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Communication

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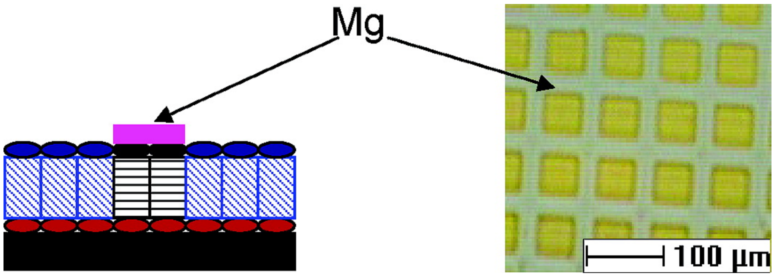

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Toward Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces

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Understanding and controlling the interaction of metals with organic thin films is critical to many technological applications, including polymer light emitting diodes (PLEDs)[1] and organic/molecular electronics.[2−7] Although a number of approaches have been developed to assemble simple organic/molecular electronic devices,[4,5,8] it remains difficult to incorporate these structures into complex circuits. Furthermore, device-to-device performance variations have been observed which stem from the structural integrity of the molecular monolayer, contaminants, and the quality of the metallic contacts.[9]

In this paper, we demonstrate a simple and robust method to construct stable metallic structures on functionalized self-assembled monolayer (SAM) surfaces, which could potentially be used as interconnects in molecular electronic devices. Our approach is to employ UV-photopatterning and the reaction of deposited metals with self-assembled monolayers (SAMs). UV-photopatterned SAMs are ideal tools for the construction of nano- and microscale structures since their surface chemistry can be easily tuned to provide the needed features. The process is shown schematically in Figure 1.

First, an image in one SAM is created using UV light shone through a mask (UV-photopatterning) and a second SAM adsorbed in the areas where the first SAM has been removed. Physical vapor deposition (PVD) or chemical vapor deposition (CVD) is then employed to deposit metal atoms on the SAM surface. By using SAMs with different terminal groups, we can control where and how metals deposit on the construct. Additional patterning/metal deposition cycles can then be used to assemble devices in layers, forming complex circuits. *This technology is, therefore, compatible with current optical photolithography technology and so provides a method by which to provide both nanoscale alignment and overlay capabilities*.

The method was demonstrated using SAMs of long-chain alkanethiols, $HS(CH_2)_xA$, where $x = 10$ or 11, and the terminal group A is one of $-COOH$ or $-CH_3$ adsorbed on Au(111). Well-ordered $-COOH$-terminated SAMs (SAM#1) were prepared on Au surfaces using standard procedures.[10] To UV-photopattern the SAM#1 surface, a mask (a copper TEM grid, Electron Microscopy Inc., Fort Washington, PA) was placed on the $-COOH$-terminated SAM. This construct was then placed under a 500 W Hg arc lamp fitted with a dichroic mirror and a narrow band-pass UV filter (280−400 nm) (Thermal Oriel, Spectra Physics Inc., Stratford CT), for 1 h. In areas of the SAM exposed to UV light, the thiolate group, $-S$, reacts to form a sulfonate group, $-SO_3^-$, which does not stick to the Au surface.[11,12] After UV-photopatterning, the SAM#1 substrate was immersed into a 1 mM solution of a $-CH_3$-terminated alkanethiol in absolute ethanol for 5−10 min. In the areas exposed to UV light, the $-CH_3$-terminated SAM displaces the photoreacted SAM#1, resulting in a patterned $-COOH/-CH_3$ SAM surface.

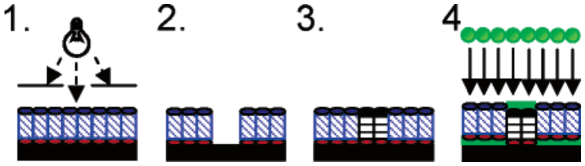

Figure 1. The four stages of the proposed selective metal deposition process. The process involves the photopatterning of a SAM (SAM#1) (step 1) and the removal of the photoreacted SAM molecules (step 2). A second SAM (SAM#2) is adsorbed on the surface (step 3). Finally, metal atoms are deposited, forming a metal overlayer on top of the second SAM (step 4) and penetrating through SAM#1 to the Au substrate. In the case of chemical vapor deposition, deposited metal only reacts with SAM#2 and does not penetrate through SAM#1.

Prior to UV-photopatterning and metal deposition, the SAMs were characterized by single wavelength ellipsometry and time-of-flight secondary ion mass spectrometry (TOF SIMS) to ensure that they were well-ordered and had no significant chemical contamination. Samples were also analyzed using TOF SIMS after UV-photopatterning and metal deposition. All mass spectra and images were obtained using a TOF SIMS IV (ION TOF, Inc., Chestnut Ridge, NY) equipped with a Au_n^+ liquid metal ion gun. Briefly, the instrument consists of a load lock, a preparation chamber, and an analysis chamber. The preparation and analysis chambers are kept at less than 5×10^{-9} mbar to prevent sample contamination. For analysis, an Au^+ primary ion beam was employed at a kinetic energy of 25 keV. The primary ion dose during acquisition was less that 1×10^{10} ions cm^{-2}. The secondary ions generated were extracted into a time-of-flight mass spectrometer and reaccelerated to 10 keV before reaching the detector.

We have employed physical vapor deposition (PVD) for the metal deposition. To selectively deposit at the SAM/vacuum surface, the deposited metal must penetrate through one of the SAMs to the Au/S interface while reacting with the terminal group and accumulating on top of the other SAM. This produces a thin metal interconnect atop the SAM, in the shape of the original pattern.

To demonstrate the process, we have vapor-deposited magnesium on $-COOH/CH_3$-patterned SAM surfaces. We have recently shown that vapor-deposited magnesium reacts with $-OH$,[13] $-COOH$,[13] and $-OCH_3$ [13,14] terminal groups of alkanethiolates to form Mg−O−R species (where R = methylene chain of the SAM). In the TOF SIMS mass spectra, this is indicated by the formation of $MgO^{\pm}$, $MgOH^-$, and $MgO_x(CH_2)_y^{\pm}$ ions. In contrast, for $-CH_3$-terminated SAMs,[13] in the TOF SIMS spectra, we observe the formation of $Au_xMg_yS_z^-$, $MgSH_x^+$, and $MgS(CH_2)_y^+$ ions, indicating that deposited Mg does not react with the methyl terminal group but penetrates to the Au/S interface. Figure 2 displays a $-COOH/-CH_3$ terminal group patterned surface after the deposition of 80 Å Mg *over the whole surface*. It can clearly be seen that Mg reacts with the $-COOH$-terminated SAM to form a metal−organic complex, most likely a carboxylate MgOO−R (R is the methylene

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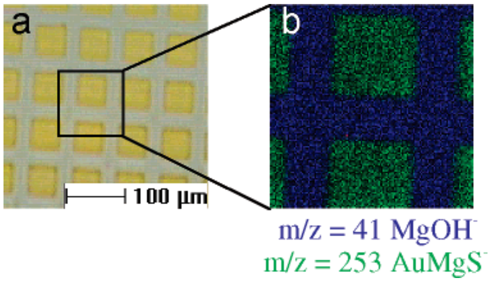

Figure 2. (a) Optical image and (b) negative ion mass spectrum image (area = 100 × 100 μm^2; 256 × 256 pixels) of a $-COOH/-CH_3$-patterned SAM after deposition of 80 Å Mg. Deposited Mg reacts with the $-COOH$-terminated SAM to form a metal−organic complex, indicated by the observation of $MgOH^-$ ions. Mg penetrates through the $-CH_3$-terminated SAM to the Au/S interface, as indicated by the formation of $AuMgS^-$ ions. Mass spectrum image: primary ion Au^+; kinetic ion energy = 25 keV.

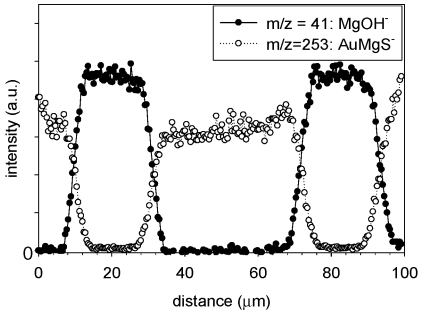

Figure 3. The signal intensities of $m/z = 41$ ($MgOH^-$) (black dots) and 253 ($AuMgS^-$) as a function of distance across the sample for the mass spectrometric image shown in Figure 2.

chain) and then accumulates on top of the SAM, turning these areas a pink−brown color (Figure 2a). We also display a negative ion TOF SIMS image, showing that Mg reacts with the terminal group of the $-COOH$ SAM (Figure 2b; $MgOH^-$ ions colored blue) and penetrates through the $-CH_3$-terminated SAM (Figure 2b; $AuMgS^-$ ions colored green). The vapor-deposited Mg structure is conformal to the underlying $-COOH/-CH_3$-patterned SAM. The lateral resolution of the profile is 2.7 ± 0.5 μm (defined as the distance corresponding to ion intensity levels of 84 and 16%), which is the same as the lateral resolution of the UV-photopatterned SAM surface (Figure 3). We note that the lateral resolution of the photopatterned SAM is determined by the optical lithographic process used. Features as small as 80 nm have been reported using optical lithography.[15]

This approach is generally applicable to a wide variety of metals and deposition processes and can be used with technologically relevant substrates, such as GaAs. There are several other metal/monolayer systems that have the required properties for PVD. We have recently investigated the interaction of vapor-deposited zinc with $-COOH$- and $-CH_3$-terminated alkanethiolates and observed that Zn reacts with the $-COOH$ terminal group but penetrates through the $-CH_3$-terminated SAMs.[13] Vapor-deposited Al and Cu both penetrate through a $-CH_3$-terminated SAM to the Au/S interface and react with the $-COOH$-terminated SAM to form a metallic overlayer.[16−18] Other systems with the desired properties are Al, Cu, and Ag deposited on $-CH_3$- and $-OCH_3$-terminated SAMs.[10,16,18] These metal atoms penetrate through both SAMs and also interact with the terminal methoxy group to form an overlayer. Chemical vapor deposition (CVD) can also be used to selectively deposit metals on patterned substrates. Mittler et al. observed that for Al deposition the CVD precursor reacts with $-OH$- and $-COOH$-terminated SAMs, but not with a $-CH_3$-terminated SAM.[19] They also observed that for Au deposition the CVD precursor reacted only with a $-S$-terminated alkanethiol, and not with an $-OH$- or $-CH_3$-terminated SAM.[20,21] CVD will deposit a metal overlayer without metal penetration through the film and may be preferable in certain applications.

In summary, we have demonstrated a simple, reliable, widely applicable method to construct metallic structures on functionalized self-assembled monolayer (SAM) surfaces by exploiting UV-photopatterning and the reaction of deposited metals with SAMs. This approach enables the development of new ways to create molecular electronic devices, sensors, and other nanotechnological devices. It has important advantages over previous methods since it affords precise nanoscale placement, is parallelizable, and is extensible to many different metals, semiconductors, and organic molecules.

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Supporting Information Available: High-resolution TOF SIMS mass spectra and mass spectral images of patterned surfaces (with and without metal deposition). This material is available free of charge via the Internet at http://pubs.acs.org.

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