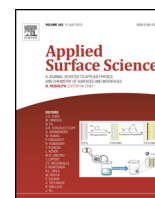




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Electrodeposition of gold templated by patterned thiol monolayers

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ABSTRACT

The electrochemical deposition of Au onto Au substrates modified by self-assembled monolayers (SAMs) was studied by linear sweep voltammetry (LSV), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Patterned SAMs exhibiting electrochemical contrast were prepared by two different methods. One used microcontact printing (μ CP) to generate a binary SAM of ω -(4'-methylbiphenyl-4-yl)-propane thiol ($\text{CH}_3\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_3\text{-SH}$, MBP3) and octadecane thiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$, ODT). Templated by the SAM, a gold microelectrode structure was electrodeposited featuring a line 15 μm wide and 3 mm long. After transfer to an epoxy substrate the structure proved to be electrically conductive across the full length. The other patterning method applied electron beam lithography (EBL) where electrochemical contrast was achieved by crosslinking molecules in a single component SAM of MBP3. An electron dose above 250 mC/cm^2 results in a high deposition contrast. The choice of parameters for the deposition/lift-off process is found to be more critical for Au compared to Cu studied previously. The origin of the differences and implications for nanoscale patterning are discussed.

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1. Introduction

The optical and electrical properties of metallic micro- and nanostructures are of interest for a wide range of applications which comprise plasmonics and metamaterials [1–4], energy conversion [5], displays [6], and sensing [7–13]. Besides their technical specification, one important criterion influencing their technological implementation is the effort required to generate such structures and in search for viable routes a widely adopted strategy is based on templating. One variant of this approach is the use of masks such as colloidal layers [10] which are single-use but easy to fabricate by exploiting self-assembly. The self-assembly process allows the generation of the metal structure directly on the substrate of choice, although it limits the templating to periodic patterns and imposes constraints with respect to the accessible geometries and dimensions. Freely definable patterns are accessible using templates which are generated by conventional lithography. However, the effort required to generate them represents a bottleneck and might even become prohibitive for the routine generation of small scaled structures. A solution to this dilemma is the templated deposition using a reusable master

pattern followed by a transfer of the structure to another substrate [14–18]. Patterning can either be achieved by a topographic pattern [16,19] or by a selective deposition onto a flat substrate. The latter is exploited in a scheme where a self-assembled monolayer (SAM) controls the electrodeposition of metal as illustrated in Fig. 1 [17,20]. An electrode is modified by a patterned SAM which defines electrochemically active and passive areas (1) in the sense that the onset of deposition is at a more negative potential in the passive compared to the active areas as indicated by schematic linear sweep voltammograms (LSV) in Fig. 1. Selective deposition (2) is achieved by setting the deposition potential E_D to a value which is between the onsets of the deposition in the active and passive areas. As illustrated by the cartoon showing a cross-section of a deposit in an active area, there are point contacts between the deposited metal and the substrate. They are located at defects in the SAM at which the deposition starts. After the initial stage where the metal nucleates at the substrate it grows beyond the SAM in a mushroom like fashion until a closed layer is formed. The decisive point is that the area of direct contact between the deposited metal and the substrate metal is very small compared to the area between the deposited metal and the SAM. Since the adhesion energy associated with the metal–organic interface is low the structure can be lifted off by breaking the necks of the deposit [21]. This is accomplished by attaching another substrate (3) which adheres well to the metal deposit but poorly to the blocking SAM. Using mechanical force the secondary substrate with the pattern is separated from the master electrode (4) which might then be reused (5).

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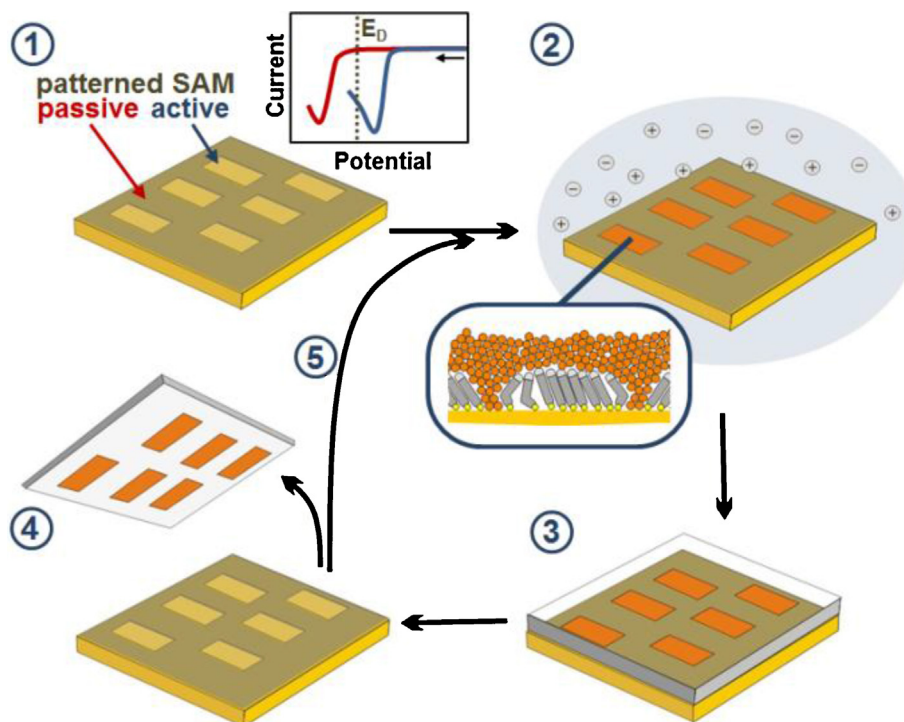


Fig. 1. Scheme to generate metal structures by SAM templated electrodeposition (1, 2), transfer to another substrate (3, 4) and reuse of the original template (5). The difference between the electrochemically active and passive areas is illustrated by the LSVs in (1). A model of the metal deposited on the SAM modified electrode is shown in (2). For details see text.

Since the contrast between blocking and non-blocking areas is determined by differences in the defects, selective deposition can be accomplished in two ways. One strategy is based on a binary SAM of thiols where the pattern is defined by two different types of molecules which differ in their ability to block electrodeposition such as a long chain aliphatic thiol (blocking) and a shorter aromatic thiol (non-blocking) [20]. The other one uses chemical modification of a single component SAM for which different strategies are available. One option is the fragmentation of a SAM molecule which can be done in a well defined way by e.g. photolytic cleavage [22] or less selectively by electrons [23] to alter the thickness and/or structure of the SAM and, thus, its ability to block electrodeposition. A complementary possibility exploiting the opposite effect is the electron induced crosslinking of molecules which occurs in aromatic SAMs [24–26]. The crosslinking eliminates defects or at least reduces them in size to the extent that a sufficient electrochemical contrast compared to the non-irradiated areas is established [17,27–29]. Notably, employing this negative resist behaviour of aromatic molecules offers the advantage that the deposition occurs on the native layer, i.e., deposition behaviour and adhesion are defined by the intact SAM molecules. This contrasts thiols comprising aliphatic chains which exhibit positive resist behaviour [23,30] by undergoing fragmentation, thus, making the control of properties more difficult. For larger scale patterns the binary SAM seems a good choice as patterns can be easily generated by microcontact printing (μ CP) [31]. Crosslinking molecules in a single component SAM is the choice for the nanoscale as the high resolution of electron beam lithography can be harnessed [17,32].

So far defect mediated metal electrodeposition on SAM modified electrodes has mostly been applied to Cu [17,20–23,27–30,33–43] whereas other metals such as Au [44–48], Ag [40,49–54], Ru [55], Ni [35,56], Co [27,57] or a magnetic CoNiFe alloy [14] have been studied more sporadically. Even narrower is the range of metals for the combination of electrodeposition with the lift-off and transfer where with the exception of the CoNiFe alloy [14] only Cu has been

studied [17,20,21]. While Cu is of interest for its electrical properties, other metals such as Au and Ag are preferred for optical applications. As part of our efforts to widen the knowledge base and the scope of the deposition/lift-off scheme we studied the Au deposition on both binary SAMs and e-beam patterned SAMs. From evaporation experiments it is well known that the propensity to penetrate a SAM depends on the type of metal as well as the structure and terminal group of the molecular layer [58–60]. Therefore, it was of interest to see to what extent differences between metals exist.

Applying μ CP the generation of electrodes with one dimension in the micrometre range and a large length to width ratio was studied which was motivated by a simple access to inert microelectrodes suitable for electroanalysis [61]. In this case the challenge was the uniform deposition over millimetre distances to yield conducting wires. The experiments using e-beam lithography is motivated by its high spatial resolution and, thus, its possibility to generate Au nanostructures.

The type of thiols used in this study has been successfully applied to the deposition of Cu and Co in the past [20,27–29]. For the binary SAM, octadecane thiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$, ODT) and 3-(4'-methylbiphenyl-4-yl)-propane-1-thiol ($\text{CH}_3\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{SH}$, MBP3) served to define electrochemically passive and active areas. MBP3 is a representative of a class of thiols which combine a short aliphatic chain with an aromatic moiety, a molecular architecture which has been shown to yield high quality monolayers [62,63]. Furthermore, the aromatic moiety accounts for a negative resist behaviour upon irradiation with low energy electrons [29,64], thus, making it suitable for high resolution patterning.

2. Experimental

2.1. Fabrication of PDMS stamp

The PDMS stamp used for making the two component SAM by μ CP was fabricated by moulding a silicon/SU8 master pattern.

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