Study of Latex sphere mask dry etching in oxygen

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Abstract. Nanosphere lithography is well suited for quick and easy formation of ordered structures on the entire silicon wafer. After coating of close packed mask of spheres, they must be reduced in diameter. In various studies, the main method used for spheres diameter reducing is dry etching using capacitively coupled plasma (CCP) mode. In this paper, we present the possibility of spheres etching using inductively coupled plasma (ICP) mode, comparing the results obtained with CCP mode. A strong degradation of the spheres morphology was demonstrated at CCP mode, while the degradation effect was not sufficient using ICP mode. However, the effect of spheres migration over the silicon surface during ICP etching was observed. A preliminary thermal annealing of spheres allows one to avoid this effect. Finally, a technology of reducing the spheres size with minimal degradation and preserving the original spherical geometry was developed.

1. Introduction

Modern electronics is moving from planar structures to 3-dimensional. These structures are used in various gas sensors, solar cells, and biological applications [1-3]. One of these structures are vertically aligned structures on silicon. These structures are characterized by increased light confinement that allows one to use thinner absorbing layers. Novel solar cell concept based on vertically aligned silicon nanostructures realized in flexible polymer matrix was recently proposed [4]. Recent studies show that micron size columns rather than nanometer one are required for solar cells based on vertically aligned structures [5]. One of the technological ways to form such periodic structures is a combination of polystyrene microspheres lithography [6] with dry etching [7]. Nanosphere lithography is used as a mask for etching of silicon columns. Previously, we proposed to use an etching scheme (Figure 1) with an intermediate SiO₂ layer, which is etched in a CHF₃ atmosphere through polystyrene microspheres, to form hard mask for deep silicon etching [8].

![Figure 1. Etching scheme of vertically aligned silicon structures.](image_url)

First, the surface of Si covered by a SiO₂ layer is coated by polystyrene spheres, using spin-coating technology. The diameter of the spheres determines the period of the structure. Whereas the silicon wire...
diameter could be controlled by etching of the polystyrene spheres in oxygen plasma reducing their size to the required diameter. Then the layer of SiO$_2$ is etched in CHF$_3$ plasma for forming hard mask. Silicon could be etched in cryogenic process (T < 200 K) to the required depth using SiO$_2$ hard mask. Thus, a periodic topology could be achieved with a controllable density and diameter of silicon wires. The most commonly used and simplest method for etching spheres is the capacitive coupled plasma (CCP) dry etching method [9,10]. This method allows one to reduce the diameter of the spheres, but unfortunately it does not allow one to achieve isotropic etching of the spheres. Anisotropic etching leads to the formation of too thin edges on the periphery of the spheres, which are etched too fast during next SiO$_2$ etching step. It leads to increase of wall roughness during the subsequent etching. In this paper, we explore a capability of inductively coupled plasma (ICP) mode for the sphere etching in oxygen plasma.

2. Experimental

First, the SiO$_2$ layer of 500 nm thickness was deposited in standard 250°C PECVD process on 4-inch (100) silicon substrates after HF-dip pre-treatment using Oxford PlasmaLab 100 PECVD setup. Then the surface of the SiO$_2$/Si substrates was covered by monolayer of polystyrene spheres of 0.9 or 2 µm diameter using spin coating. Initial water solution of polystyrene spheres was 10 wt. %. Polystyrene spheres were separated from water in centrifuge and diluted in isopropyl/water solution before deposition. The optimal value being equal to 13/7 was determined from the variation of the isopropanol/water volume ratio performed previously. Before spin coating, substrate surface was treated in oxygen plasma for 2 minutes. Following spin coating parameters were used for of 0.9 µm spheres: solution temperature of 60°C; deposition speed of 300 rpm; drying speed of 900 rpm; low acceleration. A full area of the substrate surface was covered by one monolayer of polystyrene spheres presented in Figure 2a.

Deposition parameters for 2 µm spheres were specially optimized for this size because the optimum parameters for 0.9 µm spheres demonstrated not acceptable results. Full area covering requires addition of propylene glycol and tune isopropanol/water volume ratio. Bigger spheres require lower acceleration speed and higher solution viscosity. Polystyrene spheres were separated from water in centrifuge and diluted in isopropyl/water/propylene glycol solution before deposition. From the variation of the isopropanol/water/propylene glycol volume ratio the optimal value being equal to 7/2/1 was determined. Following spin coating parameters were found to be optimal for 2 µm spheres: solution temperature of 20°C; deposition speed of 300 rpm; drying speed of 600 rpm; low acceleration. The described conditions provide full area covered by one monolayer of latex sphere deposition as presented in Figure 2b.

![Figure 2](image-url). Optical microscopy image of 0.9 µm (a) and 2 µm (b) latex spheres deposited on SiO$_2$ surface on silicon substrate.

Dry etching of latex spheres was performed at the temperature of -20°C using Oxford PlasmaLab 100 ICP 380 setup supplied with O$_2$ and CHF$_3$ gas lines. The both CCP and ICP modes were used. ICP and CCP power was varied from 0 to 1000 W and from 10 to 50 W, respectively. The morphology of the surface was studied by scanning electron microscopy (SEM) using SUPRA 25 Zeiss.
3. Results and discussion
To etch the spheres in the capacitive coupling mode the following etching parameters were used: ICP power was set to 0 W, CCP (RF) power was equal to 30 W, pressure was set to 20 mTorr and O₂ flow to 50 mTorr. The etching results are presented in Figure 3.

![SEM image of the etching of 0.9 micron spheres after etching in oxygen at the CCP mode.](image1.png)

**Figure 3.** SEM image of the etching of 0.9 micron spheres after etching in oxygen at the CCP mode.

CCP etching allows one to successfully reduce the diameter of the spheres and to obtain a sparse array of spheres (Figure 3). However, the strong anisotropy of the CCP process leads to strong etching of the upper part of the spheres, which leads to a strong thinning of the edges of the spheres. The thinner edges of the spheres during subsequent etching are etched much faster compared to other parts leading to formation of etching artifacts on the SiO₂ mask, such as rough edges and a decrease of the etching angle, which in turn affects the further cryogenic etching of silicon. On the other hand, the advantage of this method is that the spheres hold their position on the surface of the sample. To increase the etching isotropy, we consider to use ICP etching process. ICP etching has greater variability compared to CCP. ICP etching allows one to vary the degree of isotropy of the etching by controlling a bias voltage and plasma power density independently. To etch the spheres at the ICP mode the following etching parameters were used to obtain maximum isotropy: ICP power was set to 1000 W, CCP power was equal to 3 W, pressure was set to 25 mTorr and O₂ flow to 50 mTorr. The minimum CCP (RF) power applied on the stage and the maximum possible pressure in the chamber were chosen for maximum stability of ICP plasma. The etching results of the spheres are presented in Figure 4.

![Latex sphere dry etching at ICP mode: optical microscopy (a) and SEM (b) image.](image2.png)

**Figure 4.** Latex sphere dry etching at ICP mode: optical microscopy (a) and SEM (b) image.

The etching of the spheres in the ICP plasma led to an unexpected result. Spheres migrated over the SiO₂ surface and formed a “leopard like” pattern on the silicon surface. Seems the attraction of the spheres occurs due to electrostatic forces. However, SEM image (Figure 4b) demonstrates that the diameter of the spheres decreased significantly, while the spherical shape was kept. Thus, isotropic etching of the latex spheres was achieved being a quiet important result. To prevent the migration of the spheres over the surface it was proposed to use preliminary thermal annealing of the substrate on a hotplate after spheres coating at temperature of 120°C. The optimization
of the warm-up time was performed. The minimal time required to hold spheres positions being equal to 12 seconds was determined. The result of etching of spheres at ICP mode with preliminary annealing of spheres is demonstrated in Figure 5.

![Figure 5. Latex sphere dry etching in ICP mode: after pre-treatment optical microscopy (a) and SEM (b) images.](image)

The optical microscopy shows that the spheres have hold their positions while SEM demonstrated that the spheres also kept their spherical shape.

4. Conclusion
The way to enhance stability of latex spheres mask was demonstrated. Indeed, the developed ICP process provides controllable isotropic etching of latex spheres, while additional thermal pre-treatment step allows one to fix the distance between the spheres centers and increase SiO$_2$/spheres etching selectivity

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