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Negative Resist Monolayers of Thiols as Templates for Metal Electrodeposition

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Charge transfer and adhesion are two interfacial properties which can be conveniently controlled by self-assembled monolayers (SAMs). While patterned electrodeposition via selective passivation of electrodes by thiol SAMs is well established (1-3), the step beyond, lift off and transfer of patterns to other substrates by harnessing the poor adhesion of deposits to SAM modified surfaces (see Fig. 1), has been studied much less (4-7). However, it is only the combination of both deposition and lift off which would allow making full use of the metal patterns as electrodes or in hybrid materials such as metamaterials.

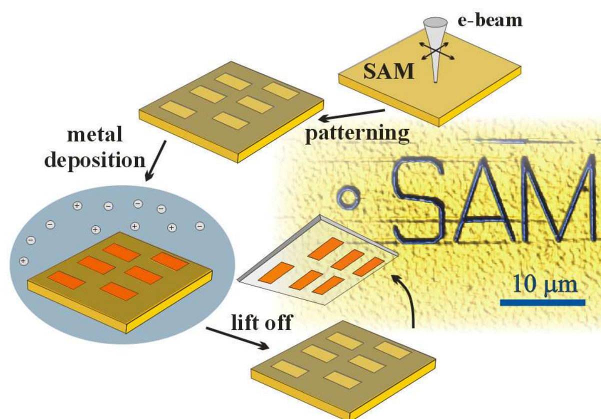

Figure 1: Scheme of SAM templated deposition and lift off of electrodeposited metal structures. Background image shows AFM micrograph of Cu deposited on an e-beam patterned SAM with letters as electrochemically passive areas.

On the micrometer scale the scheme depicted in Fig. 1 is most easily realised by SAM patterns defined by two types of molecules which differ in their ability to electrochemically passivate an electrode (8). Achieving electrochemical contrast by e-beam patterning of a SAM consisting of only one type of molecule is a promising approach to extend the scheme to the nanoscale. Aromatic SAMs are the systems of choice for this purpose as they exhibit negative resist properties (2) and, thus, compared to aliphatic SAMs, allow for a better control of charge transfer and adhesion properties. The mechanism relies on a selective passivation by e-beam induced cross-linking of the molecules which eliminates defects acting as nucleation sites in the electrodeposition process. However, implementing the scheme using e-beam modified SAMs requires a detailed understanding of the mutual influence of the parameters involved in the patterning, deposition and lift off process. The issue is illustrated by the relationship between patterning and deposition parameters which is of vital importance for quality of the electrodeposited structure. As demonstrated in Fig. 2 the contour of the deposited metal is strongly dependent on both the deposition parameters and the extent of cross-linking. With regard to the former employing different potentials for nucleation and growth drastically improves the pattern contrast as seen from Fig. 2a. The influence of the degree of cross-linking is inferred from Fig. 2b which shows a pronounced improvement in contrast with increasing dose.

Another crucial point in the process is the fidelity at which the structure can be lifted off. In the experiments epoxy glue was used to separate the deposit from the substrate and there was no observable difference in the quality of the pattern as deposited and after adhesion to the glue and subsequent lift off. The corrugation of the line seen in Fig. 2c is exactly the same as before the lift off which demonstrates that the challenge in further increasing the resolution of the process is not the lift off process but lies in the control of the deposition process. To further reduce the feature size from currently 50-100 nm, improving the nucleation process is a key issue. At present the precision of the deposition process is limited by the statistical nature of the defects where nucleation occurs. It is anticipated that controlling their position and size will enable another decisive advancement in resolution.

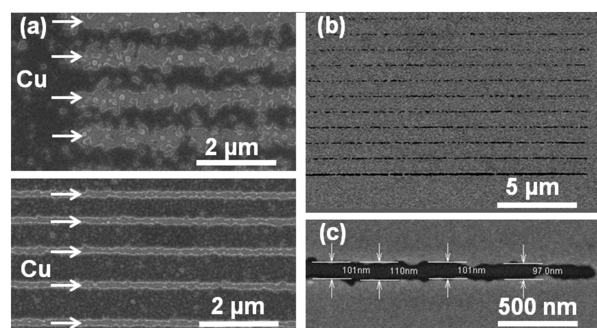

Figure 2: (a) Influence of deposition parameters on contour definition. Cu deposition at potentials of -0.5 V (vs Cu^{2+}/Cu) for 15 s (top) and –0.7 V for 1 s followed by 10 s at -0.35 V (bottom). Arrows mark e-beam written lines (b) Influence of e-beam dose on deposition contrast. Dose decreases in steps of 25 mC/cm^2 starting at 1000 mC/cm^2 for the bottom line. c) Magnified image of SAM templated Cu deposition. The passivating line was written at a dose of 750 mC/cm^2. SEM images show deposition before (a) and after (b,c) lift off.

Acknowledgements
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