Defect-Tolerant and Directional Wet-Etch Systems for Using Monolayers as Resists

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We developed strategies based on self-assembly principles to etch substrates patterned with monolayer resists with high selectivity and etch directionality. Our strategies exploit the defined composition and order of these ultrathin resists and overcome their imperfections. Defects in a monolayer can be healed by additives present in an etch bath. Alternatively, large molecules that cannot diffuse through defects can be employed as etchants. It is also possible to taper structures using the competition between etching and the side-growth of a self-assembling etch barrier, nucleating from the originally patterned monolayer. The application of these concepts lets defect-sensitive monolayers become robust and versatile resists, which should promote their acceptance and use in microtechnology.

Lithography is of paramount importance for many technological applications, including the fabrication of microelectronic devices, storage elements, displays, sensors, and microactuators. Often, lithography involves patterning a resist first and using it as a mask to protect the substrate locally during an etch step. Ideally, the etch should only dissolve the parts of the substrate left uncovered with resist. A typical resist for microfabrication is a light-sensitive material spin-coated onto a substrate to form a relatively thick layer and "baked" to eliminate solvents. The material and thickness of the polymer layer can be adjusted to allow uniform film formation and sufficient resistance during the etch process. A self-assembled monolayer (SAM) can be used as a resist but with the profound difference that it is only one molecule thick. Some of these films, obtained for example when a Au substrate is placed in an ethanolic solution of alkanethiols or disulfides, comprise only 10 nanomoles of molecules well ordered into a 2-nm-thick monolayer of 1 cm^2.[1] The ideal SAM-based resist will prevent etchants from dissolving the substrate below, Figure 1A. The order of the alkyl chains of hexadecanethiol SAMs on Au, for example, accounts for the surprising etch resistance this SAM confers to a Au substrate immersed in a bath containing CN^- and O_2.[2] Interestingly, the same monolayer will be highly permeable to iodine in solution and cannot prevent the dissolution of Au by a KI/I_2 etch bath. Obviously, as for all etch systems, the etchant matters. In addition, SAMs are high-resolution resists: the spatially controlled removal or placement of monolayers has been demonstrated using photolithography,[3] electron-beam lithography,[4–6] scanning probe methods,[7] and microcontact printing[8] (μCP) at scales sometimes well below 100 nm.

Figure 1. Etching of substrates patterned with SAMs. (A) The barrier properties of SAMs are determined mainly by their thickness, order, and density. (B) Real SAMs have defects and less-ordered regions, which compromise their resist properties.

In practice, SAMs adsorbed from solution or patterned on a Au substrate are not perfect but have flaws such as molecular defects or domain boundaries.[9] A defect in the SAM (disordered region or missing molecule) may open a path to the substrate for etchants, Figure 1B.[10] The roughness and the presence of contaminants or impurities on the substrate add defects that diminish the etch-barrier properties of monolayers. These problems are responsible for the limited contrast and small process window when monolayers are used as resist and have prevented the widespread use of SAMs as wet-etch barriers despite the unique opportunities they offer.

Here, we devise novel wet-etch systems for employing monolayers as resists based on self-assembly principles. We illustrate these strategies for monolayers patterned

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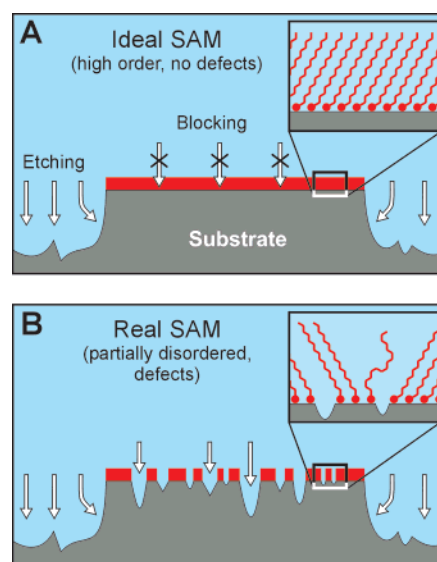(7) Piner, R. D.; Zhu, J.; Xu, F.; Mirkin, C. A. *Science* **1999**, *283*, 661.
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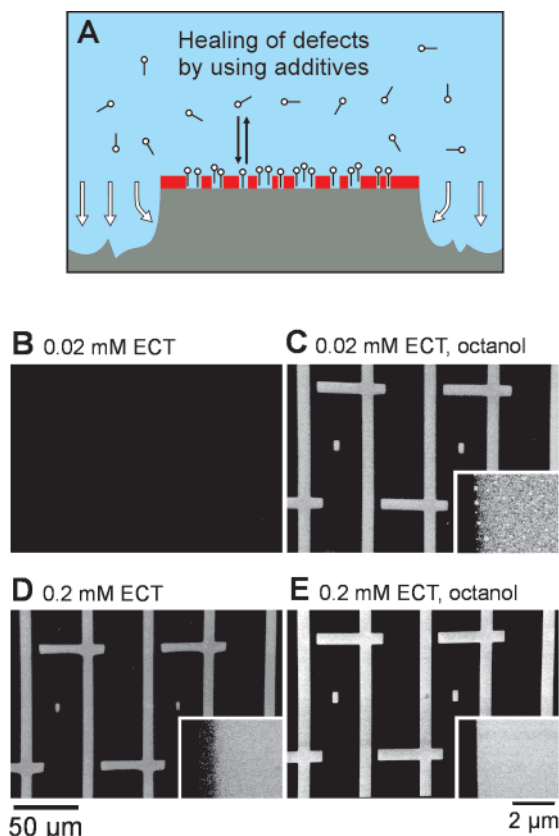(10) Zhao, X.-M.; Wilbur, J. L.; Whitesides, G. M. *Langmuir* **1996**, *12*, 3257.

Figure 2. Etch selectivity of substrates covered with monolayer resists can improve by the addition of defect-healing molecules to the etch bath. (A) Defect-healing additives, such as octanol, have a high affinity for defects in SAMs but not for the bare substrate. (B) Au printed with a poly(dimethylsiloxane) stamp inked with a 0.02 mM solution of ECT in ethanol etched entirely, except when octanol molecules were present in the CN^-/O_2 bath (C) and blocked defects in the incomplete, printed SAM. (D) Printing ECT at 0.2 mM improved the protection of the Au substrate, but this protection was optimal when octanol was present in the etch bath (E). The bright regions in these SEM images correspond to the 15-nm-thick Au film deposited onto 1 nm of Ti on a Si wafer using electron-beam evaporation. Printing and etching in all cases lasted for 3 s and 5 min, respectively.
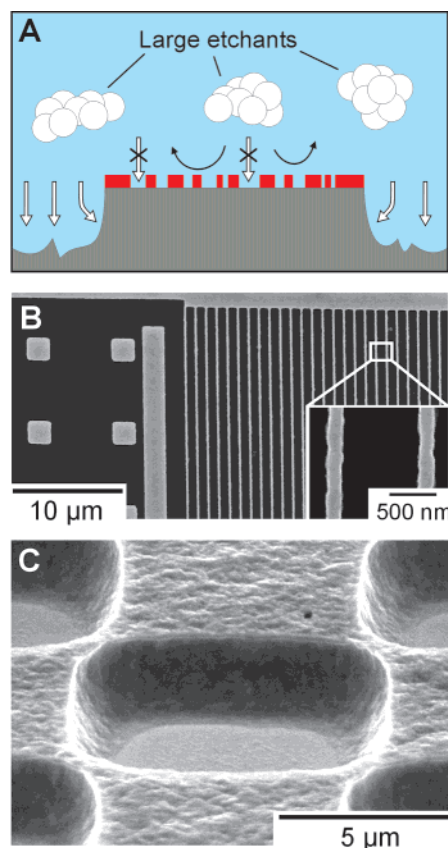
Figure 3. (A) An etch system can be made highly selective if at least one of the molecules necessary to etch the substrate cannot penetrate through defects in the monolayer resist. (B) SEM images of micrometer-sized structures and 170-nm-wide nanowires formed by etching a 100-nm-thick Cu substrate using a bath containing NBSA and large PEI molecules. The NBSA/PEI etch system remains selective even for etching a rough, 2.2-μm-thick, electrodeposited Cu substrate (C). Patterning the monolayer on Cu was done by (i) removing copper oxide present on the surface by a 10-s immersion in HCl (4% in deionized water) and (ii) printing a high-resolution stamp inked for 1 min with a 0.2 mM solution of ECT in ethanol for 30 s (B) or printing a conventional poly(dimethylsiloxane) stamp inked for 1 min with a 0.4 mM solution of ECT in ethanol for 1 min (C).

on substrates using μCP. μCP is remarkably simple and versatile, making it a method of choice for patterning SAMs on surfaces;[11] it uses a micropatterned, elastomeric stamp replicated from a lithographically prepared mold. Typically, the stamp is first inked and dried and then applied to a substrate to form a SAM using molecules from the ink in the printed areas of the substrate.

Our first strategy to achieve high-selectivity etching of substrates covered with monolayer resists relies on "defect-healing" additives in the etch bath. These additives should have the following properties: they should (i) be lipophilic to have an affinity for defects in the monolayer, (ii) insert themselves into or cover defects, (iii) be a priori incapable of self-assembling on Au, and (iv) have poor solubility in the etch bath to favor their "healing state", Figure 2A. Octanol, for example, fulfills these conditions, and the defect-healing capabilities of this compound can be important as suggested by French and Creager.[12] We verified this concept by etching a thin layer of microcontact-printed Au in a CN^-/O_2 etch bath with and without octanol, Figure 2B–E. First, we printed incomplete monolayers of

eicosanethiol (ECT). This sample was then split in half. The Au dissolved entirely when the sample was immersed in the etch bath without octanol, Figure 2B.[13] In contrast, the printed pattern on the other half of the sample was revealed faithfully when the etch bath contained octanol,[13] Figure 2C. Increasing the ink concentration resulted in the formation of a denser monolayer, which protects the Au in the printed areas, except at the periphery of the structures, Figure 2D. The presence of octanol in the etch bath proved remarkably helpful in protecting these regions and allowed the formation of Au patterns with high contrast and accuracy, Figure 2E.[14]

The converse strategy to etch substrates patterned with SAMs is to use etchants incapable of diffusing through defects in the monolayer resist, Figure 3A. We applied this strategy to etch Cu, which was microcontact-printed

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(13) The etch bath contained KCN at a concentration of 0.1 M in a NaOH/KCl buffer at pH 12. 1-Octanol (Fluka) was added to this bath for experiments on the healing of defects as follows: First, 2.0 mL (excess) of octanol was added to 250 mL of the cyanide bath. The mixture was sonicated for 30 min and stored at room temperature for ~12 h to ensure equilibration. The aqueous solution was then separated in a phase-separation funnel and diluted by 2 with a cyanide solution. Half-saturation of the etch bath with octanol was preferred over full saturation to prevent phase separation. All etch solutions were used at 25 °C with moderate stirring.
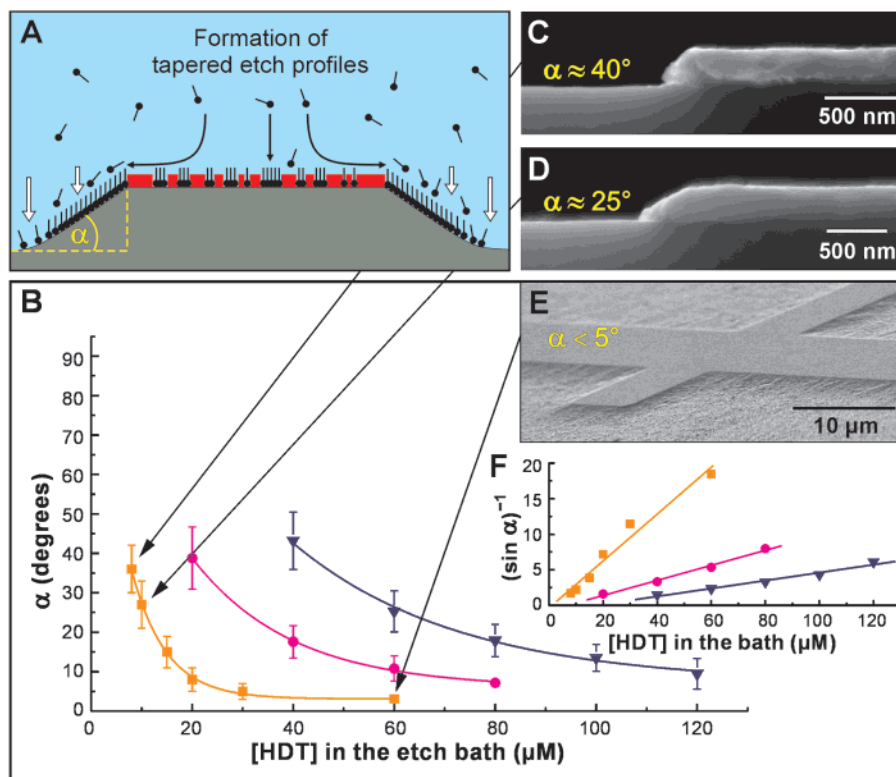
Figure 4. Competition between etching and diffusion of blocking additives can be used to taper structures. (A) A monolayer patterned on a substrate can direct the lateral growth of a resist formed from additives, resulting in a taper angle *a*. (B) The taper depends on the strength of the etch bath and on the concentration of the additives. The data were obtained using a 250-nm-thick Cu film deposited on a Si wafer, which was printed with 0.2 mM solutions of ECT and etched in a CN^-/O_2 bath containing C12E6 (0.2 mM), HDT additives, and NBSA. Concentrations of NBSA of 0 (square), 0.2 mM (circle), and 0.5 mM (triangle) were used to vary the strength of the etch bath. The lines in the graph are guides for the eye. The SEM cross-section images reveal a taper of ~40° (C) and ~25° (D) of Cu patterns formed at the conditions referenced in the diagram. (E) Using a slow bath and a high concentration of HDT, it is possible to form very low tapers, such as the one obtained in the 500-nm-thick Cu layer shown here. (F) The ratio between the spreading of the resist and the rate of etching is equivalent to $(\sin a)^{-1}$, which shows a linear dependency with the concentration of HDT in the bath.

with alkanethiols. Cu is a particularly challenging substrate because alkanethiols form films of lower quality on it than on Au, and native copper oxide interferes with the monolayer self-assembly.[15,16] The technological importance of Cu due to its high conductivity makes it desirable for etching with high resolution and selectivity, however. The etch system developed here contains the sodium salt of 3-nitrobenzenesulfonic acid (NBSA)[17] and a branched polyethylenimine (PEI). The intention was to expose Cu to a strong oxidizer and to solubilize oxidized Cu with a well-complexing agent. PEI forms stable complexes with copper ions via its primary and secondary amino groups, and the large size and branched structure of this polymer should prevent its diffusion through defects in the monolayer resist.

The scanning electron microscopy (SEM) images in Figure 3B,C reveal striking results: The 100-nm-thick Cu structures in Figure 3B were fabricated by microcontact-printing ECT onto Cu and etching it selectively using

NBSA and PEI.[18] The Cu structures have no defects, and 170-nm-wide Cu nanowires as well as large Cu squares could be made simultaneously without adverse dependency of the pattern geometry on the etch selectivity.[19,20] This result could not be achieved using a CN^-/O_2 etch bath or even using a bath with NBSA and complexing agents having a significantly lower molecular weight than PEI, such as ethylenediamine or pentaethylenehexamine. In this example, the complexing agent is the principal determinant of the performance of the etch system.

We probe the limits of this etch system by using a rough and thick Cu substrate, Figure 3C. The roughness of a substrate provides a simple way to manipulate the barrier properties of SAMs:[21] monolayers on rough substrates tend to have lower order than those on smooth substrates, and a rough substrate is challenging to protect well. By use of the NBSA/PEI etch system, a 2.5-nm-thick printed monolayer was sufficient to etch a 2.2-μm-thick and rough electroplated Cu substrate without creating defects in the

(14) Elucidating on the molecular level how octanol contributes to the protection of Au covered with ECT is difficult. The insertion of one or a few octanol molecules in defects in the monolayer is plausible and may occur concurrently with the formation of a film of octanol over the alkanethiol monolayer. Octanol does not seem to form a film on Au alone because even adding a large excess of octanol to the etch bath does not significantly slow the etching of the Au.

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(18) One liter of etch bath was composed of 11.25 g (50 mmol) of 3-nitrobenzenesulfonic acid (sodium salt, Fluka), 225 g of polyethylenimine (average MW $\approx$ 800 g mol^{-1}, branched type, Aldrich), and deionized water. We operated the bath at temperatures ranging from 60 to 80 °C, at a pH of 11.4, and with strong stirring.

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protected regions. This demonstrates an etch selectivity of at least 800, which is not even typical for dry reactive-ion etching systems.[22]

The virtue of the above-described etching systems is their remarkable selectivity, but the etched structures exhibit sidewalls with a geometry typical of an isotropic wet etch. For many technological applications, however, it is desirable to control the etch profile of structures so as to create tapered profiles allowing conformal coverage by overlayers.[23] A tapered structure may be easily formed when anisotropically etching a Si single crystal but requires advanced strategies when applied to metals.[24]

We developed a directional wet-etch system for forming tapered metallic structures based on the competition between isotropic etching of the substrate and the formation of a spreading etch barrier. This etch barrier self-assembles from additives in the bath, first over the patterned regions of the substrate, and then expands laterally toward unprotected regions of the substrate similar to the way phospholipid membranes can form and grow on hydrophilic surfaces.[25] Consequently, zones of the substrate adjacent to the monolayer are blocked first, which results in the formation of etched structures with tilted sidewalls, Figure 4A. We selected hexadecanethiol (HDT) as the additive because it can form etch-protective SAMs on Au, Ag, and Cu, and the lipophilicity of this alkanethiol favors its deposition from aqueous solution onto the hydrophobic regions of microcontact-printed substrates. A homogeneous distribution of HDT in the aqueous solution was ensured by adding a micelle-forming compound (hexaethyleneglycol monododecyl ether [$CH_3-(CH_2)_{11}-(OCH_2CH_2)_6OH$, C12E6] to the bath, which served as a carrier for HDT molecules.[26,27] Tapering Cu lines provides an example of our strategy: the Cu substrate

was first microcontact-printed with ECT and then etched using a CN^-/O_2 bath containing variable amounts of NBSA and HDT to adjust the etch characteristics, Figure 4B. We were able to fabricate Cu microstructures having excellent protection and tapers ranging from ~40° to less than 5°, Figure 4C−E. The geometrical expression of the competition between the spreading of the resist and vertical etching is given by $(\sin a)^{-1}$, which equals the length of the taper sidewall divided by its height. The linear dependence of $(\sin a)^{-1}$ on the concentration of HDT, Figure 4F, helps in predicting the composition of the bath required for a desired taper. The size and geometry of a pattern can influence its efficiency in collecting HDT molecules from the bath, thus also determining the degree of protection and the taper angles that can be obtained.

Self-assembling techniques are very appealing but also inherently difficult to drive to perfection. Even small "errors" such as a molecule missing in a SAM can lead to a catastrophic failure such as poor etch protection of a substrate. As imperfections can have such a profound impact, repairing, healing, or redundancy must be applied to self-assembled systems. We demonstrated the experimental validation of enhancing the resist properties of SAMs by orders of magnitude using self-assembly principles. These results, when combined, suggest the use of self-assembled monolayers as reliable and high-contrast resists for wet-etch processes with the potential to challenge conventional resists in many areas.

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