Nanofabrication Process by Reactive Ion Etching of Polystyrene Nanosphere on Silicon Surface

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Abstract: Nanospheres made of organic polymer have been applied to generate various patterning mask in fabricating functional nanostructures. The patterning and generation of semiconductor nanostructures through nanospheres mask provides a potential alternative to the conventional top-down fabrication techniques. Polystyrene nanosphere was modified using reactive ion etching (RIE) with O2 plasma at various duration of exposure (0, 20, 40 sec) and further extended to produce nanostructure by employing combination of O2 and mixed CHF3/SF6 gases. These edge PS nanospheres are later reduced as nanostructures and characterized using various characterization techniques such as Field Emission Scan Electron Microscopy/Energy Dispersive X-ray Spectroscopy (FESEM)/EDS, Atomic Force Microscopy and Fourier Transformation Infrared Spectroscopy (FTIR). The potential for multi stages etching procedures of O2 and later with SF6/CHF3 plasma etching are found to modify the nanospheres shapes and sizes which are important either as secondary mask for metal evaporation or as direct patterning of carbonaceous materials when exposed to irradiation sources. The nanofabrications made using RIE will have applications in low power high performance electronic devices, optoelectronic, photovoltaic, biosensors and lithium ion battery devices.

Keywords: Polystyrene; Nanostructure; RIE; O2 gas; SF6 gas; CHF3 gas.

1. Introduction

Nanostructured materials have attracted a lot of attention these days because of their new electric, magnetic, optical [1], [2] or biological characteristics which are not obtainable with conventional non-structured materials. The applications range over many areas of science and technology, such as low dimensional electronic and magnetic systems, photo detectors, photo emitters, enhanced Raman scattering, filtration, bioreactors, biosensors, and high-density magnetic recording [3]–[5]. Polymers play an important role in nanofabrication of materials either as mask for lithography or its own unique properties, owing to its repetitive molecular unit, simple processability, low cost tunable properties and diverse functionalities [2],[6]–[10]. Polystyrene (PS) is one of the important polymers that exhibits many good properties, such as easy process, rigidity, low water absorbability, transparency, and that it can be produced at low cost [11]–[13]. The PS films have wide applications and are mainly employed in surface protection of metals, optical biosensor and humidity sensor, coatings for biomaterials and barrier films for pharmaceutical packaging.

Many methods have been used in modify PS nanospheres shapes and sizes, such as reactive ion etching [2], [14], laser irradiation [12], [15], x-ray lithography, electron beam, ion beam and annealing [16]. One of the most popular methods for fabrication of nanomaterials is Reactive ion etching (RIE). It can also be used to modify PS nanospheres mask to create secondary lithography mask but it is also suitable to control the surface morphology and roughness of PS nanospheres especially in investigating surface hydrophobic and hydrophilicity of polymers for application as in electronics and biological applications [2]. The used of PS nanospheres
as mask and fabricating arrays of nanostructure materials through the aid of self-assembly of polystyrene nanospheres is called Nanospheres Lithography (NSL) technique, where the mask created can be varied through the single or multi-layer for metal evaporator mask. The arrays of metal nanostructures deposited through voids of PS nanospheres are dictated by the sizes used as mask and also by combining with other techniques such as RIE, secondary phase of lithography mask are able to be created. In the conventional NSL method, the nanostructure size can be controlled by the diameter of nanospheres used [17]. The array pitch is determined by the size; however, the nanostructure size can be arbitrarily selected by subsequent dry etching of the PS nanospheres. The ability to control size is important for obtaining a profound understanding the properties of nanostructured material and for improving characteristics in terms of technological applications [18].

Many studies have been reported for fabrication of nanostructure using PS spheres for examples He et al [19] fabricated vertical nanostructure arrays (VNAs) by plasma etching processes and their applications in biology, energy and electronics. Evtimova et al., [20] fabricated one-dimensional diamond nanostructures using nanocrystalline diamond films (NCD) as a starting material, where fabrication processed through electron beam lithography (EBL) and reactive ion etching in inductively coupled O₂ plasma (ICP-RIE) was used to increase precise patterning of the diamond nanostructures. Wang et al., [21] reported facile and fast nano-fabrication technique for creating nanostructures based on combining the nanoimprint lithography (NIL) and nanosphere lithography (NSL) techniques, where monolayer self-assembled polystyrene colloidal particle as a mask for dry etching of SiO₂ to create periodic ordered nano-plates on glass substrates.

In this article, approach of producing nanostructure using reactive ion etching (RIE) with three different gases: pure O₂ and mixture CHF₃/SF₆ consisted of 3 stages, first stage: coating method using PS nanospheres to form hexagonal close-packed single or double layers. Second stage, reducing the size and separation of the PS spheres by reactive ion etching with O₂ plasma etching for different etching duration (20 and 40 s). Third stage, using couple capacitive plasma (CCP) with mixture of CHF₃ and SF₆ to etch the PS films with the following conditions: CHF₃ flow 80 sccm, SF₆ flow 40 sccm, RF power 50 W for 20 and 40 s. Investigations of treated and untreated were analyzed using field emission scan microscopy (FE-SEM), Energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and Fourier Transformation Infrared (FTIR).

2. Experimental Details

Polystyrene (PS) nanospheres with the diameter of 500 nm were drop-coated onto silicon wafer with the following procedure: in order to obtain a monolayer of PS nanospheres, the silicon wafer p-type with orientation (100) surface was made hydrophilic by immersion in a piranha solution of 3:1 concentrated H₂SO₄/H₂O₂ at 80 °C for 40 min, rinsed thoroughly with ultra-pure water and dried in a stream of nitrogen, thus created hydrophilic surfaces. The PS nanosphere solution was diluted in deionized water then coated on the substrate surface with the volume-controlled pipette. Finally, the PS monolayer was uniformly distributed within the area of 1x1 cm². Reactive ion etching (RIE) (SnTEK Technology) with couple capacitive plasma (CCP) was used, where nanostructures were made by two stages of etching process. PS was etching with O₂ plasma at flow rate 50 sccm, pressure 200 m Torr and 50 W RF power. This procedures were taken to tailor the size and separation of the PS nanospheres by adjusting the etching duration for 20 and 40 s. Afterward, a mixture of CHF₃/SF₆ with ratio of 2:1 sccm 80/40 sccm plasmas at the fixed chamber pressure (200 mTorr) and RF power (50 W) was employed with the etching durations of 20 and 40 s respectively. Morphologies and elemental composition of the samples were observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500) and the energy dispersive spectroscopy (EDS) and coated with platinum before characterization. Topography and roughness of the samples were studied using atomic force microscopy (AFM) XE-100 Park systems. The measurement was carried out using non-contact mode under the room temperature.
conditions with scan size of 5 μm x 5 μm, high resolution 256 pixels x 256 pixels. FTIR analysis was performed using a Perkin Elmer FTIR Spectrometer LR 64912C N3896 equipped with a universal Attenuated Total Reflectance (ATR) sample stage. The sample molecular structure was determined within the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

3. Results and Discussion

3.1 Morphological Analysis

Fig. 1 (a-f) show analysis of SEM images obtained for untreated and treated polystyrene. Fig. 1(a) shows the morphology of the untreated PS nanospheres. At initial states, the self-assembled monolayers of PS are found to form in hexagonal close-packed arrangement on the silicon substrate. Treated PS for the first RIE stage, using O₂ gas plasma etching process, average diameter of the individual PS nanospheres are found to be reduced in sizes and shapes. The PS nanospheres average diameter reduction through O₂ gas plasma etching process are found to corresponded linearly with etching duration as can be seen in Fig. 1(b-c). Since the position of each PS nanospheres remain the same after the oxygen RIE, the separations between each PS nanospheres increased as the sizes of nanospheres decreased. Though, the etching process caused a minor increase in surface roughness on the etched beads that is in general PS nanospheres were etched evenly in the lateral dimension within the duration of 20 and 40 s. The heights of nanospheres were decreased gradually during the RIE process. Fig. 1 (e-f) corresponds to images of PS nanospheres etched with CHF₃/SF₆ gas mixtures. The Si substrates are believed to be etched too as the mixture of CHF₃/SF₆ are commonly used to gives highly anisotropic Si etching. This is due to the fact that with the addition of CHF₃ to SF₆ gas, CF₂ radicals are produced a blocking layer on the Si sidewalls during etching. The differences of etching rate PS nanospheres and Si, where the higher etching rate of CHF₃/SF₆ compared with O₂ plasma etching and the isotropic nature of process in the case of O₂ gas could be further used to fabricate nanostructures such as nanopillars, nanotriangulars and nanorings.

![Fig. 1: FESEM images of untreated and treated PS with O₂ plasma etching](image)

3.2 Elemental Composition Analysis

Elemental composition analysis was carried out using EDS (Energy Dispersive Spectroscopy) to determine the weight and atomic percentage of carbon and silicon present for untreated and treated O₂ plasma etching. Results are summarized in Table 1;
The PS nanospheres show 81.52 % by weight & 91.16 % for carbon and silicon element before any plasma treatment. The treated PS with 20 and 40 s of O₂ plasma etching were found to reduce in weight and atomic %, reduction of carbon, silicon are 74.06 % & 86.97% and 51.35 % & 71.17% respectively. Fig. 2 (a-c) shows the EDS spectrum for carbon and silicon, where reduction of carbon materials are obvious in the EDS spectrum of 40 s compared to 20 s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>C</td>
<td>81.52</td>
<td>91.16</td>
</tr>
<tr>
<td>PS</td>
<td>Si</td>
<td>18.48</td>
<td>8.84</td>
</tr>
<tr>
<td>PS RIE</td>
<td>C</td>
<td>74.06</td>
<td>86.97</td>
</tr>
<tr>
<td>20 sec</td>
<td>Si</td>
<td>25.94</td>
<td>13.03</td>
</tr>
<tr>
<td>PS RIE</td>
<td>C</td>
<td>51.35</td>
<td>71.17</td>
</tr>
<tr>
<td>40 sec</td>
<td>Si</td>
<td>48.65</td>
<td>28.83</td>
</tr>
</tbody>
</table>

### 3.3 Atomic Force Microscopy Analysis

Atomic force microscopy is a powerful tool for topography study of the films and obtain information about the roughness, height asymmetries values such as the skewness and kurtosis of the films [22]. The average roughness, root mean square (rms) and height asymmetry values are measured using a software analysis from AFM instrument and the results obtained are summarized Table 2. Fig. 3 (a-c) appears to have gradual changes the PS nanospheres where average roughness of samples decreases as the etching time increases. Fig. 4(a-c) shows the AFM images obtained both for untreated and treated polystyrene with RIE. Fig. 4a show that for untreated PS with many sharp and regular present over the whole substrate surface. The surface roughness decreased after treating PS with O₂ plasma and CHF₃/SF₆ gas compared to untreated PS. This could be caused by highly energetic ions and radicals of plasma, because exposure to the active residuals and ions of plasma could result in dissociation of some chemical bonds from the surface of polymers which results in changing morphology of the samples [5].
Fig. 3: Topography images of pre and post RIE treatment of PS during O₂ plasma for (a) 0, (b) 20 and (c) 40 s.

Fig. 4: Topography images of pre and post RIE treatment for PS with CHF₃/SF₆ for (a) 0, (b) 20 and (c) 40 s.

Table 2 AFM Statistical parameters of the O₂ plasma and CHF₃/SF₆ RIE polystyrene thin films at different duration

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Samples</th>
<th>O₂ RIE</th>
<th>CHF₃/SF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure PS</td>
<td>20 sec</td>
<td>40 sec</td>
</tr>
<tr>
<td>Average roughness (nm)</td>
<td>20.4</td>
<td>54.2</td>
<td>38.2</td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td>23.8</td>
<td>67.0</td>
<td>46.3</td>
</tr>
<tr>
<td>Skewness Sₖₖ</td>
<td>0.29</td>
<td>0.81</td>
<td>0.08</td>
</tr>
<tr>
<td>Kurtosis Sₘₘ</td>
<td>2.39</td>
<td>3.59</td>
<td>2.50</td>
</tr>
</tbody>
</table>
3.4 Fourier transformation infrared (FTIR) analysis

RIE surface modifications of polystyrene nanoparticle are confirmed by Fourier transformation infrared. FTIR spectroscopy in attenuated total reflection (ATR) mode is one of the methods used to bring out the finer surface information. This technique was used to characterize the polymer surface. The spectra of the treated and untreated samples are compared to observe the changes. Fig. 5(a-c) shows the ATR-FTIR spectra of untreated polystyrene and treated with oxygen plasma. Fig. 5a show the characteristic bands at 3023 cm\(^{-1}\), 1601 cm\(^{-1}\), 1490 cm\(^{-1}\), 1447 cm\(^{-1}\), and 902 cm\(^{-1}\) correspond to the phenyl group, the peaks at 2924 cm\(^{-1}\) and 2846 cm\(^{-1}\) are assigned to the methylene and methenyl groups, the peak at 1023 cm\(^{-1}\) is correspond to the C–O bond [15], [23]. When untreated polystyrene spectrum is compared with the oxygen-treated polystyrene spectrum, it is seen that broad band occurs around 3698 cm\(^{-1}\) and 2970 cm\(^{-1}\), which led to formation of oxygen-based functional group on the surface due to collision of the radicals components of oxygen to the polystyrene surface [24]–[28]. Etching of the polymer surface through the reaction of atomic oxygen with the surface carbon atom, giving volatile reaction products and other one is the formation of oxygen functional groups at the polymer surface through the interaction between the active species from the plasma and the surface atom [18],[22], [23]. Fig. 6(a-c) shows the spectra of PS treated and untreated with mixture of CHF\(_3\)/SF\(_6\) gases. Treated PS with CHF\(_3\)/SF\(_6\) bands are found to be affected, bands reduced some intensity and become broader compared with O\(_2\) plasma treated and untreated PS which indicates the structural changes as a result of CHF\(_3\)/SF\(_6\). It’s clearly show that new peak appear at 1207 cm\(^{-1}\) for 20 s, intensities of band at 1601 cm\(^{-1}\), 1490 cm\(^{-1}\), 1447 cm\(^{-1}\), 1023 cm\(^{-1}\), disappear after 40 s and created new peaks at 3863 cm\(^{-1}\), 3674 cm\(^{-1}\), 2275 cm\(^{-1}\) due to CHF\(_3\)/SF\(_6\).

![FTIR spectra of untreated and treated PS with O\(_2\) plasma etching for (a) 0, (b) 20 and (c) 40 s.](image)
Fig. 6: FTIR spectra of untreated and treated PS with mixture of CHF₃/SF₆ gases for (a) 0, (b) 20 and (c) 40 s.

4. Conclusion

In conclusion, polystyrene nanosphere was successfully prepared by drop coating method onto substrate and developed a low cost with high throughput fabrication process for nanostructures with modification of the PS nanosphere by plasma treatment and RIE at different etching time. The size and separation of the fabricated nanostructures can be independently adjusted by selecting different etching time and by using an optimum plasma modification process. Also, the new modified fabrication of nanostructures can lead to new applications in electronics, optoelectronics and biosensor devices.

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Letters, 6, 1–5.


