CONTROLLED STRUCTURING OF SELF-ASSEMBLED POLYSTYRENE MICROSPHERE ARRAYS BY TWO DIFFERENT PLASMA SYSTEMS

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Abstract
Nanosphere lithography is a simple and time-efficient technique which is often recognized as an alternative to conventional top-down approaches standardly used in nanofabrication. In this study we present a successful manipulation of microspheres by reactive ion etching (RIE). A self-assembled monolayer close-packed array of monodisperse polystyrene microspheres (PM) with diameter of 471 nm was used as the primary template. The PM templates were processed in two different RIE systems: (i) capacitively coupled radiofrequency plasma (CCP) and (ii) dual plasma system which combines CCP and pulsed linear-antenna microwave plasma (PLAMWP). The influence of process conditions on the PM geometry was systematically studied by scanning electron microscopy (SEM). The process conditions were controlled by varying radiofrequency (RF) power, gas mixture (O\textsubscript{2}:CF\textsubscript{4} ratio) and process duration. A clear correlation between RIE conditions and the final PM geometry is found. In comparison to CCP-RIE, the PLAMWP system is less aggressive due to different plasma character and it allows smoother etching steps, thanks to which some conditions led to formation of long necks toward adjacent spheres. It was found out that choosing optimal parameters results in a tunable diameter of PM with various shapes (from spheres to pyramid-like structures) while keeping their periodic hexagonal ordering.

Keywords: nanosphere lithography, reactive ion etching, pulsed linear-antenna microwave plasma, polystyrene microspheres, Langmuir-Blodgett monolayers

1. INTRODUCTION
Nanofabrication means designing and production of nanoscale devices either by top-down or bottom-up strategy. The top-down strategy involves creating nanoscale structures with desired geometries starting from larger dimensions and scaling them down to the required values. Technologies include lithographic and etching methods (wet, plasma, focused ion beam etching, etc.). In conventional lithography, the required material is usually protected by a mask and the exposed material is etched away. Many techniques have been developed by using a variety of exposure radiation sources (photons, X-rays, electrons, ions, and neutral atoms). Present photolithography systems allow mass replication of nanostructures with sizes under 50 nm. X-ray lithography utilizes shorter wavelengths (0.04 to 0.5 nm), therefore a higher lateral resolution. However, X-rays cannot be focused through a lens, it requires special masks and resists which makes it very expensive compared to photolithography. Electron beam lithography (EBL) is a computer-controlled scanning electron microscopy (SEM), operating directly without a physical mask, it uses the electron beam as a "pencil" to "write" the pattern on the sample. Therefore, it is very time consuming method, nevertheless its best achievable resolution is ~20 nm in polymer resist. Focused ion beam lithography is similar to EBL, with higher writing speed, it capitalizes on the reduced lateral scattering of ions (such as H\textsuperscript{+}, He\textsuperscript{++}, Li\textsuperscript{+}, Be\textsuperscript{++}), compared to electrons. A quite different alternative route to overcome the lateral resolution limitations imposed by diffraction is to use no radiation at all, such as nanoimprint lithography and nanostamping. Compared with conventional lithography, they are far simpler, faster and less costly techniques. \cite{1, 2}
As we described, all of these techniques suffer from certain limitations. Such techniques tend to be cumbersome and slow, requiring prohibitively expensive equipment to produce small scale and often only two-dimensional structures, and almost all require a clean room environment.

The bottom–up methods have been developed to produce structures of even smaller scale and more complex architecture, that are difficult to achieve by the usual top–down processes. These structures can be achieved by the use of powerful microscopes, which allow nanomanipulation, or by techniques of molecular synthesis, colloid chemistry and polymer science.

Both approaches have their own disadvantages, therefore a method which serves as a bridge between the two would be the ideal solution. Nanosphere lithography seems to be a promising technique in this regard, because it takes advantage of the combination of bottom-up growth with top-down patterning. It is inexpensive, it allows high spatial resolution, large patterned area wafer-scaling with relatively low density of defects (can generate structures with true three-dimensional order) and high throughput. It also does not require expensive equipment like EBL. The NSL technique is composed of two stages, the first of which is mask preparation. In this stage the substrate is coated with monodisperse spherical particles and a colloidal crystal mask is formed (monolayer or bilayer). Several techniques have been successfully developed for the homogenous spreading of spheres over substrate, such as drop-coating, dip-coating, spin-coating and self-assembly at the gas-liquid interface. Self-assembly is a “fabrication tool” of nature, i.e. the molecular or atomic components spontaneously build up into stable well defined structures through non covalent interaction. Spherical particles are commercially available in suspension in a variety of sizes (from ~30 nm to 20 µm) and produced from various materials, e.g. silica, polystyrene (PS) or polymethyl methacrylate (PMMA) [3]. The second stage of the NSL uses well-known nanomachining techniques – etching and metal deposition – to create desired geometrical patterns suitable for optical devices such as metamaterials, photonic crystals or SERS-active substrates. Different types of structures can be formed: arrays of pillars, holes, rings, crescents, etc [4].

In this article the dry plasma etching of the polystyrene microsphere monolayer mask was studied by two different etching systems: (i) capacitively coupled radiofrequency plasma (CCP) and (ii) dual plasma system which combines CCP and pulsed linear-antenna microwave plasma (PLAMWP) [5]. Both etching systems have their advantages and disadvantages which are discussed regarding to experimental results.

2. EXPERIMENTAL PART

Silicon (100) wafers in size of 1x1 cm² were used as substrates for nanosphere lithography. First, Si substrates were ultrasonically cleaned with isopropyl alcohol for 10 min and by deionized water for 5 min and dried in nitrogen stream. Periodic arrays of PS microspheres 471 nm in diameter (purchased from microParticles GmbH, Berlin, Germany) on Si substrates were achieved from their aqueous dispersion (10 weight %). The colloidal suspension mixed with ethanol (1:1 v/v) was spread onto a water surface, then the microspheres self-assembled on the air-water interface into a hexagonal-close-packed monolayer. Finally, the resultant floating arrays were transferred onto the Si surface and left to dry [6]. Such prepared samples were plasma treated by two different RIE systems: (i) capacitively coupled radiofrequency plasma (CCP-RIE, (CCP-RIE; Phantom III, Trion Technology)) and (ii) dual plasma system which combines CCP and pulsed linear-antenna microwave plasma (PLAMWP; modified AK 400, Roth and Rau, AG). In the first set of experiments CCP-RIE was applied with varied RF power (60 W or 100 W) and changed gas mixture (pure O₂ 20 % and 50 % of CF₃ in O₂) while the other parameters were kept to constant: total pressure 12 Pa and process duration 30 s. In the second set of experiments the etching duration was varied from 30 s to 7 min. The third set of experiments were carried out in PLAMWP system a) only with RF power (357 W), b) combination of RF and MW (600 W and 1200 W, respectively) for 1 min and 3 min in O₂ atmosphere at 10 Pa of process pressure.

CCP-RIE (Phantom III, Trion Technology) system operates at frequency of 13.56 MHz and is characterized by a two parallel plate electrode configuration [7]. The bias voltage is determined by process parameters, i.e.
total pressure, gas mixture and RF power; therefore, the ion density is directly coupled to the ion energy (RF bias). This means relatively high RF power must be employed to obtain high ion densities. In comparison to CCP-RIE, the PLAMWP system (modified AK 400, Roth and Rau, AG) is so-called dual plasma system, which combines both RF and MW plasma, and the bias voltage can be controlled independently on other parameters [8]. Combined RF and MW plasma means also independent control of ion density. Moreover, it is characterized by cold plasma due to large distance of microwave antennas (i.e. high-density plasma region) from substrate holder. Thus, overheating of the substrate from plasma is minimized [9].

The surface morphology of samples after plasma treatment was characterized by scanning electron microscopy (SEM, eLine writer, Raith and JEOL JSM-7500F) and atomic force microscopy.

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of pressure and CF₄:O₂ ratio on the structuring of the PS microsphere array in CCP-RIE plasma. It is obvious, that during the plasma treatment the close-packed arrays (shown in Fig. 3a) are converted into a non-close-packed template with preserved period of the initial microsphere array (i.e. the center-to-center distance is the same). The plasma treatment led to homogeneous etching over the whole sample area and reduced the diameter of the spheres. Increased RF power from 60 to 100°W enhanced the etching rates (Fig. 1g) for each ratio of CF₄:O₂. This means more extensive ion bombardment of the samples which was also confirmed by increased bias voltage from ~ 18 V to ~ 57 V. For example, plasma treatment in pure oxygen plasma at 100 W reduced the PS diameter to 340 nm (in comparison to plasma treatment at 60 W, which was 364 nm). Of course, the evaluated etching rates of samples etched at different RF power are relative values, since at higher RF power not only the diameter decreased, but also the surface morphology of PS microspheres became roughened (as it can be seen on SEM images, Fig. 1).

![Fig. 1. a) - f) Top view SEM images of plasma treated polystyrene microparticle array by CCP-RIE at different pressures and CF₄:O₂ ratio (upper row represents samples treated at RF power of 60 W, bottom row at 100 W, respectively). g) Diameter of microspheres (red solid lines) and attributed etching rates (blue dotted lines) as a function of CF₄:O₂ ratio (triangles represents samples treated at RF power of 60 W, squares at 100 W, respectively).](image)

In earlier studies of the plasma treatment of PS microsphere arrays primarily pure O₂ atmosphere was used, because O₂ does not etch the Si or SiO₂ substrates, while CF₄ reacts with them and makes some polymers; moreover it changes the surface potential of the PS microspheres, which is undesired for several applications. However, addition of CF₄ into the O₂ atmosphere makes the surface of the PS microspheres much more smooth.

Interesting result was found out, when we increased the etching time from 30 s to 7 min. Figure 2 shows the effect of time in the case of pure O₂ and 100 W of RF power. We found out that the plasma treatment has non linear behaviors, it can be divided into two regions, where the breakpoint is between 45 s and 1 min (see Fig. 2e). For etching times up to 30 s, the shape of the PS spheres is similar to initial sphere-like shape, while for
longer etching times (>1 min) the sphere patterns collapsed, they lost their spherical shape and inhomogeneous PS residue are observed. These structures regarding to AFM images (Fig. 2f) will be referred as pyramid-like structures. While the etching rate seems to be linear until 1 min of etching time, for longer etching times nearly no change is observed (only slight decrease).

Fig. 2. Top view SEM images of plasma treated polystyrene nanoparticle array on Si substrates a) as prepared (before etching) and after CCP-RIE treatment for b) 30 s, c) 3 min and d) 7 min in O₂ plasma at 100 W and 90 mTorr. e) Sphere diameter as a function of the etching time, and f) typical AFM image of pyramid-like structures for longer etching times (>1 min).

Aforementioned experiments showed that the process parameters need to be chosen carefully, especially in term of short process durations, because of the soft material and thin monolayer. Moreover, as it was mentioned, the bias voltage in the case of CCP-RIE plasma can not be controlled independently, therefore we studied the PS microsphere plasma treatment in PLAMWP system, which combine both RF and MW plasma, and allows independent control of the bias voltage, which is corresponding to surface bombardment. Several experiments were carried out, in Fig. 3 are shown only few of them only with RF plasma (Fig.3a) and with the combination of RF and MW plasma for 1 min (Fig. 3b) and 3 min (Fig. 3c), respectively.

Fig. 3. Top view SEM images of plasma treated polystyrene microparticle array on the Si substrates by PLAMWP system a) only with RF power (357 W, 7 V) and combination of RF and MW power of 600 W and 2×1200 W, respectively for 1 min (b) and 3 min (c) at 10 Pa in pure O₂ atmosphere.

First of all, after 1 min or even after 3 min the PS microsphere array is not damaged and has sphere-like structures. The microspheres were shrunk from their initial diameter of 471 nm to 433 nm after etching for 1 min; and with further etching (3 min) the diameter was reduced to 403 nm. Moreover, this array of sphere-like structures are each other connected with thin necks creating a net even after 3 min of plasma treatment. This net-like structure is not observed for etching times longer than >3.5 min (not shown here).

Formation of net-like structure is probably due to the cold plasma character and lower plasma densities (N_e) near to the sample surface in PLAMWP system comparison to CCP-RIE, as it was shown in Ref. [10].
observed that even at 10 Pa of total pressure the effective electron temperature \( T_{\text{eff}} \) is strongly dependent on the distance from the microwave antennas, and this influence further increases with increasing pressure (i.e. for the substrates localized at \( z = 70 \) mm it means a drop of \( N_b \) by three orders of magnitude in the range of 10 to 150 Pa) [10]. In the close vicinity to the antenna (16 mm) the \( T_{\text{eff}} \) reaches the value of 4.5 eV and for higher distance it drops by 2 eV for the same pressure value of 10 Pa. This dependence of the electron temperature and electron density on distance in similar surface-wave plasma systems was observed also by Tsugawa et al. [11]. Secondly, formation of net-like structure in PLAMWP system can be caused also by lower bias voltages. In PLAMWP system two independent MW and RF power supplies are applied. MW plasma is responsible to enhance the ion density, while RF plasma accelerates the ions (and electrons) toward to sample. In the case of PLAMWP, the bias does not exceed 15 V even at 600 W of RF power, while in the case of CCP-RIE it is 18 V and 57 V for 60 W and 100 W of RF power, respectively.

CONCLUSIONS

We studied the plasma treatment of self-assembled monolayer polystyrene (PS) microspheres using two different RIE systems. It was shown that in comparison to capacitively coupled radiofrequency plasma (CCP-RIE) the dual plasma system (PLAMWP), which combines CCP and pulsed linear-antenna microwave plasma, is less aggressive, it allows smoother etching steps with longer process time, thanks to which a formation of a net-like structure (long necks towards adjacent spheres) is possible. It is supposed that this feature of the PLAMWP system is based on the different plasma character (cold plasma), lower ion and electron temperature, and lower bias voltages (in comparison to CCP-RIE), which can be controlled independently from ion densities. We found out that in the CCP-RIE system only short-time processes are allowed since after > 1 min of process time only PS residues remain, and pyramid-like structures are formed. Choosing optimal parameters results in a tunable diameter of PM with various shapes (from spheres to pyramid-like structures) while keeping their periodic hexagonal ordering.

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