Strategies for Etching Microcontact-printed Metal Substrates

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Microcontact printing (μCP)[1] is a novel, convenient, simple and inexpensive lithographic technique that is enjoying rapidly growing interest and causing a good deal of excitement in today's scientific and technological research. This technique uses micropatterned, elastomeric stamps which are first inked, then dried, and finally placed on a substrate to localize a chemical reaction between molecules from the ink and the substrate. The capability of μCP to replicate accurate patterns was first demonstrated by printing alkanethiols on gold. This particular ink/substrate system still represents probably the best-explored variant of μCP because thiols react rapidly with gold and the alkyl chains of the molecules self-assemble into a well-ordered, dense monolayer.
Although these films usually have a thickness of only 1-3 nm, they can constitute a very efficient barrier to protect their substrate against etchants from solution due to their order and density.[2] Like for conventional lithography, an etch step is necessary to transfer the printed pattern into the underlying substrate. In practice, etching printed substrates with high selectivity and accuracy is very challenging and easily leads to disastrous results when printed SAMs provide the resist: a single molecular defect in a SAM can open a path to the substrate for etchants and it is not possible to form ideal monolayers by printing. So far, all conventional etch systems, such as an alkaline solution with dissolved CN^-/O_2 that has been widely used to etch microcontact-printed Au, Ag and Cu, have not shown sufficient selectivity.

For this reason we developed a set of strategies to etch microcontact-printed metal substrates with very high selectivity and, additionally, with control of the etch profile.

One strategy is based on having additives in the etch bath. These additives have a high affinity for the printed monolayer resist and can "heal" defects in this monolayer, thus preventing etching in these regions of the substrate. This effect was demonstrated by etching a thin layer of microcontact-printed Au with and without a surfactant in the CN^-/O_2 etch bath. In the most spectacular case, a printed monolayer, which was not a good resist for its Au substrate, provided excellent protection when a few microliters of a surfactant have been added to the etch bath.

An alternative strategy is to increase the size of the etchants to tolerate certain defect levels in the printed monolayer pattern. This can be achieved for example by etching printed Cu with an oxidizer and a large complexing polymer. This approach is promising because it enables for the first time microcontact-printed Cu to be etched with high resolution and contrast and, additionally, it enables several micrometers of microcontact-printed Cu to be etched with excellent selectivity.

The third strategy involves additives in the etch bath to etch microcontact-printed patterns with high selectivity and with control of the etch profile. This strategy is of particular interest because (i) patterning thick metal deposits is always compromised by an underetch, and (ii) some applications require tapered structures or structures with well-defined profiles. The latter strategy relies on the competition between etching and the continuous lateral propagation from the printed area of a blocking film of additives: the printed monolayer serves as a template to collect the additives from the bath and direct their growth over the rest of the substrate. Here, the ratio between the etch rate and the growth of the additional layer mainly determines the degree of protection and the angle of the taper that can be obtained. Interestingly, the formation of tapers depends also on the size and the geometry of the printed patterns.

These selective etching strategies expand the possibilities of microcontact printing to the multiple printing and etching of substrates to form complex structures.

References

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