

Narrow features in metals at the interfaces between different etch resists

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The ability to create structures on length scales below 100 nm easily is a challenging feat. We report here a facile technique for the fabrication of such structures in gold (Au) with feature sizes smaller than 50 nm, utilizing two families of Au etch resists in conjunction. The first resist family consists of self-assembled monolayers (SAMs) of alkane thiols on Au, which provide substantial resistance against cyanide etch solutions. The second class consists of metals deposited on the surface of Au, which also provide similar resistance of the Au film to CN etchants but are not conducive for the formation of SAMs. Selective etching is initiated at the interface between these resists, proceeds into the Au layer, and results in narrow trenches in the Au film. Our protocol allows for the sequential removal of both resists and thus permits the creation of planar Au surfaces with well-defined sub-50-nm etch patterns. © 2003 American Institute of Physics. [DOI: 10.1063/1.1611640]

Nanostructure fabrication on length scales below 100 nm is a challenging goal, especially when it needs to be done in a cheap and scalable fashion.^{1–3} While techniques exist to create such features with remarkable fidelity using scanning microscopy like e-beam writing⁴ or dip-pen lithography,⁵ such techniques are inherently serial and are not amenable for reproduction on large scales. More recent work has concentrated on the development of nontraditional lithographic methods such as imprint and contact lithography as techniques for the formation of smaller features.^{6,7} Recently, active research has been done in utilizing self-assembled monolayers (SAMs), formed from long-chained alkanethiols, as resists on the surfaces of coinage metals.^{8–11} While their high degree of order enables these SAMs to function as highly efficient resists,¹² it has been also suggested to exploit disordered regions in SAMs, at the interface of two topologically patterned coinage metals, to create narrow trenches much below the diffraction limit encountered in optical lithography or the capabilities of the standard microcontact printing with SAM resists.^{13,14} However, this approach, also known as topologically directed etching (TODE), leaves behind a nonplanar metal surface, which is impractical for many applications.

We expand on the idea of using the active edge regions in SAMs and demonstrate the formation of sub-50-nm lines on *planar* surfaces of Au. The key concept here is utilizing not only SAMs, but also non-SAM-forming metals (e.g., Ti) as etch resists. At the interface of these two families of resists, there exists a region of disorder in the SAM, from which the more labile SAM thiols are easily removed and nucleate etch pits. As the region of disorder is present only on the Au side, the corresponding etch lines are narrower than those formed in TODE. Finally, the lack of SAM formation on Ti allows for Ti removal and yields flat Au substrates patterned with trenches.

A schematic outline of the various processing steps in our approach is presented in Fig. 1. The deposition of an Au

layer on a silicon substrate [Fig. 1(a)] is followed by the patterning of a photoresist layer [Fig. 1(b)]. Deposition of a second, SAM-resistant metal (e.g., Ti) [Fig. 1(c)] and liftoff (d) result in the formation of a patterned Au substrate. (e) SAM formation on the exposed Au regions is accomplished by dipping the substrates in a 10 mM HDT solution in ethanol for at least 2 h. Right (magnified view): The disordered SAM region in this approach is expected to be narrower than the disordered SAM region in TODE, as the HDT can only self-assemble on top of the Au surface. (f) Au substrate is etched in cyanide solution with 1 M KOH, 10 mM ferricyanide, 1 mM ferrocyanide, 100 mM sodium thiosulfate. Right (magnified view): As a result of the narrower disordered SAM region, the etched linewidths are thinner in this approach than in the case of the TODE approach. (g) Both etch resists are removed by sequential treatment in a 3% HF solution (30 s) and 10 s oxygen plasma etching. Right (magnified view): The presence of a SAM layer on both metals in TODE prevents the removal of one metal and results in a nonplanar topography.

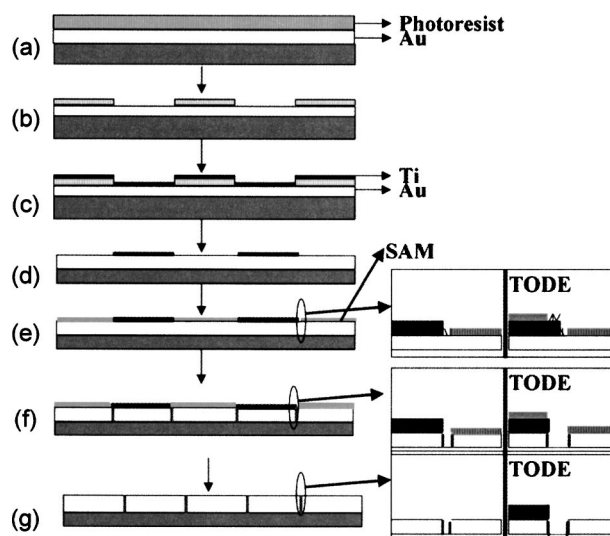


FIG. 1. Schematic presentation of multiresist fabrication strategy. (a) Deposition of Au (20 nm) by e-beam evaporation is followed by spin-coating of Shipley 1805 photoresist (4 K rpm). (b)–(d) Photolithographic patterning (b), Ti deposition (3 nm) (c), and liftoff (d) result in the formation of a patterned Au substrate. (e) SAM formation on the exposed Au regions is accomplished by dipping the substrates in a 10 mM HDT solution in ethanol for at least 2 h. Right (magnified view): The disordered SAM region in this approach is expected to be narrower than the disordered SAM region in TODE, as the HDT can only self-assemble on top of the Au surface. (f) Au substrate is etched in cyanide solution with 1 M KOH, 10 mM ferricyanide, 1 mM ferrocyanide, 100 mM sodium thiosulfate. Right (magnified view): As a result of the narrower disordered SAM region, the etched linewidths are thinner in this approach than in the case of the TODE approach. (g) Both etch resists are removed by sequential treatment in a 3% HF solution (30 s) and 10 s oxygen plasma etching. Right (magnified view): The presence of a SAM layer on both metals in TODE prevents the removal of one metal and results in a nonplanar topography.

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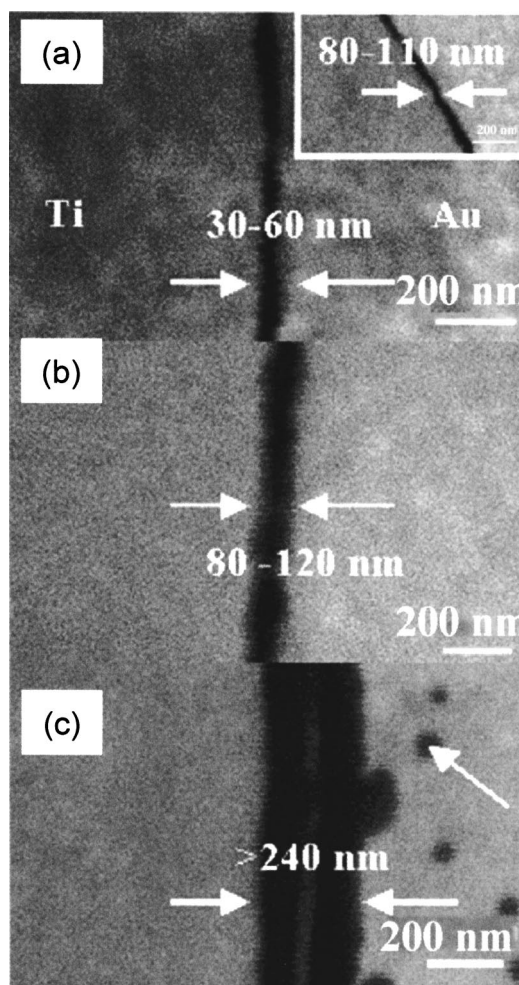


FIG. 2. Line patterns formed at the interface of SAM/Ti systems. (a) Minimum linewidth observed after 6 min in the etching solution is 30–60 nm and is likely limited by the grain size of Au in e-beam-evaporated samples. Inset: Linewidth increases in curved regions as compared with straight edges (~80–110 nm for the same sample) indicating greater disorder at curved areas. (b) Width of etch pattern is controlled by the etching time and is seen to increase to 80–120 nm within 16 min. (c) After etching for 30 min, the linewidth is seen to rise to >240 nm. The formation of pin-hole defects through the SAMs are also seen (indicated by arrows). No visible defects form within the Ti etch resist layer.

1(e)]. As a result, the disordered SAM region in this approach is expected to be narrower than those in the TODE experiments [Fig. 1(e), right]. Subsequent etching of the Au layer is done with a cyanide etch solution, which results in the formation of narrow lines at the interface of the two etch-resistant layers [Fig. 1(f)]. Again, the patterns etched in the surface are expected to be narrower than those seen in TODE [Fig. 1(f), right]. The final step involves the removal of the Ti and the SAM to yield a uniform Au surface patterned with narrow trenches [Fig. 1(g)].

As hypothesized, the patterned Au surface was selectively etched only at the interface between the SAM and the Ti resists. Figures 2(a)–2(c) present scanning electron micrographs (SEMs) of Ti/SAM-covered Au substrates after being treated with the cyanide etchant for different times. The narrowest, trenchlike features, which were reproducibly formed, ranged between 30 and 60 nm in size, and were narrower than the linewidths previously seen using the TODE approach. The trench linewidths were seen to rise either when the patterned regions were curved [inset, Fig. 2(a)] or if the

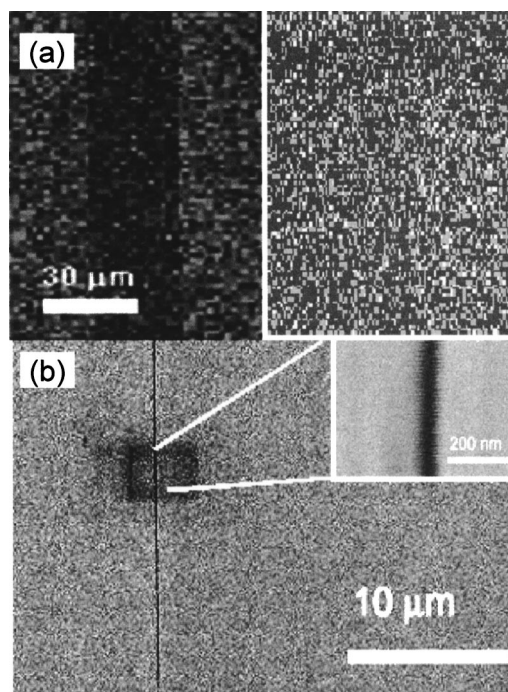


FIG. 3. Evolution of the pattern after the removal of etch resists. (a) Left: EDX map showing distribution of Ti after Au etchant treatment. Photolithographic pattern is reproduced. Right: EDX distribution of Ti after HF treatment (3% HF for 30 s). No Ti presence detected. (b) SEM images of substrate after removal of Ti layer and SAM layer shows a homogeneous surface profile. Inset: Linewidth of etch pattern (~60 nm) is not affected by the HF and plasma treatment.

etching times were increased [Figs. 2(b) and 2(c)]. Using different etch times, we were able to tune the linewidths in Au between 30 and >240 nm (long etch times). At very long etch times [Fig. 2(c)], however, defects were seen to form in the SAM etch resist, and the Au surface was pitted (shown with arrows) at locations away from the interface as well. These results indicate that our approach utilizing two different types of etch resists in conjunction makes it possible to create features in Au far narrower than previously possible.

Another advantage of the proposed method is our ability to subsequently remove the Ti and SAM etch resist layers. Figure 3(a) shows energy dispersive x-ray (EDX) images of substrates before (left) and after (right) HF treatment. The initial Ti maps corresponds quite well with SEM images and optical micrographs of the photolithographically patterned substrates. Post-HF treatment, however, no Ti signal is evident from the samples, indicating removal of this resist layer. Lastly, exposure of the substrate to reactive ion etching (oxygen plasma) effects the removal of the SAM resist layer as well. No noticeable degradation in the etch lines is seen during the course of these two steps [Fig. 3(b)]. A rise in the film resistivity indicates that these trenches extend through the entire Au film to the underlying substrate.

Our approach provides a facile route to the creation of narrow trenches in the surfaces of Au films, whose linewidths are easily tuned by varying the etching times in Au etchants. The narrow linewidths result from two distinct characteristics of the chosen resists. The variance in linewidth is in accordance with the expected grain size distribution of Au in an e-beam-deposited sample. It should be possible, therefore, to obtain even narrower linewidths using this

approach with metals that have smaller grain size (for example silver).^{14,15} Moreover, this approach can be extended to generate patterns in noncoinage metals like palladium (Pd) that are compatible with complementary metal–oxide–semiconductor processing. As Pd has an enhanced affinity towards thiols, no differential etch resistance is evident between SAMs of different chain lengths.^{16,17} As a result, previous TODE-based strategies could not be adapted to form narrow trenches. Here, however, as the etch selectivity proceeds from different families of etch resists, it should be possible to create narrow trenches in Pd as well. Current research efforts are exploring this possibility.

An additional strength of this approach results from the chemically distinct nature of the two etch resists. First, we exploit the selective reactivity of Ti towards HF to effect the removal of the Ti layer without disrupting the underlying Au film. Next, as small organic molecules are easily removed from Au surfaces by oxidative ion etching, we are able to sequentially remove both types of etchants and obtain topographically and chemically uniform Au films, unlike previous works [shown schematically in Fig. 1(g), right]. The films developed in this work are being evaluated in the formation of narrow channel length transistors and other applications where a flat surface is critical.

In conclusion, an approach exploiting disordered SAMs to direct chemical etching is presented here. The use of different sets of resists, as opposed to the *same* resist with different substrate-induced ordering patterns, enables the formation of features that are narrower than previously

reported. More generally, this approach represents another example in using chemical etching and optical lithography together in a bottom-up fashion. Such hierarchical patterning permits the creation of long-range patterns using optical lithography, while nanoscale patterning is controlled by chemical etching techniques.

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