Grafted Polystyrene Monolayer Brush as Both Negative and Positive Tone Electron Beam Resist

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ABSTRACT: Although spin coating is the most widely used electron-beam resist coating technique in nanolithography, it cannot typically be applied for nonflat or irregular surfaces. Here, we demonstrate that monolayer polystyrene brush can be grafted on substrates and used as both positive and negative electron-beam resist, which can be applied for such unconventional surfaces. Polystyrene is a popular negative resist when using solvent developer but solvent cannot be used for grafted polystyrene brush that is firmly bonded to the substrate. Instead, we employed two unconventional development methods to lead polystyrene brush to positive or negative tone behavior. Negative tone was achieved by thermal development at 300 °C because exposed thus cross-linked polystyrene brush is more thermally stable against vaporization than unexposed linear one. Surprisingly, positive tone behavior occurred when the brush was grafted onto an aluminum (Al) layer and the film stack was developed using diluted hydrofluoric acid (HF) that etched the underlying Al layer. By transferring the patterns into the silicon (Si) substrates using the thin Al layer as a sacrificial hard mask for dry etch, well-defined structures in Si were obtained in two different electron-beam resist tones as well as in nonflat surfaces.

1. INTRODUCTION

In order to fabricate nanostructures, lithography methods are used for both industry and research purposes, such as electron beam lithography (EBL) and photolithography. These lithography methods use resists on which patterns are drawn or duplicated from the mask or mold. The most widely used method for resist coating is spin coating because of its simplicity, cost efficiency, and high resist uniformity. However, spin coating does not coat a uniform resist layer on nonflat substrates that is required for some applications such as patterning on atomic-force microscope (AFM) tips for tip-enhanced Raman spectroscopy or lab-on-fiber technology. Therefore, fabrication methods that are applicable in these nonflat surfaces are desired.

Several methods have already been demonstrated to pattern nanostructures on irregular or nonplanar surfaces. For example, as EBL resists coating techniques on such surfaces, ice lithography, evaporative resists, spray coating, spin coating using low viscosity resists, float coating, and dip coating have been developed. For ice lithography, an amorphous ice layer is formed on the cooled substrate inside a vacuum e-beam (or ion beam) chamber and then patterning is performed by focused electron beam or focused ion beam. The drawback of this method is that it requires specially modified scanning electron microscope (SEM) system. Also, the sensitivity of ice resist is extremely low compared to the typical electron beam resist such as PMMA. Evaporated polystyrene resist can also be used as electron beam resist on irregular surfaces. Uniformity of the film coated by this method is much better than that of spin-coated film because evaporated resists do not suffer from the edge beak effect, which deteriorates the uniformity of spin-coated film. However, resists choices that can be thermally evaporated are limited. For example, the popular positive tone electron beam resist, PMMA, cannot be used for this method because its thermal decomposition mainly relies on depolymerization, or end-chain scission. Also, thermal evaporation system is costlier than spin-coating system. Another method that can be used for nonflat surfaces is spray coating. It can be applied even on sharp edges of trenches. However, it requires optimization of resist solution to achieve a proper mobility of resist, and the resist thickness varies significantly between flat surfaces and slanted surfaces. Next, spin coating using low viscosity resists can be applied for nonflat surfaces. Resist can be coated even on nearly vertical surfaces by using this method. However, in order to obtain uniform thickness, sides of the substrate should be parallel to the radial direction of the spinning. Float coating is another method that can be applied on nonflat surfaces. In this method, resist is dried on the surface of wafer in which substrate is submerged. Then, water is extracted and the resist covers the substrate. The patterning on AFM tips has been demonstrated by using this method. Lastly, dip coating can cover irregular surfaces with resist, but it suffers from the difficulty to make uniform film.
There are several other methods to make nanopatterns on irregular, nonflat substrates. Nanoimprint lithography can be used for nonflat or irregular surfaces with or without using spin-coating.\textsuperscript{12–14} Spin coating of imprint resist can only be applicable for slightly curved but smooth surface. Resist coating on nonflat surfaces can also be achieved by transferring the prefabricated nanopatterns on rigid substrates to unconventional substrates by using an intermediate polymer layer.\textsuperscript{15,16} The transfer of metal nanostructures to fiber facet and silica microsphere has been demonstrated by using this method. Transferred hard mask lithography can also be applied for unconventional substrates.\textsuperscript{17} Si membrane hard masks are made by conventional nanofabrication method like electron beam lithography or photolithography and then transferred onto substrate. Because the substrate should be smooth enough to be covered with membranes, it cannot be applied for sharp structures.

Using self-assembled monolayer (SAM) resists\textsuperscript{18–20} is another well-known method that would be capable of patterning irregular substrates. The most popular SAM resist is based on trichloro-silane that bonds readily to –OH terminated substrate.\textsuperscript{21} However, SAM resists are too thin (typically 1–2 nm\textsuperscript{22}) for acting as dry etching mask; and they have very low sensitivity, typically one order lower than that of PMMA.\textsuperscript{23} Additionally, long-term stability of SAMs is limited for a range of reagents/media.\textsuperscript{24,25}

Although many methods have been developed for nanofabrication on unconventional substrates, each method has the limitation on its applicability and there is no universal method. Therefore, a new method to fabricate nanostructures on irregular, nonflat surfaces is still desired to be developed. Previously, we have shown that PMMA polymer brush grafted on substrates can be used as resists for EBL, and it can be applied for nanofabrication on irregular or nonplanar surfaces.\textsuperscript{26} In this paper, we will show nanopatterning on AFM cantilever using monolayer polystyrene (PS) brush. Although thick PS film is known as a negative electron beam resist when solvents are used as developer,\textsuperscript{27–29} we have found that PS monolayer brush layer can be used as both negative and positive resist depending on the development condition. Negative tone behavior was achieved using thermal development that preferably desorbs the unexposed linear PS; whereas positive tone behavior was unexpectedly attained when PS was coated on Al and the film stack was “developed” using diluted HF that etches Al, indicating electron beam exposure weakened PS capability of protecting the underlying Al against HF etch.

2. EXPERIMENTAL SECTION

Figure 1 shows the schematic representation of the fabrication process to utilize PS brush as electron beam resist. First, a silicon substrate was cleaned by RCA cleaning, and a thin layer of Al (~8 nm) was deposited on substrate as a sacrificial hard mask layer because the brush layer is too thin for pattern transferring. The surface was then treated by oxygen plasma for 1 min. Afterward, carboxyl-terminated polystyrene PS-COOH (Scientific Polymer Products, Ontario, New York State, molecular weight (Mn) 13 000 g/mol) was dissolved in toluene with a concentration of 10 w/v%. After spin/drop coating (spin for flat substrate (at 4000 rpm for 40 s), drop for AFM cantilever), the thick resist film was baked at 160 °C for 24 h to promote the adsorption of PS-COOH onto the substrate, presumably via the reaction of the –COOH end group and the hydroxyl group on the substrate with the release of H₂O. Then, the substrate was soaked in toluene for 1 min to remove the bulk of PS film that could be very nonuniform if the substrate was nonplanar. Therefore, only a grafted monolayer of PS-COOH with extremely uniform thickness remained on the substrate. Here the coating condition is not critical for our process, because anyway the thick/ungrafted part of the PS will be washed away by a solvent after the thermal annealing.

Next, electron beam exposure was performed using LEO 1530 field emission SEM (Carl Zeiss) integrated with the nanometer pattern generation system (NPGS, JC Nabiity Lithography Systems). The brush layer was developed with different conditions to obtain recessed or protruded structures. To achieve protruded structures, the PS brush layer was used as a negative resist. First, the resist was thermally developed on a hot plate at 300 °C for 60 s to preferably vaporize the unexposed PS, and then the aluminum layer was etched by diluted hydrofluoric acid (HF/H₂O₂, 1:500 volume ratio) for 70 s. Finally, the pattern was transferred to the silicon substrate by dry etching in CF₄ and O₂ plasma (20 sccm CF₄ gas, 3 sccm O₂ gas, 10 mTorr pressure, 50 W RF power) using the aluminum layer as a hard mask. On the other hand, to obtain recessed structures, the PS brush layer was used as a positive resist. In this case, without thermal development, the exposed area of the PS brush layer was lifted off by soaking for 15 s in diluted HF solution (HF/H₂O₂, 1:25 volume ratio) that etched away the underneath Al layer. This implies that the exposed PS became less effective in protecting the underneath Al against HF etching. Finally, the pattern was transferred in the same way as fabricating protruded structures.

To evaluate the thickness of the brush monolayer (see Figure 2), PS-COOH was grafted on a silicon substrate after a brief oxygen
plasma treatment to form hydroxyl group on the surface. Next, a layer of chromium (Cr) was evaporated simultaneously on the grafted silicon and bare silicon substrates which are partially shadow-masked. Afterward, unmasked brush layer was removed by O₃ RIE, and then the brush including Cr thickness measured by AFM was compared with Cr thickness on the bare silicon in order to obtain the brush layer thickness.

3. RESULTS AND DISCUSSION

The monolayer brush thickness was measured as 15 nm from which the packing density/surface coverage for the PS monolayer can be calculated as 0.723 chains per square nanometer using the following equation

\[ \sigma = \frac{(hN_A)}{M_n} \]

where \( h \) is monolayer thickness, \( \rho \) is bulk density of polystyrene (1.05 g/cm³), and \( N_A \) is Avogadro’s number. This surface coverage is in the high surface density regime. Formation of denser surface coverage is possible, too, using the “grafting from” approach where polymer brushes are generated in situ. In this work, the “grafting to” approach was preferred because it is an easier way to coat a surface, and it works well enough for our e-beam lithography application.

The molecular weight of the PS-COOH was chosen according to its commercial availability, and other \( M_W \) would also work for our purpose. Generally, for higher resolution polystyrene with lower molecular weight would be preferred; for higher sensitivity (at the cost of resolution), higher molecular weight would be preferred. As for grafting temperature, it is chosen as 160 °C that is well above the glass transition temperature of PS and well below its decomposition temperature. Annealing time was selected as 24 h to ensure grafting with a high packing density, as it is reported that long annealing time will increase the number of grafted chains.

Moreover, as we pointed out in our previous study, carboxyl group might not bond chemically to –OH terminated substrate and we were not able to show unambiguously the chemical bond formation. According to some studies, an intermediate layer that contains epoxy group should be coated before polymer brush formation in order to form strong chemical bonding. To test the adhesion of the PS monolayer, PS monolayer-coated samples were soaked in xylanes, toluene, and tetrahydrofuran solvents for an hour with ultrasonication. The monolayer could not be dissolved after this process, which shows that PS monolayer adhered strongly to the substrate, well enough to be used as a stable monolayer e-beam resist regardless whether it was chemically bonded to the sublayer or not.

When thick PS film is used as resist for EBL, it behaves as a negative resist because cross-linking is induced by electron beam exposure. Likewise, the PS brush layer may work as a negative resist, yet solvent cannot be used as developer because the firmly grafted brush cannot be dissolved by a solvent. Because cross-linked PS has higher thermal stability against vaporization than linear one, thermal development can be used to carry out the development. However, if the development temperature is too high (≥350 °C), even cross-linked areas are decomposed and vaporized. On the other hand, if the development temperature is too low (≤250 °C), the unexposed areas are not fully vaporized. It was found that thermal development at 300 °C for 1 min was the optimal condition. Figure 3 shows the SEM images of the pattern obtained by using the PS brush as a negative resist with thermal development. We have previously precisely demonstrated thermal development of thick polystyrene resist. EBL was carried out with 5 keV at a line dose range of 2.2–3.8 nC/cm. Here low electron energy was selected to minimize proximity effect to achieve better resolution, and the optimum dose was determined experimentally where a range of line arrays with pitches from 50 nm to 1 μm and doses from 1 to 15 nC/cm were exposed. In order to perform pattern transferring, we etched the underneath Al by very diluted HF (1:500 dilution ratio); otherwise, if less diluted HF was used the remaining PS brush could not protect well the Al film underneath. After pattern transfer by RIE for 2 min, line array in silicon with 110 nm width was obtained at 2.2 nC/cm exposure dose. Figure 3c shows AFM measurement of the line array that gave a 135 nm line height.

Positive behavior of PS brush layer was also achieved by changing the development condition. The SEM images of patterns using PS brush as positive resist are shown in Figure 4. EBL was carried out at 5 keV and a dose range of 0.2–3.8 nC/cm. These electron beam energy and dose values were also

![Figure 3. SEM images of the line array pattern obtained by using PS brush as negative resist: (a) 500 nm period, 2.2 nC/cm exposure dose; (b) 1 μm period, 3.8 nC/cm; (c) AFM image of line array presented in (b). Here Al layer was kept for high-contrast SEM imaging, yet its thickness should be under 5 nm.](Image)

![Figure 4. SEM images of the pattern obtained by using PS brush as positive resist: (a) 300 nm period, 0.2 nC/cm, (b) 1 μm period, 0.2 nC/cm, (c) 500 nm period, 3.8 nC/cm, (d) AFM image of line array presented in (c).](Image)
determined experimentally. To achieve positive behavior, the sample was developed by HF/H2O (1:25 volume ratio) for 15 s without thermal development. HF washed away only the exposed area of PS layer together with the underneath aluminum layer, whereas the unexposed area remained. Next, to transfer the pattern into silicon, 2 min RIE has been carried out. AFM measurement of the trench depth resulted in 40 nm as shown in Figure 4d. It should be noted that AFM probe could not reach to the bottom of the trenches, so the measurement is not accurate; yet the trench depth should be approximately the same as the line height mentioned above (135 nm) because the two samples were etched using the same RIE recipe.

Although (thick) PMMA can also be used as both positive and negative resist,35 our results indicate that the mechanism that changes the tone behavior of PS brush layer is very different from that for PMMA in which the increase of exposure dose changes the reaction induced by exposure from chain scission to cross-linking. In the case of PS brush, the tone behavior of resist was changed according to the development process even though the exposure dose was the same. Our results imply that, contrary to intuition that exposed thus cross-linked PS would behave as a better mask material, exposure actually made PS a weaker mask against HF etching of the underneath Al film.

Next, the process with positive tone behavior was applied on an AFM probe to demonstrate that PS brush is applicable to nanofabrication on irregular substrates. Periodic line arrays with 500 nm period were exposed at 5 keV and doses of 2 nC/cm and 6 nC/cm which resulted in 75 and 120 nm wide lines, respectively (Figure 5).

Figure 5. SEM images of grating patterns on AFM probe: (a) top view; (b) close-up view, 500 nm period, 2.6 nC/cm dose; (c) 500 nm period, 1.2 nC/cm dose.

Figure 6 shows contact angles of bulk (thick) PS, non-cross-linked PS brush, and cross-linked PS brush, as 91°, 91°, and 65°, respectively. The results indicate that the cross-linked brush becomes more hydrophilic that would allow aqueous HF to penetrate through the brush to etch the underneath Al and thus lift-off the brush, so only the cross-linked area is removed and the resist behaved as positive resist. Similar behavior has been obtained for SAM of octadecyltrichlorosilane on SiO2 and Cr substrates after electron beam exposure.20,36 Therefore, it is reasonable to believe that the working mechanism behind the pattern transferring for the positive tone behavior is hydrophilicity of the polymer brush.

There might be some concerns regarding usage of HF depending on the application, but it should be noted that for negative tone, different etchants can be used to etch the sacrificial layer. For example, PAN etching (a mixture of phosphoric acid, acetic acid, nitric acid, and water) also worked well for pattern transferring into Al layer. Moreover, we have performed pattern transferring using Cr as the sacrificial layer that does not involve HF. Therefore, the process is not HF dependent. On the other hand, if one wants to completely avoid the usage of wet etching, clean dry etching process can also be carried out. The etching selectivity between Cr and PS is approximately 1:1, so 15 nm PS is enough to etch 15 nm Cr layer that is sufficient for etching 1 μm deep into Si.

The results show high-resolution capability of 110 nm wide lines for the negative tone and 20 nm wide lines for positive tone. In the case of negative tone, resolution is limited by the random nature of PS brush vaporization (desorption) and proximity effect, and higher resolution could be obtained by reducing the proximity effect, such as by using high energy (e.g., 100 keV) exposure, exposure on thin membranes that are transparent to electrons, or designing very sparse patterns.

Lastly, because the brush layer is thin, there is a certain risk of pinhole formation that may cause unwanted etched holes into the substrate. However, the risk would be far less than the well-known SAM resists, which is commonly used as mask to etch gold layer for microcontact printing, because monolayer brushes are usually around ∼10−15 nm thick whereas SAMs are usually only ∼1–2 nm thick.

4. CONCLUSION

We successfully showed that PS brush layer can be grafted on nonflat substrates and used as both positive and negative resist for EBL. Unlike PMMA which is known for changing its behavior from positive tone to negative tone depending on the exposure dose, the tone behavior of PS brush changes depending on the development conditions. Negative tone was achieved by thermal development, and positive tone was achieved by using diluted HF as a “developer”. After the pattern transferring to the substrate using the thin aluminum layer as an intermediate hard mask layer for dry etch, we obtained well-defined structures for both positive and negative cases on silicon substrates, as well as on an AFM cantilever. Therefore, the process can provide a simple way to fabricate both recessed and protruded structures on those nonflat surfaces which can be applied to tip enhanced Raman spectroscopy3 and lab-on-fiber technology.25

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