

Morphology and Contact Angle Characterization of Deposited PE-PEO Diblock Copolymer on Silicon Wafer

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Abstract

Micro/nano-patterns of the diblock copolymer, PE-PEO, have been created to change and adjust the surface properties of a silicon wafer. Results show that the surface of pure silicon renders hydrophilic after thermal oxidation. Further treatment with alkoxy silane coupling agent, the water contact angle becomes 130° and the oil one, 28°. The root-mean-square roughness, Rq, increases from sub-nanometer to 1.2 nm calculated using atomic force microscopy (AFM), indicating a high surface coverage of the coupling agent over the silica layer and the formation of covalent bonds. In addition, the hydrophilic PE-PEO coatings with thermal fused hydrophobic chains of the PE blocks and the alkyl tails of silane could be deposited by the dipping method and annealing. The modified surface gives a water contact angle of 110° and an oil one of 35°. Self-assembled striated patterns driven by heat have been found for the PE-PEO diblock copolymer coatings in the phase images of AFM.

Keywords: Diblock; Silane; AFM; Annealing

1. Introduction

Wettability is an important property of a solid surface, and is dependent on the surface compositions and microscopic structures. Hydrophobicity normally means low wettability of water on a surface. Since the advent of the era of nanotechnology, the “lotus effect” has unveiled the natural hydrophobic product comprising nano-structured hydrophobic surface which could resist dirt staining easily. However, for practical use, a surface which could resist smears of both mud and grease is called amphiphobic and being sought vigorously. Hence, micro-phase separation of diblock copolymers [1-3] has been applied to substrates for rendering amphiphobic surfaces to repel both organic and aqueous droplets. Normally the diblock copolymers such as PS-*b*-PMMA have one hydrophilic segment and the other is hydrophobic. When coated on a substrate and annealed, different patterns of micro-segregated PS blocks and PMMA blocks could be formed inside and on the deposited films depending on the ratio of PS to PMMA in chain length, the substrate wettability, and other processing factors.

In addition, surface coatings with sub-micrometer to micrometer pores could also render amphiphobicity [4]. The method utilizes microphase separation induced by the rapid solvent evaporation and polymerization. It was reported that the pore size can be controlled and the mesoporous copolymer film with hydrophobic convex and hydrophilic concave structure exhibits surface amphiphobicity. Such surface property could be applied to many field especially self-cleaning products in utensils and clothes.

To enhance the competitiveness of commercial textiles by creating nano-structures on them for rendering special surface properties such as amphiphobicity, a common diblock copolymer, poly(ethylene-*b*-ethylene oxide) (PE-PEO) [5], was utilized to form micro/nano- patterns on a pretreated silicon wafer as a

model for textile functionalization. Characterization includes surface morphological study using the atomic force microscopy (AFM), as well as surface hydrophile study by water and oil contact angle (CA) measurement. Experimental variables include reagent concentrations, time duration for each processing step, dipping speed, and annealing temperature.

2. Experimental

2.1 Materials

Poly(ethylene-*b*-ethylene oxide) (PE-PEO, Aldrich, average Mn ca. 1400; 50 wt% ethylene oxide) was used with DI water as solvent. Octadecyl trimethoxy silane (OTMS, Tech, 90%) was used as received and with hexane as solvent. Silicon wafer was used as substrate and cleaned with acetone before use.

2.2 Equipment

The film morphologies of the PE-PEO diblock copolymer were obtained using the AC or semi-contact mode AFM (Angscope SPM-A-100 from Angs NanoTek, Taiwan). High temperature furnace (MC-2838P, Max Thermo) was used in oxidizing the silicon wafer to form a SiO₂ layer on the wafer surface.

3. Results and Discussion

Fig. 1 is the chemical formula of the diblock copolymer, PE-PEO. Fig. 2 is a plot of water and oil contact angles against variously treated silicon wafer surfaces. In addition to the bare Si wafer, wafer 1 is thermally oxidized; wafer 2 is thermally oxidized plus the silane coupling agent; wafer 3 is PE-PEO spin coated and annealed based on wafer 2. The samples are found to exhibit increasing hydrophobicity as high as 130° and slightly decreasing lyophilicity over 30°. The slow increase in oil contact

angle shows the potential to form an amphiphobic surface.

Fig. 3 shows the surface morphology of a pure silicon wafer. The scan size is 500 nm by 500 nm. The local surface roughness is calculated by AFM as $R_q = 0.10$ nm, indicating that the surface is very smooth with a sub-nm roughness and that the calculated roughness has fallen within the hardware noise range. In addition, the contact angles show the surface is hydrophobic as expected.

Fig. 4 shows the AFM image of the thermally treated silicon wafer surface. The scan size is 500 nm by 500 nm. The thickness of the oxide layer is estimated to be about 148 nm from the depths of the pinholes. After thermal oxidation, the surface became more hydrophilic with the water contact angle decreasing from 55° to 45° (Fig. 1). The root-mean-square surface roughness R_q increased from 0.10 nm to 0.74 nm, indicating the formation of silica oxide. The pinholes may result from the chip-off defects due to expansion of the silicon surface layer on oxidation.

After thermal oxidation, the silicon layer was modified by OTMS. The water contact angle jumped up to 130° due to the hydrophobic tails of silane (Fig. 1). The coupling agent underwent the sol-gel reactions with the oxide layer of silicon to form the Si-O-Si covalent bonds. After washing the silane layer with solvent for a few times, the surface hydrophobicity still retained, indicating the success of modification. Although the hydrophobicity increased a lot, it did not increase the lyophilicity accordingly. The oil contact angle did not decrease after the surface modification. Surface nano-structures, exposed oxide layer, or scattered fine particles of silica gel from silane might contribute to this phenomenon.

Fig. 5 shows the AFM image of the silane layer over the oxide layer. The scan size is 500 nm by 500 nm. The morphology is quite different from that of Fig. 4 to the naked eye. Further, the surface roughness R_q increased again from 0.74 nm to 1.2 nm, implying a relatively high surface coverage by the silane agent. The oxide pinholes are not as dense in number as observed in Fig. 4, indicating the filling up by silane.

Fig. 6 shows the AFM image of the annealed PE-PEO layer over the silane layer. The scan size is 500 nm by 500 nm. Morphology of netted polymer films with pinholes could be observed. However, the outlook of the pinholes in this layer is quite different from that in the silicon oxide layer. The local surface roughness R_q has increased to 5.7 nm, indicating a relatively rough surface.

Contact angle data show that the hydrophobicity drops a little bit while the lyophobicity keeps increasing (Fig. 1). On annealing the film, the PE segments of the PE-PEO copolymer are expected to move and entangle with the alkyl tails of the silane layer. Such a thermal fusion should be able to push the more hydrophilic PEO segments to the surface of the coating, thus to lower the surface hydrophobicity, which explains the change in water contact angle.

In Fig. 7, the AFM phase image reveals the micro-phase separation of the PE-PEO diblock copolymer after annealing. The scan size is 500 nm by 500 nm. The different color shades in the image normally refer to different components in the sample as well as the regions of large slope. Fig. 7 gives a striated pattern which might denote domains of PE, PEO, and silica. Hence, the surface wettability is determined by all the materials exposed on the surface. The PEO blocks might take the form of hydrophilic islands on the surface. By improving and utilizing such self-assembled micro/nano-structures, a better surface amphiphobicity is expected and currently being sought in our lab.

In the future, the concentrations and relative lengths of the two blocks in PE-PEO and the temperatures of thermal oxidation and annealing will be studied to understand their effects on the self-assembled patterns and amphiphobicity. Further, a similar process will be applied to real textile to study the effects of the surface modification.

4. List of Figures

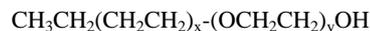


Fig. 1. Chemical structure of PE-PEO

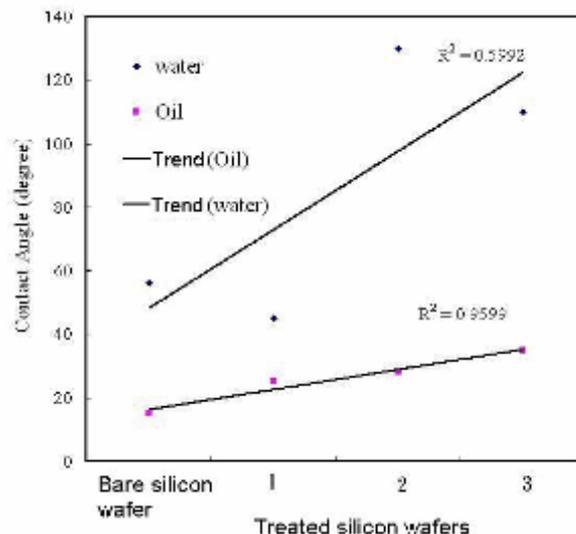


Fig. 2. Plot of contact angles of oil and water against treated silicon wafer surfaces. Wafer 1 is thermally oxidized; wafer 2 is thermally oxidized and then coated with the silane coupling agent; wafer 3 comprises PE-PEO diblock copolymer spin-coated on wafer 2 and annealed. The scan size is 500 nm by 500 nm.

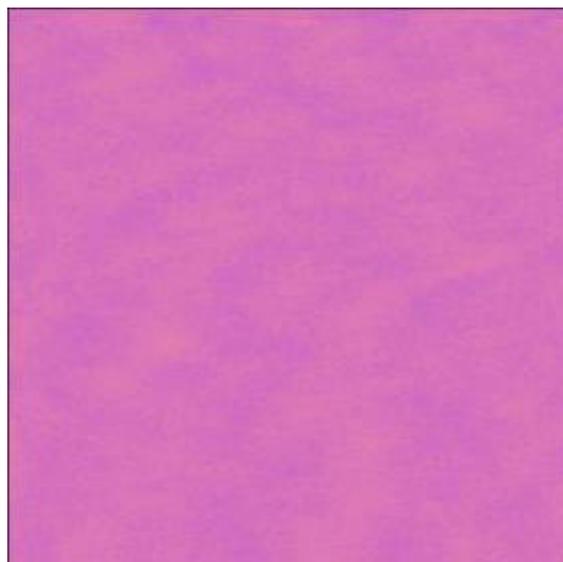


Fig. 3. AFM image of bare silicon wafer surface. The scan size is 500 nm by 500 nm.

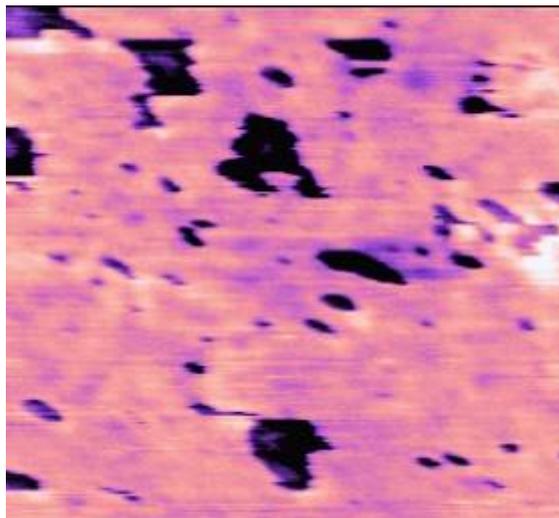


Fig. 4. AFM image of thermally oxidized silicon wafer surface. The scan size is 500 nm by 500 nm.

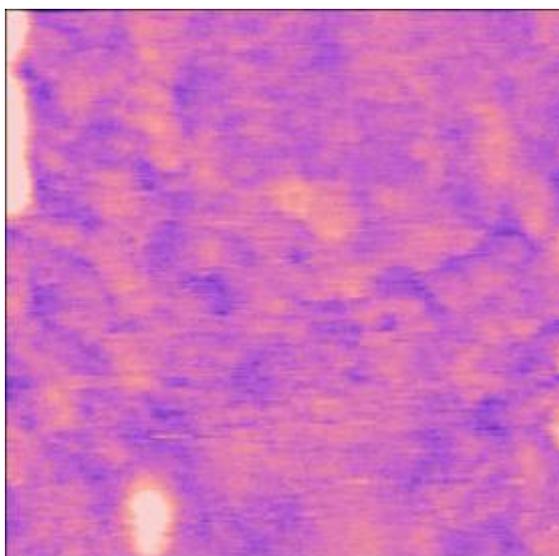


Fig. 5. AFM image of silicon oxide surface modified by alkoxy silane coupling agent. The scan size is 500 nm by 500 nm.

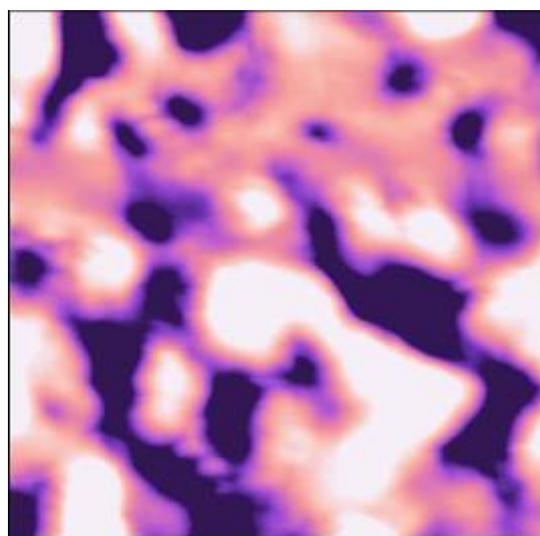


Fig. 6. AFM image of PE-PEO layer deposited and annealed on the silanol/oxide/silicon wafer surface. The scan size is 500 nm by 500 nm.

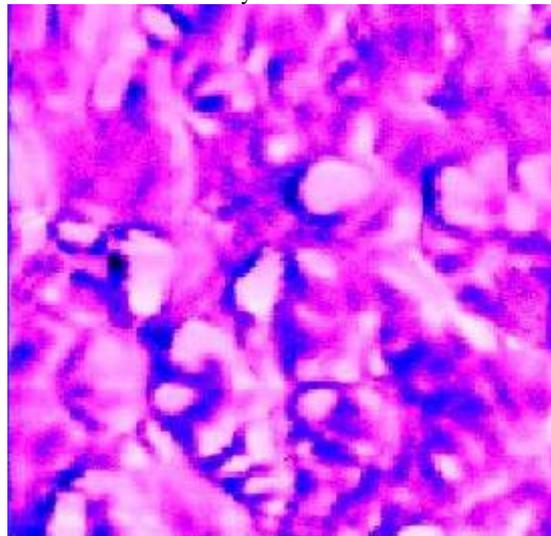


Fig. 7. AFM phase image of PE-PEO layer deposited on the silanol/oxide/silicon wafer surface. The scan size is 500 nm by 500 nm.

5. Conclusions

Micro/nano-patterns of the diblock copolymer, PE-PEO, have been created to change and adjust the surface properties of a silicon wafer. Results show that the surface of pure silicon renders hydrophilic after thermal oxidation. Further treatment with alkoxy silane coupling agent, the water contact angle becomes 130° and the oil one, 28° . The slow increase in oil contact angle shows potential in creating amphiphobic surface coatings. The root-mean-square roughness, R_q , increases from sub-nanometer to 1.2 nm calculated using AFM, indicating a high surface coverage of the coupling agent over the silica layer and the formation of covalent bonds. In addition, due to the thermal induced entangling of the PE blocks and the alkyl tails of silane, the hydrophilic PEO blocks could be moved to the top of the coating, rendering a more hydrophilic surface while holding down the oil contact angle. Self-assembled striated patterns indicating mixed but separated hydrophilic and hydrophobic regions have been found for the PE-PEO diblock copolymer coatings in the phase images of AFM.

Acknowledgements

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