

Supporting Information for:

The Influence of Defects on the Electrical Characteristics of Mercury-Drop Junctions: A Study of Self-Assembled Monolayers (SAMs) of *n*-Alkanethiolate on Rough and Smooth Silver

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Experimental Procedures. *Materials.* Hexadecane (99+% anhydrous), ethanol (200 proof, >99.5% anhydrous), 1-decanethiol, 1-dodecanethiol, 1-tetradecanethiol, and heptadecafluoro-1-decanethiol were obtained from Aldrich. The alkanethiols were passed through neutral alumina prior to use to remove polar sulfur compounds (e.g., sulfonic and sulfuric acids). Mercury (99.9998%, electronic grade) was obtained from Alfa Aesar. Silicon (100) wafers were obtained from Silicon Sense (Nashua, NH). Glass slides (6 cm x 2 cm x 1.2 mm) were obtained from VWR. Optical adhesive (61) was obtained from Norland Products, Inc., and stored in a refrigerator at 4° C.

Electron Beam Evaporation. All evaporations were conducted in a cryogenically pumped electron-beam deposition system (Temescal, base pressure $\sim 2 \times 10^{-6}$ Torr, operating pressure = $(2-5) \times 10^{-6}$ Torr). To deposit the thick (600-nm) silver films, we evaporated at a rate of 1 Å/s for the first 5 nm, and then increased the rate by 0.5 Å/s every 30 s, until we reached 8 Å/s, the rate at which we completed the evaporation. To deposit the AS-DEP films, a 2 nm-thick titanium adhesion layer was evaporated at 1 Å/s, followed by a 40 nm-thick layer of Ag at 4 Å/s.

Formation of SAMs of n-Alkanethiolate. The SAMs were formed by immersing the TS and AS-DEP surfaces in 1-mM ethanolic solutions of $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$ ($n=10, 12, 14$) for ~ 8 hrs. The ethanol was deoxygenated by bubbling argon through it for 2 hours prior to adding the thiol. The solutions containing the samples were stored under argon in 20-mL glass scintillation vials (obtained from VWR International, Inc.). The surfaces were removed from the solutions, submerged in a bath of anhydrous ethanol, and dried in a gentle stream of nitrogen gas.

Atomic Force Microscopy. The grain size and roughness of the AS-DEP and TS surfaces were determined by contact-mode AFM (Digital Instruments Dimension 3100). Scan sizes were $25 \mu\text{m}^2$ and were analyzed using the Nanoscope IV v5.12b18 software package (Digital Instruments, Santa Barbara, CA) and home-made software.

X-ray Photoelectron Spectroscopy. Spectra were obtained using a Surface Science SSX-100 photoelectron spectrometer using Monochromatic Al K- α X-Ray radiation (1.49 kV, base pressure $\sim 10^{-9}$ Torr). Survey spectra were collected at a constant pass energy of 158 eV from a 1000 μm diameter spot size on the surface. Spectra of the S(2p)

core levels were collected at a pass energy of 27 eV with a 600 μm diameter spot size. The binding energies were corrected by referencing the C(1s) binding energy to 284 eV.

Infrared Spectroscopy. Reflection absorbance infrared (RAIR) spectra were obtained using a Nexus 670 FT-IR spectrometer (Nicolet, Madison, WI) that was equipped with a surface grazing-angle attachment (SAGA, Thermo Spectra-Tech, Shelton, CT) and a MCT detector that was cooled with liquid nitrogen. The incident reflection angle was set at 80°. The background spectra were taken from a reference silver surface that supported a SAM of heptadecafluoro-1-decanethiolate. The fluorinated SAM minimizes the contributions from the C-H stretching modes of adventitious contaminants. Spectra were obtained using 1024 scans at 2 cm^{-1} resolution. The baselines of the spectra were corrected over the range of 3100-2700 cm^{-1} .

Measurements of J-V with the Hg-Drop Junction. A silver surface supporting a SAM of SC_n was submerged in a 1 mM solution of HSC_n in hexadecane in an open-topped plexiglass box. A gold probe tip contacted the TS surface and connected it electronically to the electrometer (Keithley 6430 sub-femtoamp remote SourceMeter). A Hg- SC_n electrode was formed at the tip of a gastight syringe (1 mL; Hamilton) by exposing one drop of mercury at the tip of the syringe, submerging the drop in the same thiol solution in which the silver surface sits, expunging the drop into the solution to expose another drop, and leaving this final drop hanging from the tip of the syringe, in contact with the mercury reservoir and with the solution of thiol, for ~2 minutes. The drop was then positioned over an unused portion of the Ag- SC_n SAM, and with a micromanipulator, brought into contact with the Ag- SC_n electrode. A tungsten wire protruded through the Teflon plunger of the syringe to make electrical contact between the mercury reservoir

and the electrometer. The experiment was carried out in an aluminum box, with no measures taken to exclude air or moisture from inside the box. The box was suspended from the ceiling by rubber cords to minimize vibrations.

A camera (Edmund Industrial Optics) projected a magnified image of the junction from the side. The image was digitized by an NTSC capture card. The relationship between the size of the image of the junction on the screen and the actual size of the junctions was calibrated by imaging an object of known size. The electrometer applied a voltage (V) across the junction by holding the silver electrode at ground and changing the voltage at the Hg-SC_{*n*} electrode. The electrometer recorded the values of the current at each applied voltage (-0.5 - +0.5 V with 0.05 V, 2s steps), and we captured the data with a home-made program in LabVIEW.

XPS of Silver Surfaces and Ag-SAM Surfaces. Figure S3a shows the core-level survey spectra for the AS-DEP and TS films, and those films with a SAM of SC₁₆ adsorbed on them. The spectra show that the bare surfaces are not contaminated as a result of their preparation: the spectra for the bare films were similar, and free of technique-specific artifacts, such as titanium from the adhesion layer in the AS-DEP film or residue from the optical adhesive in the TS film. The bare surfaces were contaminated by carbon (adventitious contaminants) and oxygen (silver oxide). The films with SAMs on them showed: i) that sulfur was only present after the formation of the SAM; and ii) that the SAM reduced or prevented the formation of an oxide on the silver. Figure S3b shows that the uncleaved TS substrates can be stored for longer than one month without oxidation of the TS surface. The AS-DEP surface was significantly more oxidized than the TS surface.

Figure S1. A representative plot of the applied voltage with time for one trace. We define a trace as a sweep of the voltage from $V = 0 \rightarrow 0.5 \rightarrow -0.5 \rightarrow 0$ V in 0.05 V steps. In response to a positive voltage applied to the mercury electrode, electrons flow from the silver electrode (held at ground), through the Ag-SC_n//C_nS-Hg junction to the mercury electrode.

Figure S2. Plot of the actual area of the junction vs. the diameter of the magnified image of junction measured on the computer screen for magnifications of 250x, 300x, and 350x.

Figure S3. XP spectra of AS-DEP and TS silver films. a) Core-level survey spectra for the AS-DEP and TS films, and those films with a SAM of SC₁₆ adsorbed on them. The bare surfaces were contaminated by carbon and oxygen (adventitious contaminants and possibly silver oxide). The films with SAMs on them showed that the SAM reduced the amount of oxygen on the surface. The spectra were free of technique-specific artifacts, such as (b) titanium from the adhesion layer in the AS-DEP film or (c) residue from the optical adhesive in the TS film (optical adhesive is composed of C, O, N, and S; the spectra of the TS films lacked N, and S was present only on the sample that bore a SAM of SC₁₆). d) Core-level XP spectrum of the O 1s peak on the TS silver films. There was no significant change in the amount of oxygen in the TS film when stored for up to two months in its “sandwich” structure: bare TS silver contained 15% O (1 day), and 13% O (2 months) (the peak narrowed and increased in height); TS silver on which we formed a SAM of SC₁₆ contained 3% O (1 day), and 5% O (2 months).

Figure S1.

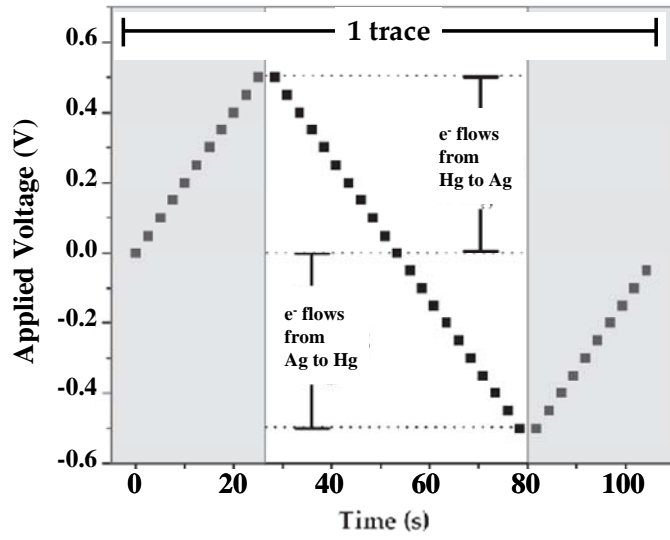


Figure S2.

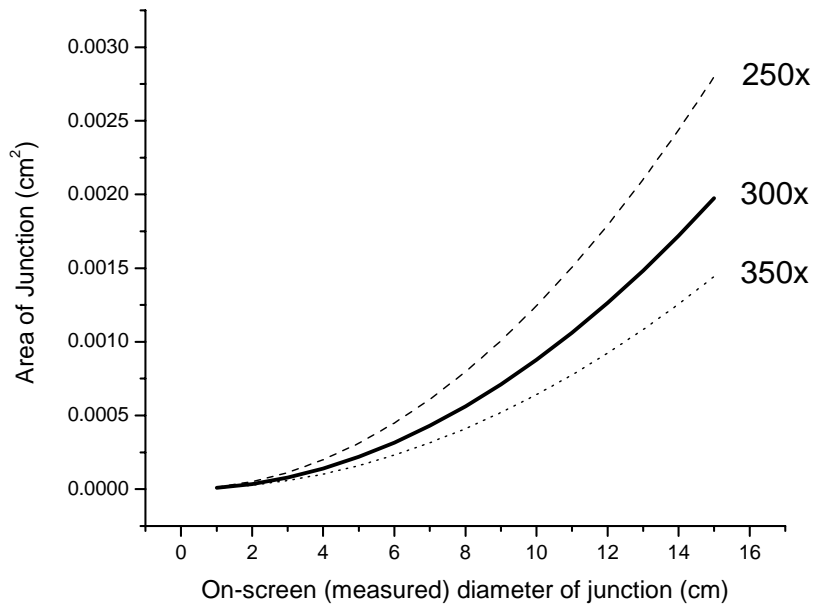


Figure S3.

