Formation of SiO₂ hard mask using dry etching and nanosphere lithography

E A Vyacheslavova¹, I A Morozov², D A Kudryashov² and A S Gudovskikh¹,²

¹Saint Petersburg Electrotechnical University "LETI", 197376 St Petersburg, Russia
²Saint Petersburg Academic University, 194021 St Petersburg, Russia
e-mail: cate.viacheslavova@yandex.ru

Abstract. The features of the formation of a SiO₂ hard mask using dry etching and nanosphere lithography are considered in the paper. A series of experiments was carried out using a variation of plasma etching parameters such as ICP and RF power, pressure as well as a substrate temperature. As a result, optimal parameters were found to obtain both good selectivity and high etching rate.

1. Introduction
Nowadays, an increased attention is paid to renewable energy sources due to the depletion of conventional energy sources as well as air pollution from industrial waste. One of the most perspective branches of renewable energy is solar energy which is studied by photovoltaics [1].

Main part of photovoltaic is related with silicon. It is due to its abundance in the Earth's crust and the well-developed silicon technology. In addition, it is possible to fabricate silicon-based solar cells with an optimal efficiency/cost ratio. Now, the great attention directed to a search of new approaches in order to improve this ratio. One of these approaches assumes the use of vertically oriented silicon nanostructures. Such nanostructures can enhance the optical absorption in the material along with a Si thickness decreasing.

Plasma etching is a promising way to solve the problem of the vertically aligned silicon structures formation. In such process, the material surface layer is removed as a result of chemical interaction between particles of the reaction gas and the surface atoms of the material. Therefore, plasma etching allows to reach a compromise between such important parameters as anisotropy, selectivity, uniformity and etching rate [2-4].

Before the silicon etching, it is necessary to create a mask (template) on its surface. The most promising way is a formation of a mask using colloidal nanospheres. This allows avoiding a usage of complex methods of lithography. Some details about cryogenic etching through a nanosphere mask and obtained silicon structures is shown [5]. Such structures have limitations in etching depth since the oxygen in the plasma affects the etching of organic spheres negatively. To solve this problem, it is necessary to use a material resistant to oxygen as a mask, for example, silicon oxide.

Thus, the aim of this work is a developing a technology and study the features of SiO₂ hard mask formation using plasma etching and nanosphere lithography.

2. Nanosphere lithography
Nanosphere lithography is a promising method for creating regular and uniform arrays of particles with various sizes. The principle of the nanosphere lithography is as follows. Micron- or nanometer size
polystyrene spheres cover the surface of the substrate. The obtained layer is used as a mask for further etching. The particle size will determine the size of the forming structure [6-8].

For the process of nanosphere lithography, silicon wafers with a deposited layer of silicon oxide are used. The initial aqueous solution of polystyrene particles with a diameter of 900 nm contains 10% spheres by weight.

It is necessary to change the initial composition of the aqueous solution of the spheres. To do this, a certain amount of water is taken from the tube (after centrifuging) by the dispenser and isopropyl alcohol is added. Isopropanol increases the viscosity of water, that allows to change the degree of fluidity and mobility of the solution by varying the ratio of water / alcohol.

Next, the resulting solution is placed in an ultrasonic bath to achieve uniformity of the solution. Using a dispenser, the resulting solution is applied to the central part of the substrate located in the spinner. After application, the spinner unwinds and a suspension of spherical particles spreads over the substrate surface. Under the action of electrostatic forces, self-ordering of the nanosphere array occurs.

To obtain the optimal volume ratio of water to isopropanol, at which a close-packed and ordered array of spherical particles is formed, a number of experiments were carried out. Results obtained at various ratios of water / isopropanol are presented in table 1.

| Sample | Volume ratio (water / isopropanol) | Surface coverage, % |
|--------|-----------------------------------|---------------------|
| 1      | 3/1                               | 30                  |
| 2      | 2/1                               | 40                  |
| 3      | 1/1                               | 60                  |
| 4      | 9/11                              | 80                  |
| 5      | 7/13                              | 95                  |
| 6      | 1/3                               | 150                 |

Figure 1 shows the distribution of polystyrene particles on the sample surface. (a) Water / isopropanol with a ratio of 3/1 and (b) water / isopropanol with a ratio of 7/13.

Figure 1 (a) shows that the nanoparticles are unevenly distributed over the surface, a significant surface area is free. Large empty areas are circled in white.

It can be seen from the figure 1 (b) that the distribution of particles is quite uniform, and a close-packed and ordered array of spherical particles is obtained.

Accordingly, with a water / isopropanol ratio of 7/13, the best result was obtained in terms of surface area, which was used in the further study.
3. Silicon oxide etching

Series of experiments was carried out to etch of SiO$_2$ in CHF$_3$ environment. All experiments were performed using Oxford PlasmaLab System 100 ICP. Different etching parameters were varied: ICP power, RF (CCP) power, pressure, temperature and cyclic mode for nanospheres etching. Variations of ICP power, RF (CCP) power, pressure and temperature were made using substrates with pre-deposited photoresist mask to prevent sphere etching impact on the experiment. Table 2 and Figure 2 (a) present experimental results with ICP power variation.

| Process | ICP power (W) | Etching rate (nm/min) | Selectivity (a. u.) |
|---------|---------------|-----------------------|---------------------|
| ICP 609 | 500           | 40                    | 1.74                |
| ICP 608 | 700           | 79                    | 1.55                |
| ICP 582 | 1000          | 100                   | 1.8                 |
| ICP 591 | 1500          | 200                   | 0.7                 |
| ICP 592 | 2000          | 250                   | 0.4                 |

Figure 2 (a) shows that increase of ICP power with a constant bias voltage on the stage leads to an increase in the etching rate, while the selectivity with respect to the resist decreases. Best-achieved etching rate is 250 nm/min with a selectivity ratio of 10:4 for 2000 W source. Based on the obtained data, a process with a power of 700 W was selected as the optimal one for selectivity and etching rate. Table 3 combines the processes in which the power supplied to the table (RF power) was changed.

| Process | RF power (W) | Etching rate (nm/min) | Selectivity (a. u.) |
|---------|--------------|-----------------------|---------------------|
| ICP 615 | 30           | 80                    | 0.79                |
| ICP 616 | 35           | 84                    | 0.95                |
| ICP 617 | 40           | 98                    | 1.61                |

Figure 2 (b) shows the dependence of selectivity and etching rate on RF power. An increase of RF power leads to an increase in the etching rate and also increases selectivity with respect to the resist. However, with a further power increase, the resist can be redeposited. This is due to the high energy of volatile radicals, i.e. the micromasking effect may occur.

![Figure 2. (a) - Dependence of selectivity and etching rate on ICP power. (b) - Dependence of selectivity and etching rate on RF power.](image-url)
Table 4 summarizes the experiments carried out at various pressures. Table 5 presents the experiments obtained at different substrate temperatures.

**Table 4. Dependence of selectivity and etching rate on pressure.**

| Process  | Pressure (mTorr) | Etching rate (nm/min) | Selectivity (a. u.) |
|----------|-----------------|-----------------------|---------------------|
| ICP 611  | 3               | 132                   | 1.28                |
| ICP 610  | 5               | 126                   | 1.11                |
| ICP 581  | 7               | 92                    | 1.08                |

**Table 5. Dependence of selectivity on substrate temperature.**

| Process  | Temperature (°C) | Selectivity (a. u.) |
|----------|------------------|---------------------|
| ICP 581  | -20              | 1.08                |
| ICP 580  | 0                | 0.77                |
| ICP 579  | 20               | 0.35                |

It can be seen from figure 3 (a) that an increase of pressure leads to a decrease of the selectivity and etching rate. It is assumed that the number of particle collisions increases with increase of pressure. It turns out that the average electron energy decreases. Since the energy of electrons determines the rate of generation of active particles, the etching rate decreases with increasing pressure.

Figure 3 (b) shows that with decreasing substrate temperature, the etching selectivity increases.

![Figure 3](image)

**Figure 3.** (a) - Dependence of selectivity and etching rate on pressure. (b) - Dependence of selectivity and etching rate on temperature substrate.

Comparing the etching profiles obtained at different substrate temperatures, it can be noted that lower temperature (-20 °C) leads to less degradation of the mask as demonstrated by SEM (Figure 4, b).

![Figure 4](image)

**Figure 4.** Cross section of the samples at (a) 20 °C and (b) -20 °C by SEM.
Based on the data obtained during the described above series of experiments with a variation of the plasma etching parameters, the optimal recipe for silicon oxide etching through a mask of nanospheres was determined. The optimal parameters of the plasma etching process are presented in table 6.

**Table 6.** Optimal parameters of the process of plasma etching of silicon oxide.

| Parameters             | Etching step | Cyclic mode | Cooling step |
|------------------------|--------------|-------------|--------------|
| Temperature (°C)       | -20          | -20         |              |
| Flow CHF$_3$ (sccm)   | 30           | 30          |              |
| Time (sec)             | 30           | 60          |              |
| Pressure (mTorr)       | 3            | 7           |              |
| RF power (W)           | 40           | 0           |              |
| ICP power (W)          | 700          | 0           |              |

However, etching in continuous mode leads to a strong degradation of polystyrene spheres due to the heating during the process. To avoid this problem, a cyclic mode was developed. In cyclic mode, the etching step alternates with a cooling step. Plasma discharge is maintained for 30 seconds and, accordingly, spheres etch is carried out. Then the plasma power is turned off for 60 seconds to provide sample cooling. The etching step time was selected to take minimal time, taking into account transients during ignition of the plasma. The cooling time was chosen to be larger than the etching step.

Table 7 presents the performed etching process parameters of silicon oxide in CHF$_3$. The first three processes were carried out in continuous mode and the last one in the cyclic.

**Table 7.** SiO$_2$ etching processes in CHF$_3$.

| Process | ICP power (W) | RF power (W) | Pressure (mTorr) | Cycle | Etching rate (nm/min) |
|---------|---------------|--------------|------------------|-------|-----------------------|
| ICP 583 | 1000          | 30           | 7                | No    | 100                   |
| ICP 618 | 700           | 30           | 3                | No    | 86                    |
| ICP 619 | 700           | 40           | 3                | No    | 107                   |
| ICP 629 | 700           | 40           | 3                | Yes   | 103                   |

In Figure 5 SEM images of samples after silicon oxide etching at a continuous and cyclic mode are shown. As noted earlier, etching in continuous mode (Figure 5, a) leads to a strong degradation of polystyrene spheres. In cyclic mode (Figure 5, b) an effect of plasma on latex spheres is less pronounced. Spheres are etched more evenly, respectively and the top layer SiO$_2$ is forming properly. Therefore, the process of oxide etching in cyclic mode is preferred.

![Figure 5. SEM images of the structures obtained after etching of SiO$_2$ in (a) continuous mode and (b) cyclic mode.](image)
make it possible to obtain vertically oriented silicon structures with the required geometry after subsequent cryogenic etching.

Acknowledgments
This work was supported by the Russian Scientific Foundation under grant number 18-79-10059.

References
[1] Devabhaktuni V, Alam M, Shekara Sreenadh Reddy Depuru S, Green R C, Nims D and Near C 2013 Solar energy: Trends and enabling technologies J. Renewable and Sustainable Energy Reviews 19 555–64
[2] Anurov A E, Zabotin Yu M and Podgorodetsky S G 2015 Specifics of Silicon Deep Anisotropic Etching in trench MOSFET Manufacturing Technology J. Rocket-Space Device Engineering and information Systems 2 66–73
[3] Vinogradov G K, Nezvorov P I and Slovetsky D I 1982 Kinetics and mechanisms of chemical reactions in non-equilibrium-plasma etching of silicon and silicon compounds J. Vacuum 32 529–37
[4] Flamm D L 1990 Mechanisms of silicon etching in fluorine- and chlorine-containing plasmas J. Pure Appl. Chem. 62(9) 1709–20
[5] Morozov I A, Gudovskikh A S, Uvarov A V, Baranov A I and Kudryashov D A 2019 The study of Latex Sphere Lithography for High Aspect Ratio Dry Silicon Etching J. Phys. Stat. Sol. 217 1900535
[6] Peng K, Zhang M, Lu A, Wong N-B, Zhang R and Lee S-T 2007 Ordered silicon nanowire arrays via nanosphere lithography and metal-induced etching J. Appl. Phys. Lett. 90(16)163123
[7] Colson P, Henrist C and Cloots R 2013 Nanosphere Lithography: A Powerful Method for the Controlled Manufacturing of Nanomaterials J. of Nanomater. 2013 948510
[8] Tsipotan A S 2015 Self-assembly of Nanoparticles Controlled by Resonant Laser Light, J. of Siberian Federal University 8(1) 109–22