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Fabrication of Nano-scale PMAA Polymer Brushes Appearing Fingerprint Pattern on Silicon Surface Using PS-b-P_2VP as Template

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Abstract *: A new simple and economical chemical method of fabrication of nano-scale PMAA polymer brushes appearing fingerprint pattern on silicon surface using PS-b-P_2VP as template has been established. The PS-b-P_2VP diblock copolymer micells in toluene was spin-coated on silicon surface, self-assembling a pseudo-hexagonal dot array composing of P_2VP with diameters of tens of nm in the PS matrix. The PS-b-P_2VP assembled array on the surface of the silicon wafer formed a linear or fingerprint pattern by the mixing solvent (THF/H_2O) steam after a certain amount of time. Then soaking in the dilute HCl solution of Na_2PtCl_4, removing PS-b-P_2VP by the oxygen plasma, the platinum salt was reduced to a platinum nanodot matrix line. In the end, the linear or fingerprint Si-Hx pits was obtained by anodic catalysis of HF ethanol solution with oxidant. The etching occurred exclusively beneath the hydrophilic vertical P_2VP columns via protonization of pyridine rings. The parts covered by PS was not corroded by HF and still the SiOx layer. Because of alternative arrangement of the inside (Si-Hx) and outside (SiOx) pits, the surface initiator can be introduced selectively in the Si-Hx region of the inside pits for hydrosilylation. PMMA polymer brushes were fabricated by Si-ATRP reaction. The PMAA linear or fingerprint patterns were obtained on the assigned silicon surface. Further herb active molecules with $–NH_2$ can be grafted on these patterns with acyl to attain different functionalities of integrated circuits, biological chips, and chemical micro-reactors etc.*

Keywords*: PS-b-P_2VP; Silicon surface; Patterning of nano-polymer brushes; PMAA*

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I. Introduction

It is one of the future directions to conduct accurate nano-patterning on related semiconductor surface, such as silicon and germanium surface[1]. Presently, most of patterning techniques of the polymer brush on the silicon surface are micron-sized, with less nanoscale. Most of the techniques are focused on physical methods such as stamping, lithography, and scanning probe sharpening. However, it is expensive in making nano-patterning, complicated in operation and only suitable for small area production[2-4].

Although lithography in the sub-100-nm pattern has an advantage, short wave light source such as EUV, laser exciter, synchronous radiation source, there are significant problems of these technologies in the industrialization and economic aspects. Other methods, such as electron beam lithography, cluster ion beam lithography, scanning probe tunnel-cutting such as DPN, can be used for sub-20-nm fabrication, but due to its intrinsic characteristics of technology, it is not suitable for large-scale production[5].

It can be obtained through photolithography for the processing pattern size of more than 300 nm. The pattern of size between 30 and 300 nm is usually etched by electron beam. It is difficult to achieve a pattern with a size less than 30 nm through conventional semiconductor etching[6]. With the higher pursuit of micro-nano processing technology and the constant understanding of the nature of materials, new nano-fabricating mean has emerged. The lithographic technique based on block copolymer is one of them. Block copolymer is a special polymer that connects two or more different polymers with various properties. Because of their thermodynamic incompatibility and connection of segments, phase separation of this molecule exists in dozens of nanometres, and the block copolymer self-assembly technology is based on this principle[6-9]. Different kinds of block copolymers were synthesized by polymerization [10]. Segalman described the directions of the block copolymer in the membrane relative to the substrate when the block copolymer was coated on the substrate. This is very useful for our subsequent patterning [11].

To meet the requirements of nano-scale patterning of polymer brushes on silicon surface, a new synthesis method with high accuracy and low cost is required[12-14].One of the things that has been getting a lot of attention is the use of self-assembling block copolymers to make templates. Block copolymer can be self-assembled into multiple uniform structures such as dot array, horizontal columnar, lamellar, etc., covering a

large area without special equipment[15]. The self-assembly block copolymer can make the surface chemical reaction templating. In the interface, the specificity of the block is used to bind and localize the chemical reagent.For PS-b-P4VP, P4VP column presents a hexagonal dot array, surrounded by PS[3, 4, 16-18]. For PS-b-P2VP, the P2VP column can be transformed into linear or fingerprint P2VP horizontal column by solvent annealing, which is surrounded by PS[11, 19-22].The linear or fingerprint patterns of these column arrays and horizontal columns specify locations of a surface chemical activity occurs only under P4VP or P2VP. The polymer template is then removed and the surface pattern left is similar to the mask. There are Si-Hx inside and SiOx outside the pits in the nano-scale pattern, respectively. So, parallel chemical functionalization can be achieved. Among them, different chemical modifications can be carried out inside and outside pits to obtain more complex and ordered structures. Because the spacing is controlled by the block copolymer template, the center-to-center distance of the polymer brushes can be adjusted by regulating the molecular weight of the block copolymer template[23, 24]. The size of the polymer brush can be obtained by adjusting the polymerization conditions, such as soaking time and catalyst concentration[25].

As a result, the author has developed a patterning method of polymer brushes on silicon surface, in which PS-b-P2VP was used as template, then corrosion by dilute HF, SiHx pits obtained, undecylenyl alcohol and acylbromide grafted, then ATRP polymerization[26].

II. Experimental

Theory

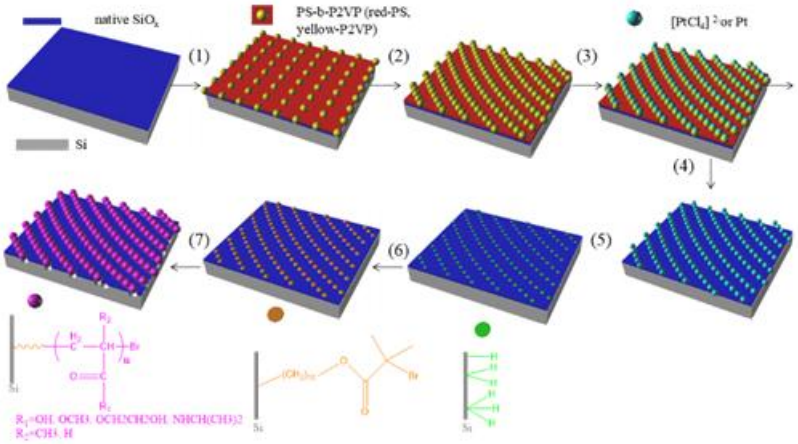


Fig. 1 Scheme of the experiment. (1) The toluene solution of

PS-b-P2VP is spin-coated on the native silicon oxide layer of the silicon wafer, self-assembling a dot array. The yellow core is P2VP, and the red peripheral is PS. (2) The spin-coated silicon wafers are annealed by a solvent vapor (THF/H2O) for a given time, and a pattern of lines or fingerprints of P2VP horizontal columns appears[27]. (3) The silicon wafers are soaked in an acidic solution and the P2VP on its surface are protonated and swollen, P2VP piercing through PS layer. When a negatively charged platinum salt is added to the solution, it will be combined with the positive P2VP by the electrostatic attraction. (4) Then oxygen plasma is used to remove the polymer, platinum salt translates platinum lines in the mean time[28]. (5) The silicon wafers with platinum lines are immersed in HF/H2O2/EtOH solution for a certain time, the Si-Hx hole will be formed in the gap position between platinum lines. (6) 2-bromo-2-methylpropionic acid-10'-undecylenate is grafted on the silicon surface by microwave reaction[29]. (7) The PMAA polymer brush is then assembled through the Si-ATRP reaction[30]. The resulting PMAA pattern is similar to that of the PS-b-P2VP fingerprint [15, 27, 31-33].

Experimental details

See Supplementary Information.

III. Results and discussion

Pattern of PS-b-P_2VP annealed by steam of mixture solvent

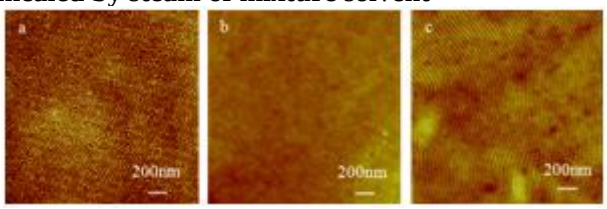
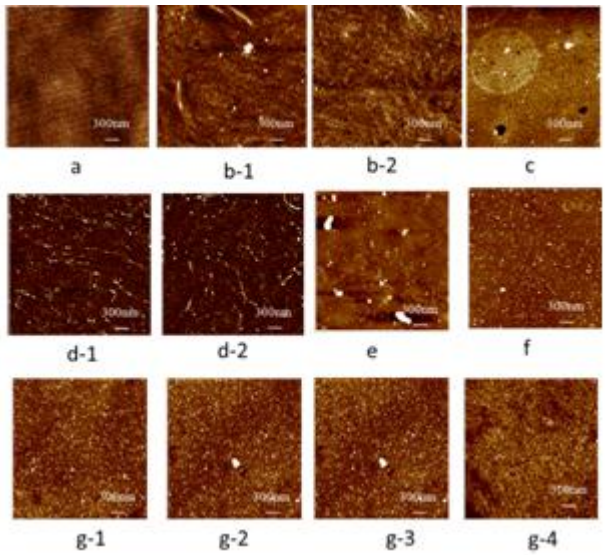


Fig. 2 AFM images: (a) PS-b-P_2VP（56000, 21000）dot matrix. (b) the line pattern of PS-b-P_2VP annealed by steam of the mixed solvent（10:1 THF/H_2O, 30h）. (c) the fingerprint pattern of PS-b-P_2VP annealed by the mixture solution（10:1 THF/H_2O, 36 h）. All the images have dimensions of 3 μm. In images b and c, the obtained patterns are different through various solvent-annealed time of PS-b-P_2VP array, because PS and P_2VP eventually move to diverse positions[15, 27, 32].



PMAA lines and fingerprint patterns were fabricated using PS-b-P2VP as templates

PS-b-P2VP forms a consistent spherical micellein toluene due to its selective dissolution for PS. Fig. 2a shows the spin-coated film. The PS block forms a crown around the less soluble P2VP core to reduce the interaction energy with the solvent. In Fig. 2b and c, AFM images were used to study the changes in the appearance of asymmetric PS-b-P2VP films in THF/H2O mixed solvents (neutral solvents for two blocks)[15, 16, 27, 32]. The morphological changes of polymer films with different solvent-annealed time were studied. On the surface of the wafer, the spin-coated film presented as spherical particle.After annealed for 36h, the P2VP column was completely transformed into a horizontal column parallel to the silicon surface[31].

Fig. 3 AFM images: (a) Thesolution of 0.5% (w/w) PS-b-P2VP(56000, 21000) was spin-coated onto the silicon oxide layer on the surface of the silicon wafer. (b) The array of PS-b-P2VPwas annealed in the THF/H2O (10:1) mixed solvent vapor for 36 h, forming a line pattern. (c) The silicon wafer was soaked in a solution of 0.9% HCl /70 mmol.L-1 Na2PtCl4 for 3h. (d) The polymer film was removed by oxygen plasma with conditions of 30W, 60s, and platinum line appeared at the same time[27]. (e) The silicon wafer with platinum lines was soaked in a solution of 1:1:4 HF/H2O2/EtOH for a certain period of time. Si-Hx pitswere formed in the gap between the platinum lines. (f) 2-bromo-2-methylpropionic acid-10 '- undecyl ester was grafted into Si-Hx pits with conditions of microwave assistance, nitrogen protection, 120℃, 30W and 20min. (g) PMAA polymer brushes were fabricated in NaMA reaction solution for 3h with nitrogen protection. The obtained PMAA polymer brush pattern is similar to that of the PS-b-P2VP line[31, 33, 34]. g-5 is 6 μm, g-6 is 9 μm, and the rest is 3 μm.

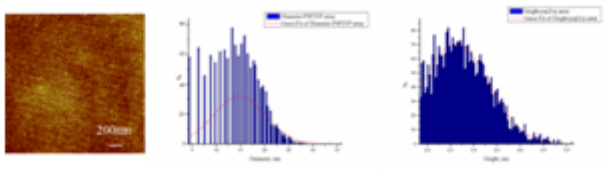


Fig. 4 The AFM image of PS-b-P_2VP (56000, 21000) dot array (left), its diameters distribution (middle) and its height profile (right).

As can be seen from Fig.4, the spin coating of 0.5% (w/w) PS-b-P_2VP presented as a dot array on the silicon chip. The core is P_2VP, and the coronal circumference is PS. Its dot diameter is 20 ~ 30 nm, its center-to-center distance is 35 ~ 45 nm, and itsdot height is about 10 nm.

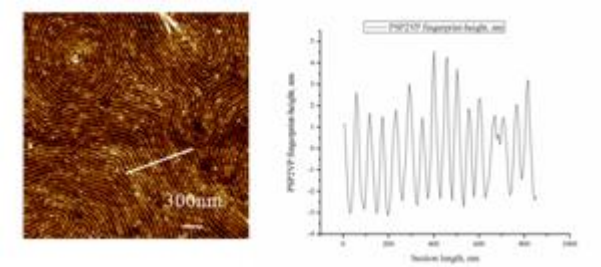


Fig. 5 The fingerprint AFM images of PS-b-P_2VP (56000, 21000) (left) and its height profile of the scribedline (right).

From Fig.5, it can be seen that the dot array was converted into lines and fingerprint patterns through the THF/H_2O mixed solvent steam annealed for 36h, in which the line width is 30～50nm, the center-to-centerspace is 50 ~ 60nm, and the line height is about 10nm.

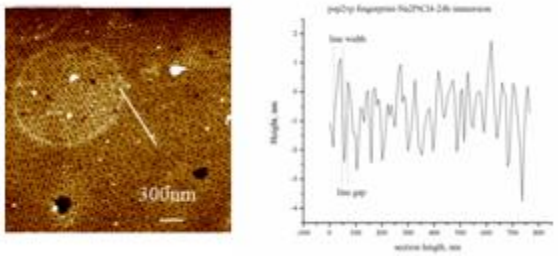


Fig. 6 The fingerprint pattern of PS-b-P_2VP (56000, 21000) was soaked in a 70 mmol.L^{-1} Na_2PtCl_4/0.9 % HCl solution for 3 h (left). The height profile of the scribed line in the fingerprint AFM images (right).

From Fig.6, after the line pattern was soaked in 70mmol.L^{-1} Na_2PtCl_4/0.9% HCl solution for 3 h, it can be seen that the P_2VP has expanded because of protonation of its pyridine ring, then punctured the PS layer and formed the dotted line.P_2VP with positive charge and $PtCl_4^{2-}$ with negative one were combined by electrostatic attraction.So the location of the original P_2VP corresponds to a platinum line formed[33]. The height of the line in the liquid phase AFM was 13nm, which was predicted by the swelling of the lines.

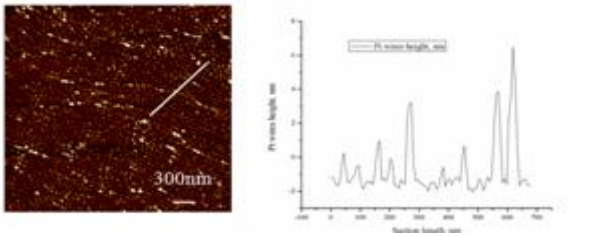


Fig. 7 The platinum lines formed by the treatment of oxygen plasma (left). The height profile of the AFM image along the marked line (right).

It can be seen from Fig. 7 that the PS-b-P_2VP line was removed after the treatment of the oxygen plasma with the conditions of 30W and 60s, and the platinum salt was reduced and the platinum lines were formed.As can be observed, the platinum line appeared a dotted line, and its pattern was similar to that after soaked in a 0.9%HCl solution.The height of platinum line was about 7nm. The height of the platinum line was related to the soaking time. When the soaking time was increased, the line height would add slightly, but the final one of the line was controlled by the altitude of P_2VP. From Fig. 3e that the silicon wafers with platinum wire were soaked in HF/H_2O_2/EtOH solution at 40℃ for 5min, and Si-Hx pitswere arranged in a dotted line, similar to platinum line pattern.The Si-Hx pitswas connected to a dotted line due to the anode catalysis of platinum lines. It can be seen from the Fig. 3f, 2-bromine -2- methyl-10 '-11 olefinic propionate were grafted to Si-Hx pits, with microwave reaction conditions of 125℃, 30w and nitrogen protection. Because the grafted molecular weight was smaller and its total number was less, the obvious relative signals can not be seen in the infrared spectrum, and the evident polymerization phenomenoncan notbe observed in the AFM images.

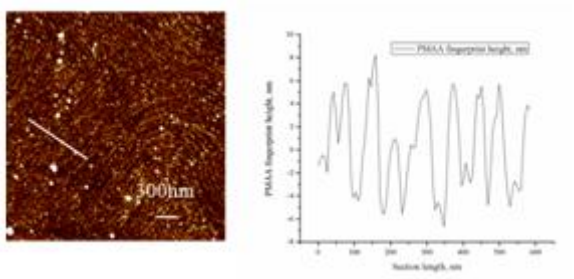


Fig. 8 The PMAA fingerprint AFM image (left) and its height profile of the marked line (right)

As can be seen from Fig.8, the PMAA pattern fabricated by Si-ATRP in the NaMA solution with initiator was similar to platinum line pattern. The width of PMAA line was 30～50nm, spacing between lineswas 60～70nm, and the height of line was 10nm. PMAA lines with carboxyl groups are a useful template for subsequent assembly of biomolecules.

IV. Conclusions

The precise positioning technology of PMAAand other polymer brushes on the surface of silicon wafer has just started in academic field.Its potential industrial applications are also very extensive, such as photovoltaic cells, photocatalysis, circuits, sensors and so on. In this paper, we used PS-b-P_2VP to assemble the double block copolymer film. The PMAA linear or fingerprint array were guided to fabricate on the surface of silicon wafer. The two block copolymer PS-b-P_2VP micelles on the surface of the silicon slice were nearly hexagonal arrays of dots. The center was P_2VP surrounded by PS.The Si-Hx hole array obtained after dilute HF etching copied the shape of the block copolymer template. The PS-b-P_2VP assembled array on the surface of the silicon waferformed a linear or fingerprint pattern by the mixing solvent (THF/H_2O) steamafter a certain amount of time.Then soaking in the dilute HCl solution of Na_2PtCl_4, removing PS-b-P_2VP from the oxygen plasma, the platinum salt was reduced to a platinum nanodot matrix line.In the end, the linear or fingerprint Si-Hx pits was obtained by anodic catalysis of HF ethanol solution with oxidant. The parts covered by PS was not corroded by HF and still the SiOx layer. Because of the difference of the chemical nature of the inside and outside pits, the surface initiator can be introduced selectively in the Si-Hx region of the inside pits for hydrosilylation[29]. PMMA and other polymer brushes were fabricated by Si-ATRP reaction. The PMAA dot array and PMAA linear or fingerprint patterns were obtained on the assigned silicon surface.

Conflicts of interest

There are no conflicts to declare.

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