

Combining Patterned Self-Assembled Monolayers of Alkanethiolates on Gold with Anisotropic Etching of Silicon to Generate Controlled Surface Morphologies

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ABSTRACT

Self-assembled monolayers (SAMs) of hexadecanethiolate were patterned onto gold films supported on titanium-primed silicon wafers using microcontact printing (μ CP). Wet etching of the gold, and subsequently of the silicon, using three systems of resists based on these patterned SAMs, denoted by the shorthand labels Au/SAM, Ni/Au/SAM, and Au/SAM/polymer, produced features in silicon having dimensions in the 1 to 10 μ m scale. In the Au/SAM system, the SAM acted as a resist to protect gold from etching by CN^-/O_2 , and the resulting, patterned gold protected silicon from etching by KOH (4M)/i-PrOH (25% by volume) at 60°C. In the Ni/Au/SAM system, the pattern in the gold layer was transferred to an underlying nickel layer by etching in a bath consisting of conc H_2SO_4 , 30% H_2O_2 , conc H_3PO_4 , and 30% aqueous solution (w/v) of NiSO_4 (5:5:1:4 by volume) at 35–40°C; in turn, the nickel acted as a resist to protect the silicon from etching. In the Au/SAM/polymer, a prepolymer of epoxy resin or polyurethane was self-assembled onto hydrophilic SAMs on the surface that was patterned into regions of different interfacial free-energy and wettability; after curing, the polymer served as the resist during etching gold by aqua regia, and etching silicon by KOH /i-PrOH. All three resists were compatible with etchants for silicon, and they masked the underlying silicon effectively.

Introduction

We describe a convenient procedure for etching patterns in the surface of silicon. The method uses well-developed etching procedures for silicon;^{1–5} the mask used to protect selected areas of silicon from the etchant is gold, or gold combined with other metals such as nickel or with an organic polymer. The gold, in turn, is patterned using μ CP^{6,7} of self-assembled organic monolayers of alkanethiolates that protect the gold from a selective etch. An advantage of these procedures is that they yield micrometer-scale features but require only one photolithographic step, to prepare the stamp for μ CP; this stamp can be used to prepare multiple copies of a patterned substrate without additional photolithography. The process of μ CP and etching yields patterned masks of gold on silicon surfaces; the silicon surfaces can, in turn, be etched. We have developed three systems of resists, and we abbreviate these as (i) Au/SAM, (ii) Ni/Au/SAM, and (iii) Au/SAM/polymer (Fig. 1). These systems are described in detail in the following sections. They have different characteristics that permit their use in both positive and negative processes, and in processes that use different types of etchants toward silicon.

The Au/SAM system that uses gold as a mask and that patterns the gold using SAMs and μ CP is the simplest to use. This process uses as substrate Si/SiO₂ whose surface has been primed with a thin layer of titanium to promote adhesion of a gold film. Our strategy was to form patterned SAMs of alkanethiolate on the gold and remove the unprotected gold by etching. The remaining gold was used to protect the silicon from etching. The Ni/Au/SAM system offers a second level of complexity. In this system, we have used nickel instead of titanium as in the Au/SAM system; nickel acts as both an adhesion promoter and resist. Patterning the SAM was followed by removal of the gold layer by etching to reveal selected areas of nickel surface; the bare nickel was removed in a separate etching step. This system was designed to be used with reactive ion etching. The third system, Au/SAM/polymer, offers a different approach to a patterned resists. In this system, we have used the different interfacial free-energies of appropriately patterned SAMs to coat selected areas of the surface with a film of organic polymer by self-assembly. This patterned polymer then protected the gold during treatment with aqua regia; this etching removed gold not protected by polymer. The polymer also protected the silicon in a subsequent etching step. This process avoids the CN^-/O_2 etching normally used to remove gold during processes based on μ CP.

We and others have developed procedures (both lithographic and nonlithographic) to form patterns of SAMs on gold, for example, micromachining,⁸ microwriting,^{9,10} and oxidative patterning with UV light,¹¹ and have used these patterned SAMs to protect the gold against selective etchants (most conveniently, CN^-/O_2 in aqueous base, although alternatives not using cyanide also exist).⁹ The most convenient and versatile of the patterning methods is μ CP. This procedure has been described in detail elsewhere,^{6,7} as have preliminary demonstrations of the ability of gold pat-

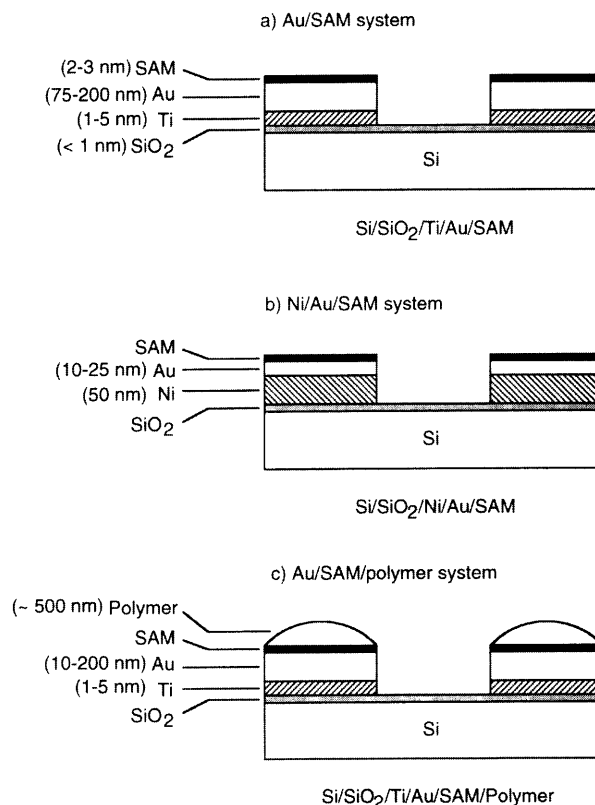


Fig. 1. Schematic representations of resists used. The approximate thicknesses of the layers are indicated on the diagrams, and they are not drawn to scale. The "polymer" in (c) was an epoxy or a polyurethane.

turned by μ CP to act as a mask that protects silicon against etching.^{7,12} Anisotropic etching of silicon offers a capability to fabricate complex structures, and it has been widely exploited. In some conditions, the rate of removal of silicon from the $\langle 100 \rangle$ face of silicon is 100 times greater than from the $\langle 111 \rangle$ face.¹³⁻¹⁹

Experimental

General.—All chemicals were reagent grade and were used as received. Gold (99.999%), nickel (99.9%), and titanium (99.99%) were obtained from Materials Research Corp. Hexadecanethiol was obtained from Aldrich, and $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ was prepared by the procedure reported elsewhere.²⁰ Stamps were made of poly(dimethylsiloxane) (PDMS)^{6,7} (Sylgard 184, Dow Corning). All etchings of silicon were done with the silicon wafers with the $\langle 100 \rangle$ orientation, except where noted otherwise. Scanning electron micrographs (SEM) were acquired by JEOL JSM-6400. Oblique views of fractured samples were taken by fracturing the silicon wafer along its $\langle 100 \rangle$ axis.

Preparation of substrates.—Prior to use, single-crystal silicon wafers with $\langle 100 \rangle$ or $\langle 111 \rangle$ orientation (Silicon Sense, Inc. test grade) were cleaned in a 1:1 mixture of conc sulfuric acid: 30% H_2O_2 and washed with copious amount of water.

CAUTION: This corrosive mixture should be handled with care. It should not be allowed to contact significant quantities of oxidizable organic materials. In some cases, it has detonated unexpectedly.²¹⁻²³

Titanium, nickel, and gold were deposited in a cryogenically pumped electron beam evaporator (base pressure = 1×10^{-8} Torr). Titanium layers (10–100 Å, deposited at 0.5 Å/s) were used as adhesion promoters. In Ni/Au systems, an adhesion promoter was not needed.

Patterning gold surfaces.—Microcontact printing^{6,7,12} was used to pattern SAMs on the gold surfaces. An elastomeric stamp made of PDMS was wet with an ethanolic solution of hexadecanethiol (1 mM) using a lint-free cotton pad. After excess solvent had evaporated, the thiol was transferred to the gold surface by the contact between the stamp and the gold.¹²

Fabricating polymeric masks.—A gold surface was patterned with the SAM of hexadecanethiolate by the procedure described above. This surface (a few square centimeters) was washed with an ethanolic solution of $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ (5 ml, 1 mM). After washing the surface with ethanol and water, it was dried with a stream of nitrogen. Epoxy resin (bisphenol diglycidyl ether and polymercaptan, Devcon) or UV-curable prepolymer of polyurethane (NOA 60, Norland) was used in preparing the films on the COOH-terminated surfaces; several other polymers were also used successfully: for example, J-91 [a prepolymer of polymethylmethacrylate (PMMA), Summers Optical] and NOA 61. A drop of polymer was placed on the patterned surface. The excess polymer was removed from the patterned region by tilting the surface and allowing it to run off under the influence of gravity. The polymer selectively wet and assembled on the hydrophilic region ($-\text{COOH}$) and dewet from the hydrophobic region ($-\text{CH}_3$). Epoxy resin was cured thermally at 60°C for 20 min, and polyurethane by exposing to a UV light (Canrad-Hanovia 450 W medium pressure, Hg vapor lamp (Type 7825-34, ACE Glass) with a water-cooled, quartz housing) for 30 min. After curing the polymer, the unprotected metallic layers (Au and Ti) were removed by dissolving in aqua regia (20 s, 40°C). The polymer-covered regions then protected the silicon from etching in a KOH/i-PrOH solution.

Etching of Au and Ni.—Selective etching of gold was done in a basic aqueous bath of CN^-/O_2 .⁹ A gold surface patterned with the SAM of hexadecanethiolate was immersed in an aqueous solution of cyanide (100 mM KCN, 0.5M KOH) through which O_2 was bubbled continuously. When the underlying layer (silicon or nickel) was exposed (~ 10 min for 250 Å gold), the sample was removed from the

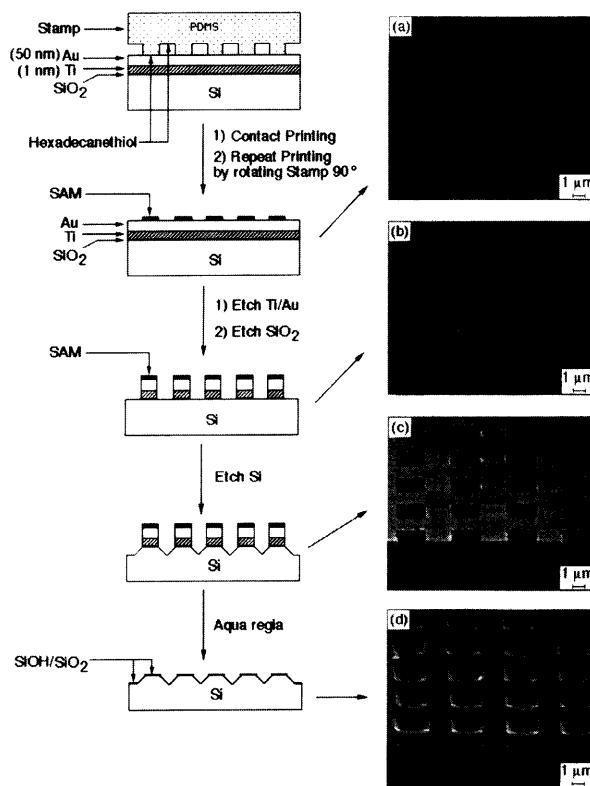


Fig. 2. Etching of silicon with the Au/SAM resist. (a) Scanning electron micrograph of SAMs of hexadecanethiolate (light region) on gold (dark region). The pattern of a square grid was made by first printing a pattern of 2 μm lines separated center-to-center by 4.5 μm . After printing this line grating, the stamp was rotated by 90° and reprinted using the same grating to make a perpendicular grid. (b) Selective etching of gold exposed the underlying silicon (dark region). The edges of gold features show < 100 nm resolution, determined by the region between gold and silicon. (c) Anisotropic etching of silicon ($\langle 100 \rangle$ orientation) using KOH/i-PrOH produced pits that were "inverted pyramids." (d) SEM of etched silicon after the resist layer was removed using aqua regia.

etching solution and washed with water and ethanol. Selective etching of nickel in the presence of gold was accomplished by a variation of the method used to etch electrolessly deposited nickel.²⁴ The etching bath was made up of conc H_2SO_4 , 30% H_2O_2 , conc H_3PO_4 , and 30% aqueous solution (w/v) of NiSO_4 (5:5:1:4 by volume) at 35–40°C. Nickel, but not gold, dissolved in this mixture.

CAUTION: The mixture of H_2SO_4 , H_2O_2 , H_3PO_4 , and NiSO_4 is highly corrosive and should be handled carefully. It should not contact oxidizable organic materials.

Nickel was etched at approximately 75 Å/s. Another efficient etchant for nickel was a mixture of 50 ml of conc H_2SO_4 , 50 ml of 30% H_2O_2 , and 100 ml of 3% (w/v) aqueous ethylenediaminetetraacetic acid (EDTA).

Etching of Si.—After the removal of metal layers was complete, the native SiO_2 layer was removed by exposure to 1% aqueous solution of HF before etching silicon. Anisotropic etching was done in a temperature controlled bath (60°C) of 4M KOH and 25% (v/v) iso-propanol.¹⁻⁵

Results and Discussion

Etching of silicon using Au/SAM resists.—Figure 2 illustrates procedure involved in fabricating and using Au/SAM masks. A patterned SAM of hexadecanethiolate was formed on a gold surface by μ CP. The SAM protected the underlying gold from etching by CN^-/O_2 . The etchants removed the unprotected gold (by the SAM) and the titanium/titanium dioxide, though at a much slower rate than gold. The residual (if any) layer of Ti/TiO₂ was removed when the surface was treated with HF. Figure 2b illustrates features formed in this process and demonstrates that μ CP

forms patterns with <100 nm edge resolution, as determined from contrast differences at the edges by SEM.

Once the pattern in the Au/SAM resist had been fabricated by removal of unprotected gold by etching, it could be used, in conjunction with anisotropic etching of silicon using KOH/i-PrOH,⁸ to form 3d structures in the silicon. During etching of silicon, the gold layer retained its integrity, although the SAM is probably destroyed. The adhesion of the gold to the silicon substrate was sufficiently strong to protect the masked parts from unselective etching, although the expected undercutting did occur. After the 3d pattern in silicon was formed, the mask was removed easily and completely by aqua regia.

This Au/SAM system has several advantages as the basis for a system for anisotropic etching of silicon. This system is easily fabricated to give uniform and reproducible masks. The pattern-transfer step is simple and allows features of 1–10 μm dimensions to be fabricated routinely, and features down to ~ 200 nm to be fabricated with more difficulty.⁷ Variations in the parameters (concentrations of etchants, temperature, humidity, atmospheric contaminants) involved in μCP and etching do not significantly affect the fabrication of mask. The structural integrity of the masks is maintained throughout during the processes used to transfer patterns.

Figure 3 illustrates the undercutting that is observed in this process. Even with significant undercutting, the adhesion between the resist and the underlying substrate remained strong. As in Fig. 3a and b, the edge resolution, which is determined by the Au/SAM resist, degrades during undercutting. As features become smaller and more closely spaced, undercutting becomes more significant. Undercutting was determined by the etching condition (etchants, concentration, and temperature) and was not controlled; however, the extent of undercutting can be varied by changing the duration of etching. "Controlled" undercutting (Fig. 3c) is useful in making microwires suspended in air between pyramidal pillars of silicon. Such systems may be useful when minimizing delay times in transmission lines.²⁵

Etching of silicon using Ni/Au/SAM resists.—We developed a second system of resist and etchant, in which nickel served as the primary mask, with the objective of exploring systems that might be useful in currently used dry-etching processes for semiconductors. One advantage of using nickel is that it resists attack by aggressive reagents such as fluorine and is thus useful as a resist in reactive ion etching. Nickel is also less expensive than gold where thick metal structures or structures with some mechanical rigidity are required. Figure 4 outlines the process used to fabricate structures of nickel and shows electron micrographs of these structures.

Although we have developed SAMs that assemble on a nickel/nickel oxide structure, the currently available systems do not have the stability, ease of formation and patterning, and reliability as masks that alkanethiolates on gold display. We have therefore used patterned SAMs on gold to generate patterns in gold; these gold patterns in turn acted as masks and protected the underlying nickel from a second etchant. This two-etch system produced patterns in nickel. The process thus has three stages: (i) pattern SAMs of alkanethiolates on gold; (ii) using these SAMs, etch gold unprotected by alkanethiolate; and (iii) using the resulting gold structure as a mask, transfer this pattern to nickel.

In this system, nickel serves two functions: as an adhesion promoter between gold and silicon dioxide and as a resist to protect silicon from etching. For this method to be successful, the etch systems must be orthogonal: that is, etchants for gold should not affect the nickel layer

and etchants for nickel ideally should not influence either gold or silicon. We used an aqueous acidic solution containing a strong oxidizing agent (H_2O_2) and stabilizing reagents for nickel (phosphates and sulfates) to remove nickel selectively.²⁴

Like the Au/SAM resist, the Ni/Au/SAM resist maintained its structural integrity during the etching process. The Ni/Au/SAM masks have been used successfully in a reactive ion etching (CF_4/O_2).²⁶ Although we illustrate this type of system using nickel, the same procedure can be used

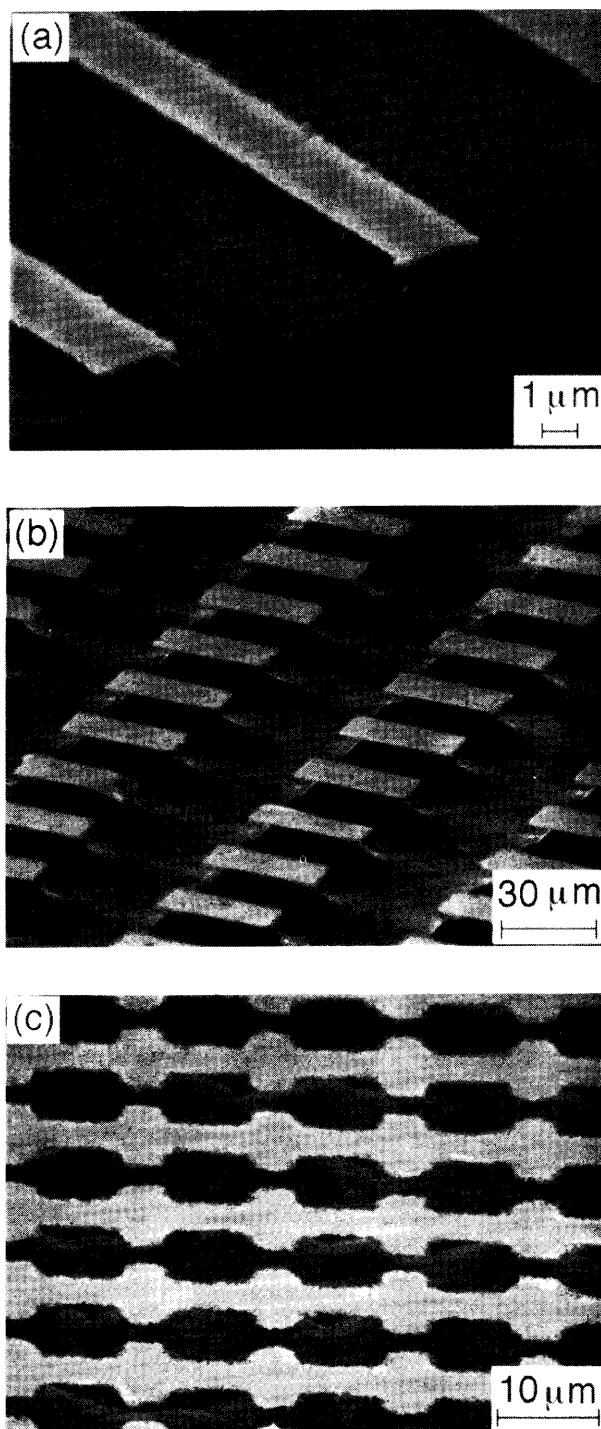


Fig. 3. Characteristics of etched structures of silicon. The mask used here was Au/SAM ($\text{Ti}/\text{Au} = 100/2000 \text{ \AA}$). Silicon was etched using KOH/i-PrOH at 60°C . (a) A view at 60° illustrating undercutting (the sample had been etched for 5 min). (b) The Au/SAM mask remained on the surface even after etching of silicon had undercut more than 40% of the mask. (c) After etching for 2 h. Undercutting resulted in the removal of silicon under the Au/SAM resist, and resulted in microwires suspended in air between silicon pillars.

⁸ Various etching conditions, hydrazine and water, ethylenediamine and water, and various concentrations of KOH at different temperatures, were compatible with the three systems of masks, and we have not examined the effects of different etchants on etched features of silicon.

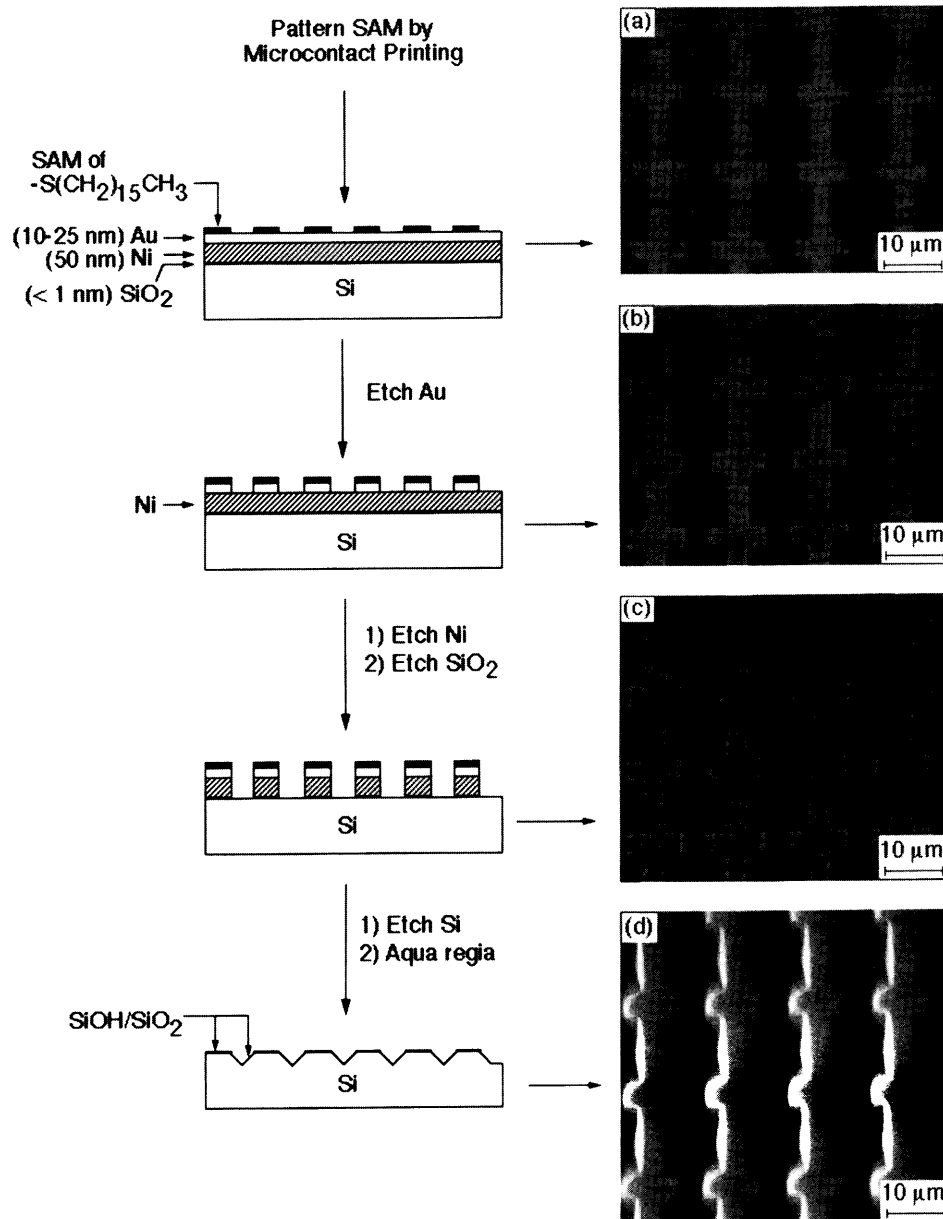


Fig. 4. Etching of silicon with the Ni/Au/SAM resist. (a) A scanning electron micrograph of the pattern of SAM (light region) on gold (dark region). (b) Gold (light) was removed by etching, and nickel (dark) was exposed. (c) Nickel was removed by etching to reveal the underlying silicon (dark). (d) A view of the surface at 30°. The pattern in (c) was used to etch silicon (<100> orientation). The metal mask was removed by aqua regia.

with other metals such as chromium and iron. At its current stage of development, etching of nickel is isotropic: that is, the rates of etching in the horizontal and vertical directions are the same. Undercutting, as much as the thickness of the Ni (50 nm in this case), is expected; consequently, some edge resolution is lost (Fig. 4c). Due to relatively large dimensions (a few micrometers) of features fabricated in silicon, this undercutting did not seem to affect the final overall structures.

Figure 5 shows the structures of silicon fabricated by anisotropic etching of silicon using the Au/SAM and Ni/Au/SAM resists. Once the masks were removed, structures produced in either system were indistinguishable. Figure 5a and b show that a complex text pattern formed by μ CP can be transferred to the gold and nickel layers, and anisotropic etching of silicon transfers the pattern of resists into the silicon substrates. Because the etch-depth is over 10 μ m in Fig. 5b, some fine details are lost; for transferring fine patterns, etching does not proceed to this extent. Figure 5d and e show anisotropic etching of a silicon wafer with the <111> orientation. Silicon wafers with different crystallographic orientation can provide an access to different structures of silicon.

Etching of silicon using Au/SAM/polymer resists.—Both systems of resists based on Au/SAMs and Ni/Au/SAMs

produce the same type of pattern in silicon: that is, the hydrophobic regions of the patterned SAMs, those usually stamped using μ CP, are protected and are not etched; these regions become raised regions in the etched silicon. The hydrophilic regions of the patterned SAM are etched.

In an ideal system of resists, the ability to produce both positive and negative resists are essential. The Au/SAM/polymer resists provide a way of producing etched silicon with the opposite sense (or a negative resist): the hydrophilic regions are protected, and the hydrophobic regions etch, whereas in an Au/SAM system (a positive resist), the hydrophobic regions are protected. In fabricating masks based on the Au/SAM/polymer system, we used the SAMs as templates for introducing another layer in a multilayer resist film, instead of using the SAMs themselves as the masks in an etching step. The new layer added in this system is an organic polymer. We accomplish the selective assembly of the organic material on a patterned gold surface by taking advantage of the differences in interfacial energies of the different regions of patterned SAM.²⁷

We have developed several ways of generating surfaces exposing patterns of different regions of hydrophobic and hydrophilic functional groups.⁸⁻¹¹ Figure 6 illustrates a way of forming such surfaces by μ CP, and the process by which a polymeric mask self-assembles selectively onto hy-

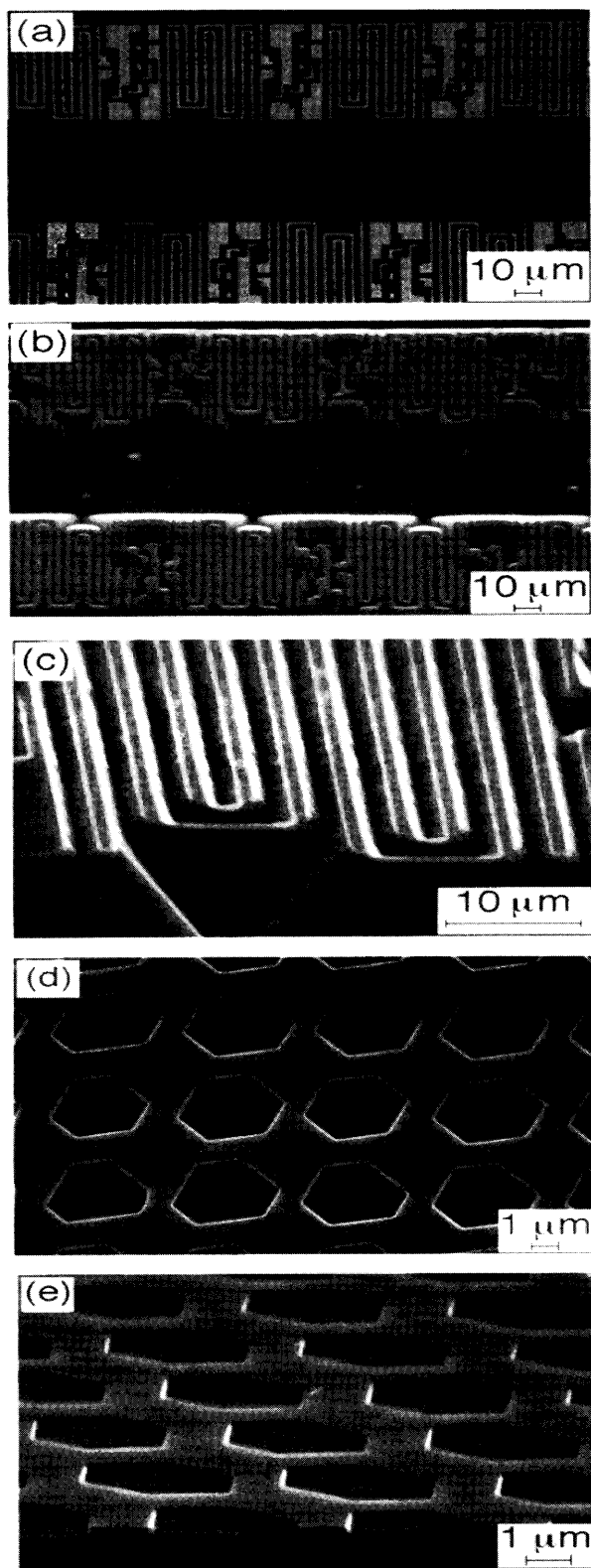


Fig. 5. Various structures of etched silicon. (a) SEM image taken normal to the surface. A test pattern had been printed on Ni/Au using a SAM. Selective etching of regions of the gold and nickel unprotected by the SAM produced the features of Ni/Au (light region) and exposed silicon (dark region). (b) SEM image taken at 15° from the top surface. The Ni/Au pattern in (a) was used as mask for etching of silicon with the $\langle 100 \rangle$ orientation. The mask was removed by aqua regia. (c) The same structure as (b) at a higher magnification. (d) SEM image of an etched pattern taken normal to the surface. An Au/SAM resist was used to control the etching of silicon wafer with the $\langle 111 \rangle$ orientation. The pattern in this figure was generated by stamping two sets of parallel lines on the surface, oriented at 90° from one another. The stamp and pattern are the same as that used in Fig. 2a. Anisotropy in etching produced the quasi hexagonal pits from the square patterns. (e) A fractured view of (d) at 60°.

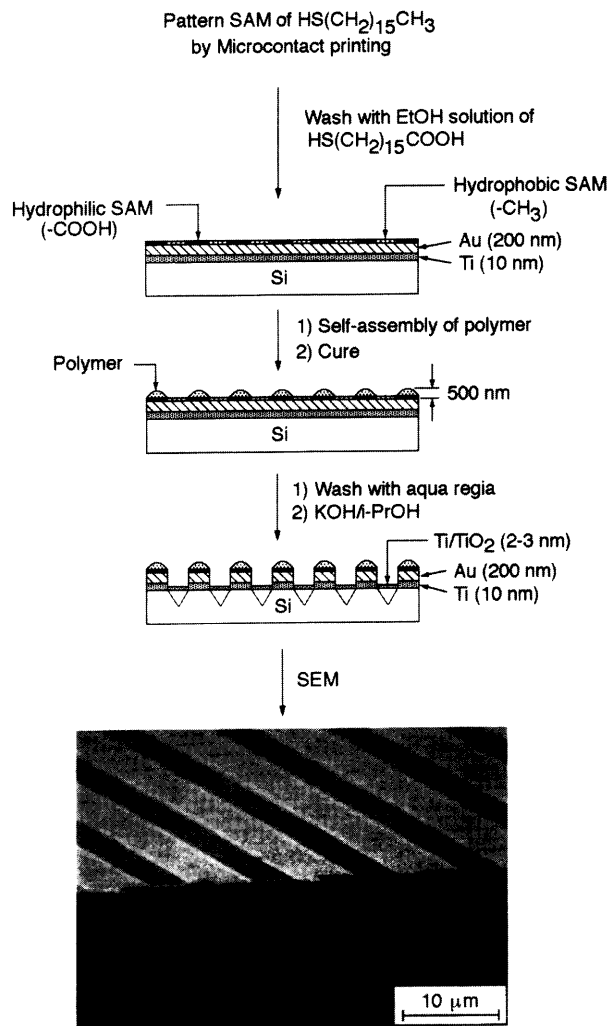


Fig. 6. Etching of silicon with the Au/SAM/polymer resist. The polymer used here is epoxy resin (bisphenol diglycidyl ether and polymericaptan, Devcon), but other polymers can be used, including polyurethane and PMMA. A fractured view at 60° by SEM shows the anisotropic etching of the silicon ($\langle 100 \rangle$ orientation) substrate by KOH/i-PrOH. The SEM photomicrograph shows the trenches that have been etched in the silicon still covered by a very thin membrane of Ti/TiO₂, originally in the adhesion layer.

drophilic regions of the patterned surface. First, we used μ CP to pattern the SAM of hexadecanethiolate that formed a hydrophobic region on the surface. Then a different thiol, HS(CH₂)₁₅COOH, was used to derivatize the rest of the surface, covering these areas with hydrophilic SAMs. When a drop of an organic polymer (most conveniently a prepolymer of polyurethane, NOA 60, Norland) was placed on the surface, the polymer assembled only on the hydrophilic region^b (-COOH) of the surface. In air, a drop of a hydrophobic liquid preferentially wets regions with a higher interfacial free-energy (in this case, the carboxylic acid-terminated regions). After curing thermally or photochemically, the polymeric layer served as a mask to protect both gold and silicon from etching by aqua regia and KOH/i-PrOH, respectively. The SEM image in Fig. 6 shows the result of anisotropic etching of silicon using the Au/SAM/polymer resist. The figure also shows a thin metallic layer (~ 2 -3 nm) that did not dissolve completely in aqua regia; this membrane was sufficiently thin and porous to allow the etchants (KOH and i-PrOH) for silicon to permeate through it. The thickness of this residual metallic film indicates that the layer is titanium/titanium dioxide; etching

^b The polymer can be assembled on the hydrophobic region if carried out under water.

with aqua regia for a longer time can remove the metallic layers completely. If desired, the residual film of Ti/TiO₂ can be removed by washing in either HF or aqua regia.

A significant difference between this system and the other two is that the gold layer can be removed using aqua regia instead of CN⁻/O₂; CN⁻ is not needed to etch gold in this procedure. An SAM does not protect gold from etching in aqua regia, but the relatively thick layer of polymer covering the hydrophilic regions of the SAM does. Because this process can be used with many organic polymers, a resist can be tailored to specific requirements in a pattern-transferring step. This polymer technique also can be extended to the Ni/Au/SAM mask; the top layer of gold can be patterned by μ CP, and the underlying metallic layer can be any metal, including Ni.

A desirable feature of this process is that negative features, that is, features not stamped in the μ CP process, can be produced. A limitation is that certain types of structures are not easily produced using the Au/SAM/polymer resists. In particular, the polymer self-assembles as a liquid, and its shape is the direct result of minimizing the interfacial free-energy.²⁸ Features that have sharp corners, right angles, and angular forms with small dimensions cannot be produced by the procedure described here. The application of this process is best applied to lines and smooth rounded structures.

Conclusion

Three systems of resists, Au/SAM, Ni/Au/SAM, and Au/SAM/polymer, have been used together with μ CP to fabricate structures in silicon. The procedure should be widely applicable to other materials and the Ni/Au/SAM system is an example of the application of the Au/SAM system to patterning and etching nickel. The procedure works routinely on structures with feature sizes of $\geq 1 \mu\text{m}$; smaller features undoubtedly can be fabricated with some development. Photolithography is used only in making the PDMS stamp for μ CP, and since other methods of making small patterned SAMs, especially micromachining⁸ and microwriting,^{9,10} are available, these methods need not use photolithography at all.

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REFERENCES

1. D. P. Clemens, Abstract 159, p. 407, The Electrochemical Society Extended Abstracts, Vol. 73-2, Boston, MA, Oct. 7-11, 1973.
2. C. Raetzl, S. Schild, and H. S. Schlötterer, Abstract 142, p. 336, *ibid.*, Vol. 74-2, New York, NY, Oct. 13-17, 1974.
3. I. Bassou, H. N. Yu, and V. Maniscalco, *This Journal*, **123**, 1729 (1976).
4. J. B. Price, in *Semiconductor Silicon 1973*, H. R. Huff and R. R. Burgess, Editors, p. 339, The Electrochemical Society, Inc., Princeton, NJ (1973).
5. A. I. Stoller, *RCA Rev.*, **31**, 271 (1970).
6. A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.*, **63**, 2002 (1993).
7. A. Kumar, H. A. Biebuyck, and G. M. Whitesides, *Langmuir*, **10**, 1498 (1994).
8. N. L. Abbott, J. P. Flokers, and G. M. Whitesides, *Science*, **257**, 1380 (1992).
9. A. Kumar, H. A. Biebuyck, N. L. Abbott, and G. M. Whitesides, *J. Am. Chem. Soc.*, **114**, 9188 (1992).
10. G. P. Lopez, H. A. Biebuyck, C. D. Frisbie, and G. M. Whitesides, *Science*, **260**, 647 (1993).
11. C. S. Dulcey, J. H. Georger, V. Krauthamer, D. A. Stenger, T. L. Fare, and J. M. Calvert, *Science*, **252**, 551 (1991); G. P. Lopez, H. A. Biebuyck, R. Harter, A. Kumar, and G. M. Whitesides, *J. Am. Chem. Soc.*, **115**, 10774 (1993).
12. J. L. Wilbur, A. Kumar, E. Kim, and G. M. Whitesides, *Adv. Mater.*, **6**, 600 (1994).
13. W. W. Harvey and H. C. Gatos, *This Journal*, **105**, 654 (1958).
14. H. C. Gatos and M. C. Lavine, *ibid.*, **107**, 433 (1960).
15. W. K. Zwickler and S. K. Kurtz, in *Semiconductor Silicon 1973*, H. R. Huff and R. R. Burgess, Editors, p. 315, The Electrochemical Society, Inc., Princeton, NJ (1973).
16. H. A. Waggener and J. V. Dalton, Abstract 237, p. 587, The Electrochemical Society Extended Abstracts, Vol. 72-2, Miami Beach, FL, Oct. 8-13, 1972.
17. R. M. Finne and D. L. Klein, *This Journal*, **114**, 965 (1967).
18. T. R. Payne and H. R. Plumlee, *IEEE J. Solid-State Circuits*, **SC-8**, 71 (1973).
19. F. Restrepo and C. E. Backus, *IEEE Trans. Electron Devices*, **ED-23**, 1195 (1976).
20. C. D. Bain, E. B. Troughton, Y. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, *J. Am. Chem. Soc.*, **111**, 321 (1989).
21. D. A. Dobbs, R. G. Bergman, and K. H. Theopold, *Chem. Eng. News*, **68**(17), 2 (1990).
22. T. Wnuk, *ibid.*, No. 26, p. 2.
23. S. L. Matlow, *ibid.*, No. 30, p. 2.
24. K. Baba, Jpn. Pat. 7,447,225 (1974).
25. E. Desurvire, *Phys. Today*, 20 (Jan. 1994).
26. T. K. Whidden, D. K. Ferry, M. N. Kozicki, E. Kim, A. Kumar, J. Wilbur, and G. M. Whitesides, Submitted.
27. H. A. Biebuyck and G. M. Whitesides, *Langmuir*, In press.
28. For an analysis of the shape of geometrically confined liquid drops, see N. L. Abbott, G. M. Whitesides, L. M. Racz, and J. Szekely, *J. Am. Chem. Soc.*, **116**, 290 (1994).