheres coated on silicon surfaces by low pressure plasma is shown in Figure 1. The discharge is carried out between two plan-parallel electrodes positioned at 9 cm one from each other. The upper electrode is connected to the RF generator (13.56 MHz) via a matching network, while the bottom one is grounded and accommodates the substrate. The system is pumped down to a base pressure of $2x10^{-2}$ mbar; oxygen is introduced afterwards in the chamber at controlled flow.

Figure 1. Image of the low pressure plasma device during PE beads treatment

The working parameters were as follows: RF power 100 W, oxygen flow rate 20 sccm, pressure $3x10^{-1}$ mbar. The exposure time was varied from 45 s to 90 s.

2.2. Atmospheric pressure plasma

2.2.1. DBD plasma source and experiments in open atmosphere

The atmospheric pressure plasma source used in the experiments is presented in Figure 2. It is based on a planar DBD (Dielectric Barrier Discharge) configuration. The inner discharge chamber is electrically insulated on the sides via Teflon components that act as spacers for the dielectric barriers, which were made from alumina. Aluminum electrodes are placed on ceramics and act as active and grounded electrodes, respectively. The applied power comes from an RF generator, working at 13.56 MHz, coupled with an impedance matching unit. The gas is inserted through one end of the device and exits as a planar plasma jet at the other end of the source. The working gas was argon or a mixture containing argon and oxygen.

Figure 2. Image of the DBD plasma

The working conditions for the experiments in open atmosphere were: RF power 15 W, Ar flow rate 5000 sccm, O_2 flow rate 0.7 sccm (injected through the plasma source).

2.2.2. Experiments in controlled atmosphere

For experiments in controlled atmosphere, the frontal part of the DBD source was mounted tightly into a specially constructed glass chamber (Figure 3). The glass chamber is provisioned with one inlet for oxygen and one outlet for allowing the resulting gas to outflow the treatment space. By flushing the chamber with argon from the DBD source and oxygen from the separate inlet, the atmosphere inside is highly controlled in order to minimize the influence of the outside atmosphere.

The experiments under controlled atmosphere of oxygen were performed using the following parameters: RF power 15 W, Ar flow rate of 5000 sccm, O_2 flow rate 350 sccm (in the chamber).

For all experiments, the DBD plasma source (and the glass chamber when working in controlled atmosphere) is mounted above an X-Y translation stage that allows substrate moving across the plasma jet.

The distance from the device (nozzle) to the substrate was kept at 2 mm for all experiments.

The scanning procedure both in open and controlled atmosphere is computer-controlled, the parameters of the treatment procedure (RF power, gas flow, number of scans) being selected in advance. The scanning route was designed to ensure a uniform treatment of the surface, with successive paths along the y axis since the source width is larger than the substrate width.

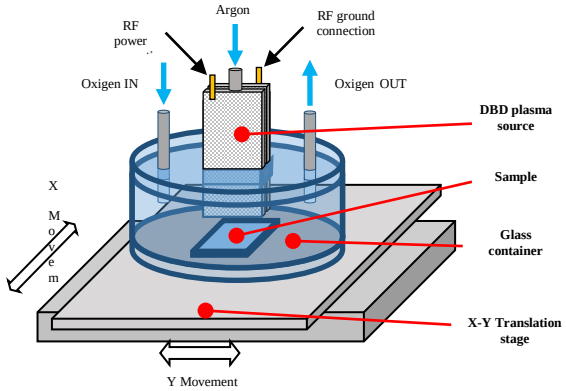

Figure 3. Schematic view of the treatment setup including the DBD plasma source

The scanning speed was 2 mm/s, which corresponds to a plasma exposure of 0.5 s along the scanning path. The used substrates (polystyrene spheres spin coated on the silicon surfaces) placed on stage were scanned over a 10 mm x 10 mm area. When working in open atmosphere with oxygen injected through the plasma source, the samples were exposed to plasma with a variable number of scans: 50, 100 and 200. When working in controlled oxygen atmosphere, the samples were exposed to a higher number of scans (up to 600).

3. Results and discussions

A SEM image of a self-assembled monolayer of the PS spheres coated on the silicon substrate is presented in Figure 4. It evidences the nearly perfect arrangement of the PS spheres, having an initial diameter of 520 nm, into a closed packed hexagonal structure with minimum spaces between the spheres. Few defects are also noticed on the surface.

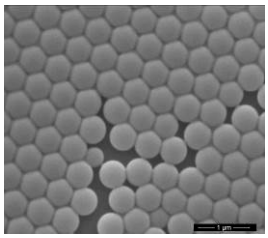

Figure 4. SEM image of the PS spheres coated on Si substrate

3.1. Effect of low pressure plasma treatment

Figure 5 illustrates by SEM images the effect of low pressure plasma treatment on the PS spheres arrays. The minimum plasma treatment time

necessary for insuring PS beads shrinkage is 60 s, which conducts to an average diameter of 490 nm.

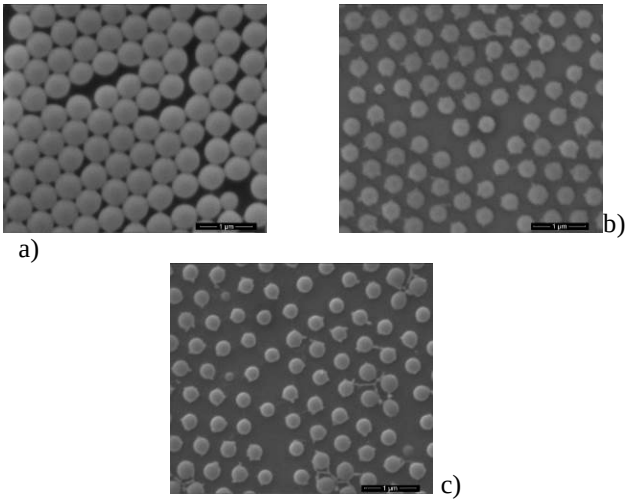

Figure 5. SEM images of the PS sphere monolayer after oxygen plasma treatment upon various exposure times: a) 60 s, b) 75 s and c) 90 s.

At larger treatment times of 75 s and 90 s, the shrinking effect becomes obvious, the average diameter of spheres being about 340 and 270 nm, respectively. The spheres remain in the same position on the substrate, the space between the spheres increases while their diameter decreases due to the oxygen plasma etching effect. Upon 120 s of treatment, the spheres are completely etched. A combined effect of thermal loading due to the plasma exposure and chemical etching due to the species formed upon excitation and dissociation processes would explain both the threshold value for treatment time needed for initiation (~60 s) and the linear decrease of spheres dimension (~7.5 nm/s) once the process started.

3.2. Effect of atmospheric pressure plasma treatment

SEM images of PS beads exposed in open atmosphere to DBD plasma generated in mixture of argon and oxygen plasma for 50 scans (a), 100 scans (b) and 200 scans (c) are presented in Figure 6.
They show a reduction of PS beads dimension accompanied by the modification of PS shape. The average dimension is reduced to 400 nm after 50 scans respectively 390 nm for 100 scans. It is observed that the PS spheres are not completely separate one from each other after a treatment time of 25 s (50 scans). Instead, they are linked by some "*bridges"* that connect the points where the spheres were initially in contact. Upon higher number of scans (100), which corresponds to a treatment time of 50 s, most of these bridges between spheres disappear while the shape of PS beads appears to be rather hexagonal, with a distance between opposite corners of around 390 nm. By further increase of treatment time (200 scans, equivalent to 100 s of plasma exposure), a combined effect of modification regarding shape and size is achieved. Figure 6 c suggests that both etching and melting of PS beads appear at larger exposure times, leading to features with approximate dimension of 340 nm, which present irregular regions of higher emission in SEM images. Such effects are most probably related to an important increase of the gas temperature within the plasma once working with reactive oxygen introduced through the DBD head.

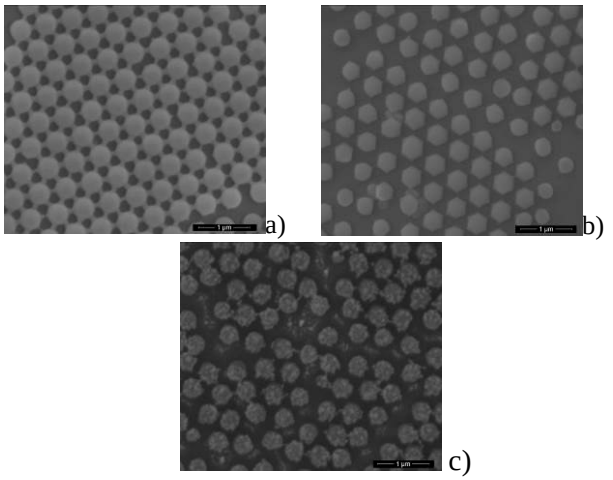

Figure 6. SEM images of the PS spheres treated in O_2/Ar plasma in open atmosphere: a) 50 scans (25 s); b) 100 scans (50 s) and c) 200 scans (100 s).

The results obtained upon argon plasma treatment of PS beads in controlled atmosphere of oxygen are illustrated by the SEM images from Figure 7 (a, b and c).

A shrinkage of the polystyrene beads, down to 482 nm, is observed after 50 scans (25 s) accompanied by a tendency of bridges formation. Compared to the case of argon/oxygen plasma in open atmosphere, a treatment time of 25 s by argon plasma in controlled oxygen environment conducted to a lower shrinking effect onto the PS beads, i.e. the diameter of the PS spheres is higher. This can be assigned to a lower amount of oxygen etching species formed when oxygen is not introduced in discharge.

For an etching time of about 200 s (400 scans) of the polystyrene spheres, the average diameter of PS spheres was reduced to 302 nm (Figure 7 b). A greater treatment time leads to a decrease in the size of the spheres as well as increasing the space between polystyrene spheres. The PS etching effect continues, leading to a reduction down to 193 nm for 600 scans (300 s). In this last situation, the PS beads diameter is decreasing linearly with the exposure

time at a rate of approximately 1.1 nm/s. At the same time, neither melting, nor shape modification are encountered in this case. This fact points out that by providing oxygen in the environment, one may control the process of PS beads modification.

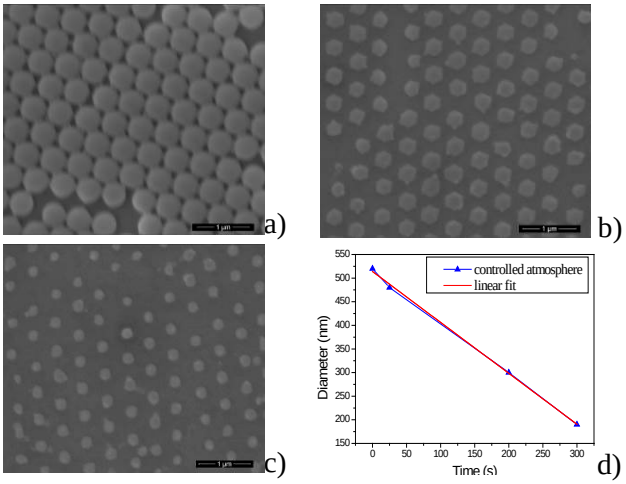

Figure 7. SEM images of size reduced PS beads in controlled atmosphere of oxygen: a) after 50 scans (25 s), b) 400 scans (200 s) and c) 600 scans (300 s) d) Modification of PS bead diameter as function of exposure time in controlled atmosphere

4. Conclusions

In this paper, we demonstrated that the diameter of self-assembled polystyrene spheres on Si wafers can be controlled and modified by using low and atmospheric pressure plasma treatments. Each of the presented approaches has some advantages, according to the desired effect. It is shown that the most effective treatment at short treatment time (of 25 s) is that provided by atmospheric pressure plasma in open atmosphere. Nevertheless, the highest etching rate, of ~7 nm/s, is obtained when working with low pressure oxygen plasma for exposures above 60 s. On the other hand, the finest control over PS beads dimension is attained when working in controlled atmosphere, where a constant etching rate of ~1.1 nm/s is obtained over a wide range of treatment times.

According to these data, one should choose among the presented approaches according to the desired effect, in order to tailor the size and shape of polystyrene beads.

Acknowledgments

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