Alkanethiol self-assembled monolayers as the dielectric of capacitors with nanoscale thickness

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Alkanethiol self-assembled monolayers (SAMs) on a mercury surface are used to build a junction consisting of two opposing mercury surfaces with interposed SAMs: Hg-SAM/SAM-Hg. The liquid mercury surface provides a support for the SAM that is smooth, compliant, free of defects, and without the incommensurate lattice properties that characterize solid metal surfaces. The thickness of the dielectric (~ 30–90 Å) in this junction can be easily changed by using alkanethiols with different lengths. From capacitance measurements, a dielectric constant of 2.7 ± 0.3 is calculated for the SAMs. The conductivity of SAMs on the Hg surface is $\sigma = 6 \pm 2 \times 10^{-15}$ Ω^{-1} cm^{-1}, a value close to that of bulk polyethylene. The junction sustains an electric field of 6 MV/cm. © *1998 American Institute of Physics.* [S0003-6951(98)03114-3]

Alkanethiol self-assembled monolayers (SAMs) on gold and silver have been extensively studied: they are stable, highly organized, and electrically insulating.[1,2] These characteristics are among the requirements for a material that is a candidate for use in nano- and molecular-scale electronic devices.[3] Connecting one-dimensional ''conducting'' molecules—so-called molecular wires—to two metal surfaces is a particularly important problem in molecular electronics, with the most successful approaches to date including those based on break junctions,[4,5] STM measurements,[6] and nanomachined junctions.[7] Additional, experimentally simple systems that would be make it more straightforward to characterize the properties of thin organic films would be a useful addition to the field of molecular electronics.

Here we describe the fabrication and characterization of a metal-SAM/SAM-metal junction that represents (i) a simple system with which to study the electrical properties of SAMs, and (ii) a step toward the connection of molecular wires to macroscopic measuring instruments.

To produce a well-characterized metal-SAM/SAM-metal junction, three problems must be solved. The first problem concerns the effect of the surface of the metal on the architecture of the SAM. The microscopic roughness of gold and silver surfaces and the presence of steps and kinks in the lattice generate defects in the SAMs.[8–10] The second problem centers on the influence of grain boundaries and other defects in the SAM itself. SAMs of alkanethiols on gold and on silver are *trans*-extended, but tilted respectively by 30° and 11° from the normal to the surface.[11,12] This tilt results in domains in SAMs even on atomically flat surfaces, and the packing of chains at the domain boundaries is critical. All of these structures studied recently by scanning tunneling microscope (STM) and EM have the potential to influence the electrical characteristics of a metal-SAM/SAM-metal interface.[13,14] The third problem is the procedure used to ''contact'' the two metal-SAM surfaces. It is not presently possible to bring two *solid* metal-SAM surfaces into contact without damaging them, nor is it possible to calculate what

fraction of the measurable contact area is in actual contact when the dimensions of the defects in the metal surface are larger than the length of the thiols. We have addressed these problems by using a liquid metal support for the SAM rather than a solid gold or silver surface.

Mercury, as liquid metal with very high affinity for thiols, offers a solution to these problems. First, as a liquid, the Hg surface is free of structural features imparting defects at the adsorbed monolayer.[15–19] Second, alkanethiols form SAMs on a Hg surface with the thiol chain axes perpendicular to the surface of Hg,[15] and the SAMs are therefore free of domain boundaries. In fact, these monolayers, as characterized by cyclic voltammetry and electrode capacitance measurements, are impermeable and free of pinholes.[14–19] Third, liquid mercury can conform to nonplanar geometries, and thereby maximize the area of contact between two surfaces. For these reasons, mercury is an excellent substrate with which to build prototype metal-SAM/SAM-metal junctions: Figure 1 shows a typical system.[20] This geometry allows the Hg-SAM/SAM-Hg junction to be characterized through measurements of capacitance, resistance, and impedance.[21]

Equation (1) describes the relation between the capacitance C and the distance d between the metal surfaces of a capacitor; ϵ_0 is the permittivity of the free space, ϵ_t is the dielectric constant of the insulating medium, and A is the area of the capacitor surfaces.

$$C = \epsilon_0 \epsilon_t A / d. \tag{1}$$

In the present case, the distance d between the two Hg surfaces was tuned by changing the thiol chain length, l: in this case, l is the thickness of the SAM.[15] The distance d ($d = 2l$) varied between 2.9 nm for HS(CH$_2$)$_{10}$CH$_3$ to 8.9 nm for HS(CH$_2$)$_{33}$CH$_3$.[22] The area A was evaluated from a photomicrograph of the contact area at $40\times$ magnification: for the system used here, $A = 1.5 \pm 0.2$ mm^2. The capacitance values for the system when ethanol was used as solvent for the thiols are reported in Fig. 2 as $1/C$ vs d.[23,24] A regression analysis of the data given a slope of 2.8 ± 0.2
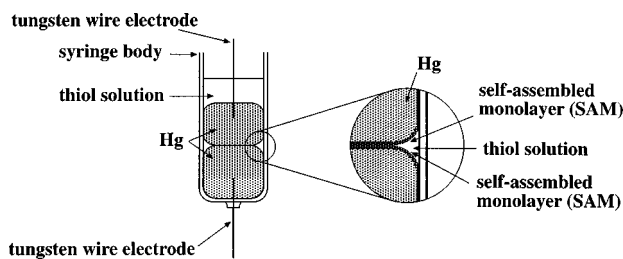
FIG. 1. Schematic representation of the geometry of the Hg-SAM/SAM-Hg junction.

$\times 10^{16}$ F^{-1} m^{-1} ($R^2 = 0.99$), from which the value of the dielectric constant for the SAMs is calculated to be $\epsilon = 2.7 \pm 0.3$. This value is in close agreement with the literature data for alkanethiolate SAMs on gold ($\epsilon_t = 2.6$)[25] and on Hg ($\epsilon_t = 2.4$).[18]

The $1/C$ intercept value of the plot represents all the capacitative contributions in series with the SAMs, and can give information about the amount of solvent that might be trapped between the Hg-SAM surfaces.[24] From the intercept value of 0.18×10^7 F^{-1} a solvent layer thickness of $\sim 1-2$ Å can be estimated, assuming that the permittivity of the solvent near and at the surface is substantially reduced relative to the bulk.[26] The conclusion that none or very few ethanol molecules are trapped between the Hg-SAM surfaces is supported by the result that the same capacitance and same intercept values are obtained when water ($\epsilon = 80$) is used as solvent instead of ethanol ($\epsilon = 25$). In contrast, solvents such as octane, heptane, and hexadecane yield capacitance values for the junction that are 50 times smaller than those obtained with ethanol. Since the dielectric constant of these hydrocarbon liquids is not significantly different from that inferred for the SAM itself, we interpret these results as indicating that thin liquid films with substantial thickness might be trapped between the Hg-SAM surfaces: the thick solvent layer in the resulting structures (Hg-SAM/solvent/SAM-Hg) would then determine the total value of the capacitance.[24] These data suggest that the polarity of the solvent (or perhaps the wettability of the SAM by the solvent) plays an important role in the interface between the two SAMs. This conclusion agrees with a recent study on the role of solvents in interfacial adhesion forces between SAM-coated metal surfaces.[27]

Figure 3(a) shows a photograph of the system used: one capacitor is formed by the Hg-SAM drop in contact with an
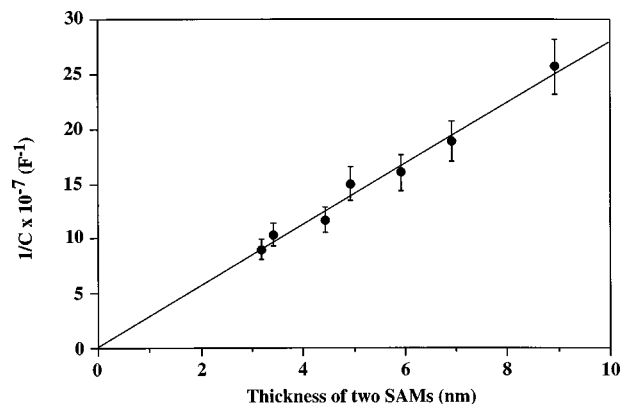

FIG. 2. Variation of the inverse of the capacitance, $1/C$, as a function of thickness of the SAMs.
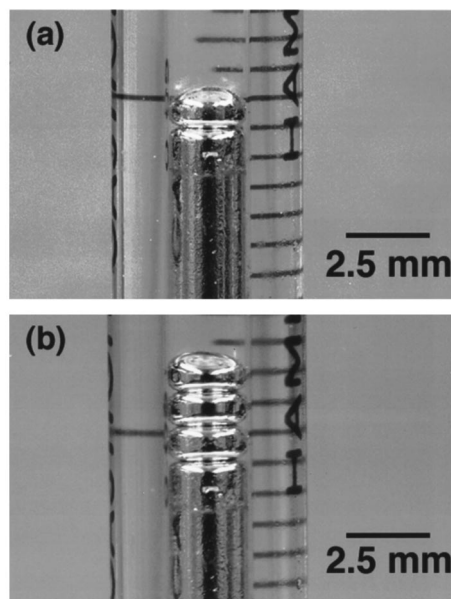

FIG. 3. (a) Photograph of the system schematized in Fig. 1: one capacitor is formed by the Hg-SAM drop in contact with the underlying Hg-SAM surface. (b) Photograph of the system where three Hg-SAM drops are stacked and create three capacitors in series.

underlying Hg-SAM surface. Figure 3(b) shows three Hg-SAM drops that are stacked to form three capacitors in series. Capacitors in series have a total capacitance described by the relation: $1/C_{tot} = \Sigma 1/C_i$, where C_i is the capacitance of the individual capacitors. In this case we expect $C_{tot} = 1/3 C_i$. The capacitance values measured when HS(CH$_2$)$_{17}$CH$_3$ is used to form the SAM are $C_i = 8.6$ nF for the single capacitor and $C_{tot} = 2.9$ nF for the capacitors in series. This result indicates that the capacitance of the SAM/SAM interfaces is the only contribution to the measured capacitance values of the system.

The Hg-SAM/SAM-Hg junction, assembled as described above, was used to measure the conductivity of the SAMs on Hg. The conductivity was obtained from current–voltage measurements.[28,29] The measurements were performed on the system for thiols of different lengths—from HS(CH$_2$)$_{15}$CH$_3$ to HS(CH$_2$)$_{33}$CH$_3$—in ethanol solution.[30] The calculated value of conductivity of $\sigma = 6 \pm 2 \times 10^{-15}$ Ω^{-1} cm^{-1} does not change with the thickness of the SAM, as expected given the absence of an electron tunneling contribution to current.[31,32] These results confirm that these SAMs on Hg are largely free of defects. The conductivity is only three times larger than that reported for bulk polyethylene and is comparable to SAMs of n-alkylsiloxanes on silicon/silicon dioxide obtained using n-alkyltrichlorosilanes with very careful control of the conditions of formation.[33] Voltages up to 1.7 V could be applied to the junction before electrical breakdown occurred. This value demonstrates that the SAMs can sustain electric fields as high as ~ 6 MV/cm.

Preliminary impedance measurements of the junction were performed using alkanethiols of different lengths.[34] The data obtained with SHG formed from HS(CH$_2$)$_{15}$CH$_3$ in ethanol are plotted on a Bode diagram (Fig. 4). The plot shows a linear relation with a slope of -0.9 over the entire fre-
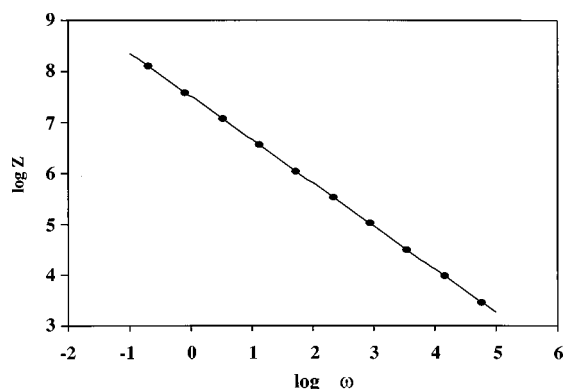
FIG. 4. Bode plot of log 1Z1 vs log ω for the Hg-SAM/SAM-Hg junction using SAMs formed from $HS(CH_2)_{15}CH_3$.

quency range examined. The plot indicates that the junction Hg-SAM/SAM-Hg can be represented by a simple equivalent circuit, where a capacitor C is connected in parallel with a resistor $R (R > 10\ G\Omega)$.[35] The dimension and the value of this electrical equivalent circuit make it similar in properties to that of bilayer lipid membranes.[36]

In summary, using the junction Hg-SAM/SAM-Hg, we have demonstrated that alkanethiols on the atomically flat surface of mercury form monolayers of extremely low conductivity—close to that of bulk polyethylene. These SAMs are capable of sustaining high electric fields before breakdown. The electrical characteristics of these systems, the simplicity with which they can be prepared, the facility of self-assembly of the alkanethiolate SAMs on mercury, and the ease with which the structures of the SAMs can be varied through synthesis of the alkanethiols make this system a convenient one with which to study the electrical characteristics of organic films having nm-scale thickness.

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[20] A microsyringe body (2.5 mm inner diameter) was used to maintain the area of the two facing Hg surfaces constant. A thiol solution was transferred to the syringe to form the first Hg-SAM interface. A calibrated drop of mercury (5 μL), previously stored in the thiol solution, was then rolled along the reclined syringe wall, bringing the second Hg-SAM surface gently into contact with the first one. Electrodes (50 μm diameter tungsten wire) were inserted into the drops. Solutions of thiols (1 mM) were prepared in ethanol, heptane, octane and hexadecane.
[21] All the electric measurements were performed in a shielded box with a micromanipulator probe station.
[22] Shorter chain thiols cause the Hg surfaces to merge.
[23] The capacitance was measured at 120, 400, 1000 Hz with a LEADER LCR-745 meter.
[24] We assume that the main contributions to the capacitance come from the contacting Hg-SAM surfaces. If a finite layer of solvent is trapped between the Hg-SAM surfaces, then the total capacitance of the system is given by: $1/C_{tot} = 1/C_{solv} + 1/C_{SAM}$. While C_{SAM} is constant, because d_{SAM} is constant, C_{solv} depends on the thickness of the solvent, d_{solv}, trapped between the Hg-SAM surfaces. The relative contribution of C_{solv} is determining the value of the capacitance.
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[28] An Axopatch 1-D with a sensitivity of 0.1 pA from Axon Instruments Inc. was used for the measurements of leakage currents. Small voltages (from -150 to $+150$ mV) were applied through the junction. Higher electric fields deform the mercury surfaces and damage the SAMs.
[29] Over a voltage range from $+400$ to -400 mV, cyclic voltammetry does not show any redox reaction occurring at the Hg surfaces.
[30] When octane is used as solvent, stationary current values are reached instantaneously after applying the voltage. When alcohol is used as solvent, even after deoxygenation, the current reaches a constant value after a slow decay ($Ixt = 10-20$ pC). We attribute this small current to traces of impurities (traces of metal cations) present in the distilled ethanol.
[31] In the limit of low electric field, electron tunneling theory predicts a linear $I-V$ dependence, and allows for the determination of conductivity ($\sigma = dI/dV$); the conductivity is expected to decrease exponentially with the film thickness [J. G. Simmons, J. Appl. Phys. **34**, 1793 (1963)]. Since the minimum thickness of the SAM/SAM dielectric is 2.9 nm, the tunneling contribution to the total current is expected to be negligible [B. Mann and H. Khun, J. Appl. Phys. **42**, 4398 (1971)].
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[34] The measurements were performed with a electrochemical interface Solartron EI 1287 and a frequency response analyzer Solartron FRA 1256.
[35] According to the theory, for such a network, $1Z1 = R/(1 + \omega^2 C^2 R^2)^{1/2}$, where $1Z1$ is the modulus of the impedance, Z, and ω is the radial frequency; the plot of log $1Z1$ vs log ω should exhibit a linear region at high ω, with a slope of -1, and a plateau at low ω, when $(\omega CR)^2 \ll 1$. Figure 4 shows that the plateau region has not been reached even at $\omega = 10^{-1}$ Hz. In fact, at this frequency, the measured values of C and R gives $(\omega CR)^2 = 25$.
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