

Supporting Information: “Towards Molecular Electronic Circuitry: Selective Deposition of Metals on Patterned Self-Assembled Monolayer Surfaces”
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1. Preparation of Self-Assembled Monolayers

Approximately 5 nm Cr and 100 nm Au were sequentially thermally deposited onto clean Si(001) native oxide covered wafers. Self-assembly of well-organized alkanethiolate monolayers was achieved by immersing the Au substrates into ~1 millimolar solutions of the relevant alkanethiol molecule in absolute ethanol for ~2 days at ambient temperature. The monolayer films were characterized with single wavelength ellipsometry, contact angle measurements and TOF SIMS to ensure that they were densely packed with clean surfaces prior to UV photopatterning and metal deposition.

2. Physical Vapor Deposition

Magnesium was deposited onto the sample at room temperature from a W-wire basket source at a rate of $\sim 0.2 \text{ atoms}\cdot\text{nm}^{-2}\cdot\text{s}^{-1}$ with the pressure below 5×10^{-8} mbar. The sample-vapor source distance was approximately 50 cm ensuring that the SAM surface was not heated during deposition. After deposition, the preparation chamber pressure was allowed to recover its base value before sample transfer to the analysis chamber. The deposited mass/area was monitored using a Maxtek, Inc. TM-400 quartz crystal microbalance (QCM) controller with a maximum error within $\pm 8 \%$.

3. High-Resolution TOF SIMS Mass Spectra a UV-photopatterned SAM

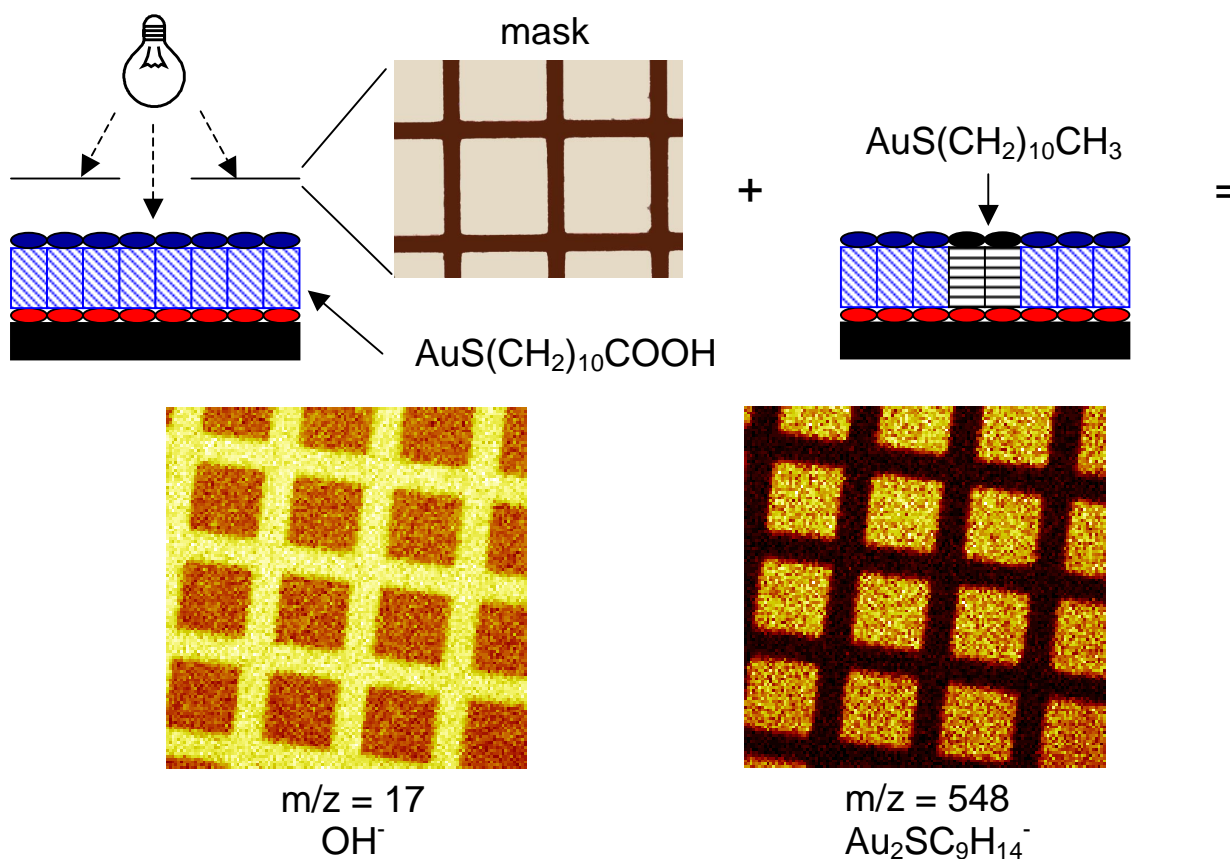


Figure 1: An example of a UV photopatterned SAM surface. First a well-ordered -COOH terminated SAM was prepared using the procedure described above. To UV photopattern the surface a mask (a copper TEM grid) was placed on the -COOH terminated SAM, and the construct exposed to UV light for 1 hour from a Hg arc lamp. The sample was then rinsed with absolute ethanol and placed in a 1 millimolar ethanolic solution of a -CH₃ terminated SAM for 5 minutes. The sample was then rinsed in absolute ethanol.

Bottom: Negative ion TOF SIMS images of the resulting UV photopatterned surface. Image size is 500 x 500 μm^2 (128 x 128 pixels; pixel size 3.90 μm). On the left is shown the intensity of the $m/z = 17$ signal, which arises from OH^- . This is a characteristic ion for the -COOH terminated SAM. On the right is shown the intensity of the $m/z = 548$ ions, which is characteristic of the -CH₃ terminated SAM. Primary ion: Au^+ . Primary ion kinetic energy: 25 keV.

4. High-Resolution Positive and Negative Ion Mass Spectra from the -COOH/-CH₃ patterned SAM after Vapor Deposition of Magnesium

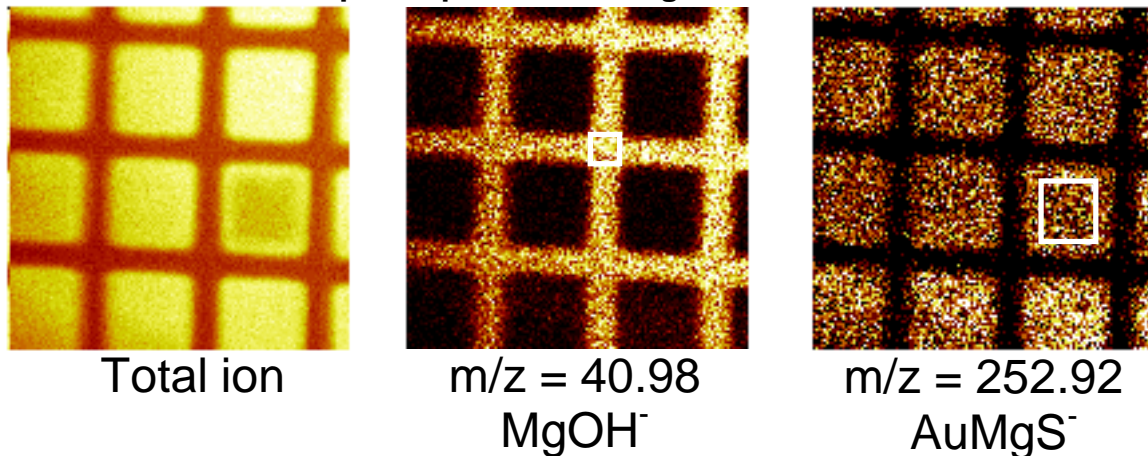


Figure 2: High-mass resolution negative ion mass spectrum images (area $500 \times 500 \mu\text{m}^2$; 128×128 pixels; pixel size $3.90 \mu\text{m}$; lateral resolution of the ion beam $\sim 3 \mu\text{m}$) of a -COOH/CH₃ patterned SAM after deposition of 100 \AA Mg. Deposited Mg reacts with and accumulates on top of the -COOH terminated SAM, as indicated by the formation of MgOH^- ions, and penetrates through the -CH₃ terminated SAM to the Au/S interface, as indicated by the formation of AuMgS^- ions. The white boxes indicate the areas from which the mass spectra shown below were taken. Primary ions: Au^+ ; primary ion energy 25 keV .

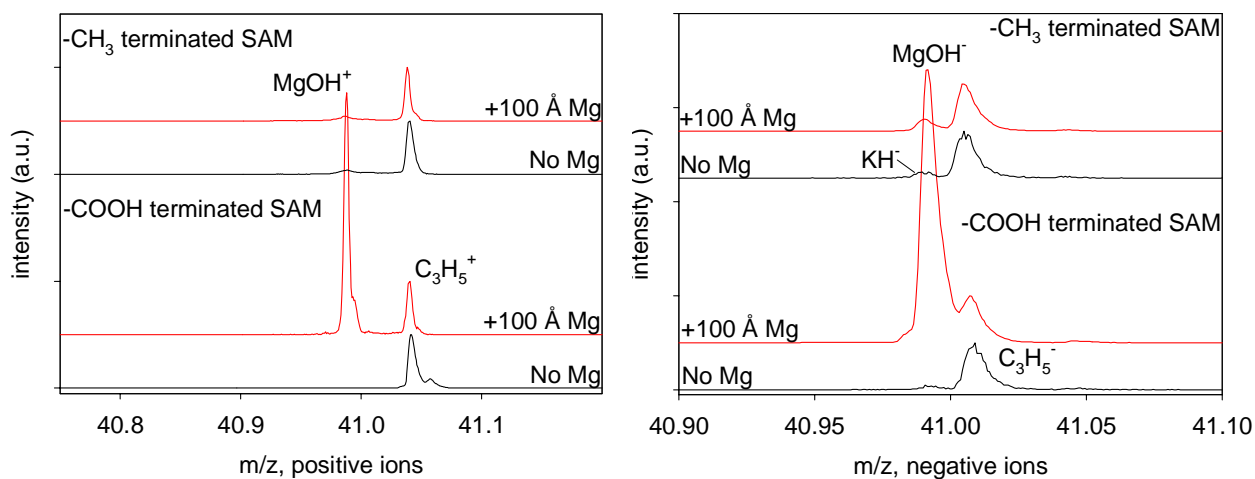


Figure 3: High resolution positive ion mass spectra of nominal mass 41 and negative ion mass spectra of nominal mass 41. In each spectrum, the peaks have been normalized to the intensity of C_3H_5^\pm to make the changes that are occurring in the mass spectra obvious. In the -COOH terminated SAM areas, we observe that MgOH^\pm ions are formed indicating that vapor deposited Mg reacts with the carboxylate group to form a metallo-organic complex. In the -CH₃ terminated SAM areas, no MgOH^\pm ions are observed.

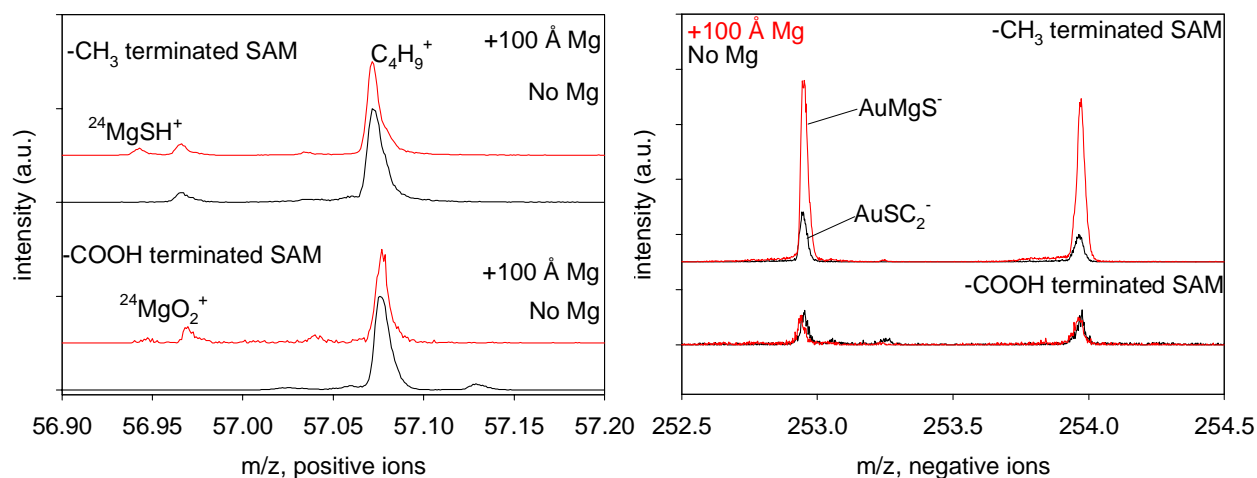


Figure 4: High resolution positive ion mass spectra of nominal mass 57 and negative ion mass spectra of nominal mass 253-254. To make the changes that are occurring in the mass spectra obvious, in the positive ion spectra, the peaks have been normalized to the intensity of C₄H₉⁺ and in the negative ion spectra the peaks are normalized to the intensity of the m/z =254 of the bare -CH₃ or -COOH terminated SAMs. We observe in the -CH₃ terminated SAM areas that MgSH⁺ and AuMgS⁻ ions are formed indicating that vapor deposited Mg penetrates to the Au/S interface. In the -COOH terminated SAM areas, no such ions are observed to form, suggesting that Mg has not penetrated through the monolayer and is accumulating on top of the SAM.

5. Stability of the -COOH/-CH₃ patterned SAM after Vapor Deposition of Magnesium

We note that these structures are extremely stable. Samples have been left in the ambient lab. environment for 9 months (at time of writing) without degradation of the sample (measured using confocal microscopy). They are also stable to rinsing in ethanol, propanol and hexane.