Korean J. Chem. Eng., **20**(5), 956-959 (2003)

Patterning Si by Using Surface Functionalization and Microcontact Printing with a Polymeric Ink

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(*Received 21 January 2003 • accepted 14 April 2003*)

Abstract−This paper describes a simple procedure for patterning Si substrate using a combination of surface functionalization and microcontact printing (μCP). The Si/SiO$_2$ surfaces were chemically modified to present self-assembled monolayers (SAMs) of siloxanes terminating in reactive carboxylic anhydride groups and then patterned with poly(ethylene imine) (PEI) by μCP. We used the patterned thin films of PEI as etch resists on Si surfaces.

Key words: Pattern Generation, Microcontact Printing (μCP), Self-assembled Monolayers (SAMs), Si Etching

INTRODUCTION

This paper describes a convenient procedure for patterning Si substrate by printing thin films of poly(ethylene imine) (PEI) using a combination of microcontact printing (μCP) [Xia and Whitesides, 1998] and surface functionalization based on reactive self-assembled monolayers (SAMs) [Yan et al., 1997]. Our approach consists of a sequence of reactions (Fig. 1): (i) preparation of vinyl-terminated SAMs of siloxanes; (ii) oxidation of the terminal vinyl groups to carboxylic acid groups; (iii) formation of reactive SAMs that present interchain carboxylic anhydride groups; and (iv) pattern delivery to the reactive SAMs using μCP. This method, the formation of interchain anhydrides, is compatible with a wide range of organic functionalities and does not require separate synthesis of each compound that is to be patterned.

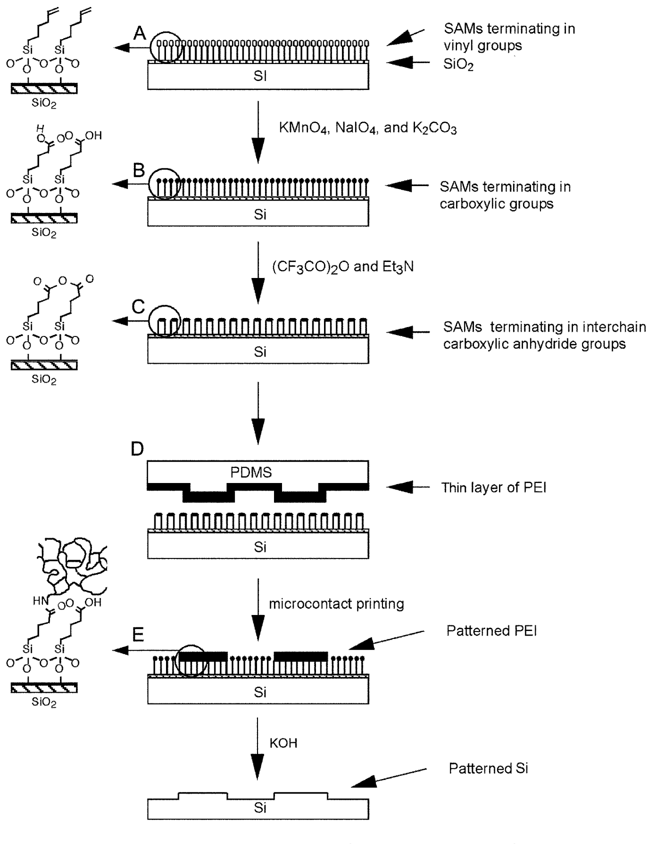

Fig. 1. Schematic representation of the procedure for patterning PEI on Si/SiO$_2$ surface.

Research on μCP and wet etching to generate micro- and nanopatterns on surfaces has been reported in pattern generations of metal films (gold, silver, copper, and palladium) [Xia et al., 1995, 1996; Love et al., 2002] and of metal oxides [Si/SiO$_2$, Al/Al$_2$O$_3$, Ti/TiO$_2$, and indium tin oxide (ITO) or indium zinc oxide (IZO)] [St. John and Craighead, 1996; Finnie et al., 2000; Breen et al., 2002]. Alkanethiolates (for metals) and organosilanes (for metal oxides) were directly printed onto the substrates and the resulting patterns of, the SAMs were used as etch resists. Although SAMs are only one molecule thick (~2-nm-thick-monolayer), they could act as an etch resist. The ideal SAM-based resist with high order and no defects would prevent etchants from dissolving the substrate below. In practice, SAMs adsorbed from solution or patterned on a substrate are, however, not perfect but have flaws such as molecular defects or domain boundaries. Defects in the SAMs (disordered regions or missing molecules) may open a path to the substrate for etchants [Zhao et al., 1996]. The roughness and the presence of contaminations or impurities on the substrate also add defects, which would deteriorate the etch-barrier properties of monolayers [Geissler et al., 2002]. These problems are responsible for the limited contrast and the small process window when monolayers are used as a resist, and have prevented a widespread use of SAMs as wet-etch barriers despite the unique opportunities they could offer.

Herein we demonstrate a procedure for patterning Si substrate with an amine-presenting polymer, poly(ethylene imine) (PEI), by μCP and using the patterned PEI as etch resists. The reaction of amines with interchain carboxylic anhydride groups on the surface is a rapid and high-yield reaction. We used a commercially avail-

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able PEI, which is highly branched, with an 1:2:1 ratio of primary, secondary, and tertiary amines [Yan et al., 1999]. Thus, these polymer films (resists) are highly cross-linked and firmly attached to the surface. Our main interest in these polymer films is to improve the etch resistance compared withe the etch resistance of a single layer of SAMs.

EXPERIMENTAL

1. Materials

Chemicals were purchased from Aldrich, Junsei, and Duksan Chemical Co. Si<100> wafers were purchased from Silicon Sense Inc. Sylgard 184 (PDMS oligomer) was purchased from Dow Corning Co. Poly(ethylene imine) (PEI, M_w 750000, 50 wt% in water, Aldrich) was dissolved in 2-propanol and passed through a 0.2-μm filter prior to use. 6-Hex-1-enyltrichlorosilane (HTS) and (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-trichlorosilane were purchased from Gelest, Inc.

2. Preparation of Reactive SAMs Presenting Interchain Anhydrides

2-1. HTS SAMs

Plasma-cleaned silicon wafer having a thin layer of native silicon oxide (SiO_2) (~20 Å) was immersed in a hexane solution of HTS (2 mM). After the formation of SAMs, the samples were rinsed with toluene and dried under a stream of argon.

2-2. Oxidation of HTS SAMs

The oxidation was performed under Lemieux condition [Wasserman et al., 1989]. The HTS-coated substrate was immersed in an aqueous solution of 0.5 mM of $KMnO_4$, 14.7 mM of $NaIO_4$, and 3 mM of K_2CO_3 for 24 h, and rinsed with pure water. The resulting COOH surfaces were completely wetted by water and the substrate was blown dry in a stream of argon.

2-3. Preparation of Interchain Anhydrides

The COOH-terminated substrate was placed in a freshly prepared solution of 0.1 M trifluoroacetic anhydride (TFAA) and 0.2 M triethylamine in anhydrous DMF without stirring for 20 min at room temperature, rinsed with CH_2Cl_2, and dried in a stream of argon. The substrates presenting the interchain anhydrides were used immediately.

3. Microcontact Printing (μCP) of PEI

PDMS stamps were prepared according to the literature method by using Sylgard 184 silicone elastomer [Lee et al., 2003]. A cleaned silicon wafer was spin-coated with a negative photoresist (SU8-50, MicroChem Co.) and processed by photolithography to develop patterns on the wafer surface. Subsequently, the master was silanized with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-trichlorosilane under vacuum for 2 h. To cast the PDMS stamp, the master was covered in a Petri dish with PDMS oligomers. After curing for 6 h at 60 °C, the PDMS stamp was peeled off from the master. Before being used, the PDMS stamp was oxidized by an oxygen plasma cleaner (Harrick PDC-002 at medium setting) for 1 min. The PDMS stamp was inked by spin-casting with a solution of PEI, and PEI was printed by contacting the PDMS stamp with the interchain anhydride-activated Si/SiO_2 for 60 sec. The stamp was carefully peeled off, and the substrate was washed with distilled water and ethanol and dried in a stream of argon.

4. Etching of Si/SiO_2

After the formation of the polymer (PEI) patterns, the substrate was immersed in an aqueous solution of KOH at 45 °C for 3 min. After the etching, the substrate was taken from the solution, rinsed with distilled water and ethanol, and dried under a stream of argon.

RESULTS AND DISCUSSION

Fig. 1 shows a schematic representation of the procedure for patterning the amine-terminated polymer (PEI in this study) on the surface of Si/SiO_2. Interchain anhydride-terminated SAMs were prepared from vinly-terminated SAMs via a two-step surface reaction [Yan et al., 1997]. Vinyl-terminated SAMs were assembled by immersing a silicon wafer having a thin layer of native silicon oxide (SiO_2) in a freshly-prepared hexane solution of 6-hex-1-enyltrichlorosilane (Fig. 1a). The terminal vinyl groups were then oxidized (under Lemieux condition) to carboxylic acid groups on the surface (Fig. 1b). Reaction of the carboxylic acid groups with TFAA and triethylamine in DMF gave SAMs of siloxanes that presented interchain carboxylic anhydride groups on the surface (Fig. 1c). Prior to inking, the PDMS stamp was oxidized in an oxygen plasma. We have found it critical for the printing of hydrophilic PEI on a substrate with high fidelity to make the surface of the stamp hydrophilic by oxidation. The oxidized PDMS stamp was immediately inked by spin-casting with an 1 wt% solution of PEI in 2-propanol and placed in contact with the substrate (Fig. 1d). The amine groups

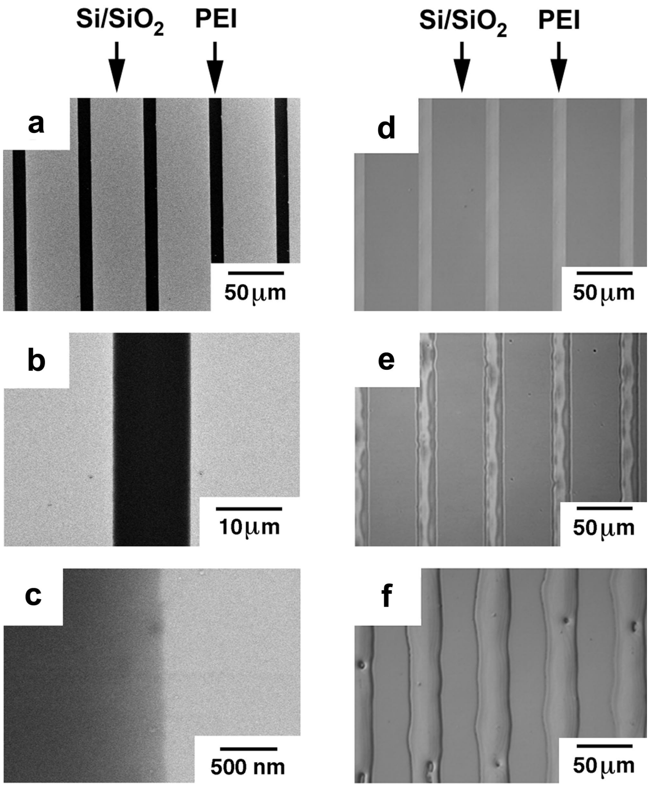

Fig. 2. Characterizations of the patterned thin films of PEI using SEM (a-c) and optical microscopy (d-f). The dark areas in the SEM images (a-c) were the films of PEI. The concentrations of PEI in 2-propanol were 1 wt% (a-d), 5 wt% (e), and 10 wt% (f), respectively. The same stamp (10-μm-lines separated by 40 μm) was used.

of the PEI polymer reacted with the interchain anhydride groups on the surface leading to the formation of amide bonds (Fig. 1e). Finally, we generated the line patterns of PEI (10 μm in width separated by 40 μm).

We used optical microscopy and scanning electron microscopy (SEM) to characterize the patterned films of PEI on Si/SiO$_2$ before etching. Fig. 2a-c show SEM images of the patterned thin films of PEI. We used a 2-propanol solution of PEI (1 wt%) for printing. The resulting thin films of PEI were nearly continuous. We also investigated effects of the concentration of PEI in 2-propanol on the morphology of printed films of PEI. The optical images (Figs. 2e and f) show that the solutions having concentration higher than 1 wt% did not yield well-defined thin films of PEI (2e; 5 wt%, 2f; 10 wt%).

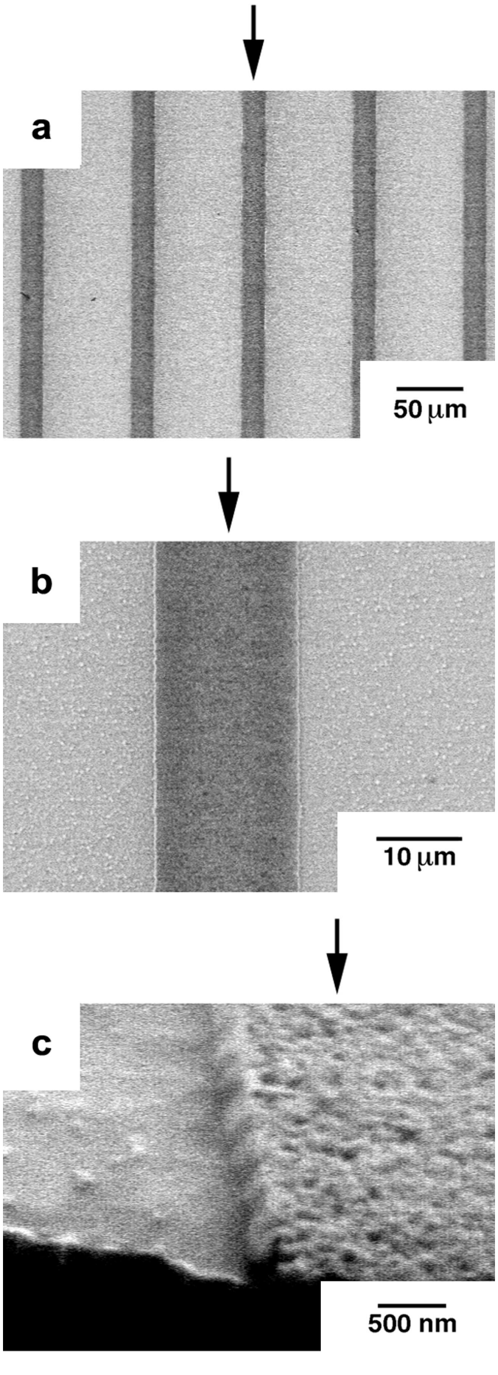

Fig. 3. SEM images of the patterned silicon after etching. The SiO$_2$ layer was etched by immersing the substrate in an aqueous solution of KOH at 45 °C for 3 min. The arrow in the figures indicates the area that has been protected with PEI.

The density of defects in patterns that are fabricated by using SAMs is too high. The defects probably originate from the domain structure of the SAMs or from intrinsic defects (pinholes) in the SAMs [Xia et al., 1995; Zhao et al., 1996]. A layer of polymer is much thicker than a layer of SAMs. Thus, we hoped that the density of defects would be lower in a layer of polymers, and that the polymer layer would be more stable under etching condition than a single layer of SAMs. Fig. 3 shows SEM images of patterned silicon lines after etching. The polymer layer is an effective etch resist (Fig. 3a and 3b). The images show that the areas patterned with a layer of PEI polymer acted as a temporary protection layer against the KOH solution. Fig. 3c shows that the edge roughness of the pattern (etch depth: ~130 nm) is less than 100 nm, which is similar to that of microcontact-printed *n*-hexadecylamine on gold surface [Yan et al., 1998]. Unfortunately, however, the surface of the area that had been protected with PEI became rough after etching, which may suggest that the printed PEI films did not have uniform thickness. The roughness of the area may be caused by the destruction from the etching solution, the surface topology of Si/SiO$_2$, and the presence of gel or dust particles in the PEI. The layers of PEI and SiO$_2$ were etched away by KOH solution leading to the Si pattern. To improve the etch-barrier property of polymer layers, Whitesides and collaborators patterned a gold surface with a PEI layer and allowed the amine-terminated surface to react with poly(octadecene-*alt*-maleic anhydride) (POMA) or poly(styrene-*alt*-maleic anhydride) (PSMA) polymers. The coupling procedure (alternating reactions with PEI and POMA/PSMA) was repeated, and the resulting polymeric multilayers were used as an etch resist [Huck et al., 1999]. They showed that increasing the number of polymer layers eliminated almost all the defects in the patterned polymer layers. This approach can also be applied to the system studied in this paper to improve the etch-barrier property.

CONCLUSION

We have demonstrated a pattern generation of Si substrate with a combination of surface functionalization and microcontact printing. The method demonstrated here could be applicable to a wide variety of surfaces of metal oxides that are amenable to surface modification. The advantages of using polymers compared with a single layer of SAMs are: (1) it is possible to make a thicker layer of etch resists than a single layer of single SAMs, which is technologically important in chemical etching processes, and (2) because the printed polymers contain chemically reactive functionality, we have a chance to further modify the surfaces.

ACKNOWLEDGMENTS

This work was supported by the Kyungnam University Research Fund (2002). We thank the Korea Basic Science Institute (KBSI) for optical microscopy.

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