Electrical Breakdown of Aliphatic and Aromatic Self-Assembled Monolayers Used as Nanometer-Thick Organic Dielectrics

Rainer Haag,[†] Maria Anita Rampi,*,[‡] R. Erik Holmlin,[†] and George M. Whitesides*,[†]

Contribution from the Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, and the Dipartimento di Chimica,Centro di Fotochimica CNR, Università di Ferrara, 44100 Ferrara, Italy

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Abstract: This paper describes a new type of metal−insulator−metal junction based on self-assembled monolayers (SAMs). The junction consists of a drop of liquid mercury supporting a SAM, in contact with a flat metal surface (M′), also supporting a SAM: that is, a Hg−SAM/SAM−M′ junction. This junction is stable, easy to assemble, and reproducible: it can generate areas of contact down to 0.01 mm^2 without photolithography. These properties suggest this junction as a useful "test bed" for experiments in molecular electronics. The junction allowed measurements of electrical properties of SAMs on different metals: M′ = Ag, Au, Cu, and Hg. The work described here focused on the electrical breakdown voltage (BDV, the maximum voltage sustained by the junction). The BDV depends on M′ (BDV$_{Ag}$ = 3.2 ± 0.5 V; BDV$_{Hg}$ = 3.1 ± 0.4 V; BDV$_{Cu}$ = 3.0 ± 0.3 V; BDV$_{Au}$ = 1.5 ± 0.2 V for SAMs formed from hexadecanethiol) and correlates with the organizational parameters of the SAM on M′: it increases as the packing density increases and the tilt angle decreases. The BDV also depends on the chain length of the alkanethiol forming the SAM for the same metal surface (M′). Alkanethiol SAMs on Ag having carbon chain lengths longer than C14 can sustain a constant electrical field up to 8 ± 1 × 10^8 V/m. This value for the BDV is similar to that of bulk polyethylene. A survey of SAMs with different chemical structures shows that the BDV correlates overall with the thickness of the densely packed hydrocarbon portion of the SAM: aliphatic and aromatic SAMs of the same thickness show similar BDVs.

Introduction

We have recently described a mercury−SAM/SAM−mercury junction (Hg−SAM/SAM−Hg) that is useful in the electrical characterization of SAMs and that behaves as a capacitor with plates separated by a nanometer-thick dielectric.[1] The procedure used in the preparation and characterization of this system is experimentally straightforward: two SAM-covered drops of mercury are brought into contact, with the spacing between the electrodes in the junction controlled by the dimensions of the SAMs at values between 2 and 10 nm. The low conductivity of alkanethiolate monolayers ($\sigma = 6 \pm 2 \times 10^{-15}$ Ω^{-1}cm^{-1} for CH$_3$(CH$_2$)$_{15}$SH) makes them excellent as nanoscale insulators and dielectrics.[1]

The development of ultrathin insulators and dielectrics having high stability against electrical breakdown is an important problem in nanoelectronics.[2] In terms of energy storage, the performance of a capacitor is limited by the dielectric constant and the breakdown voltage: the latter limits the thinness of the dielectric layer that can be used. In commercial thin-film capacitors, the two electrode surfaces are usually separated by polymer films of micrometer thickness; typical films can sustain voltages up to 1000 V (values corresponding to an electrical field at breakdown of $\sim 8 \times 10^8$ V/m).[3] The electrical strength

of the Hg−SAM/SAM−Hg junction is similar and suggests that organic monolayers may have electrical properties of substantial interest in nanodevices.

Alkanethiolate monolayers on gold have been extensively studied at metal/solution interfaces by electrochemistry.[4,5] More recently, silver, copper, and mercury have received focused attention as the supporting metal.[6,7] Electrochemical and impedance measurements provide information about electron tunneling across insulating SAMs,[8] the permeability of SAMs to ions,[7] and the resistance and capacitance of SAMs;[1,6] they do not

† Harvard University.

‡ Università di Ferrara.

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provide the information about the electrical properties and mechanical stability of SAMs as dielectric materials that would be required to evaluate their potential for small electrical devices.[9] It has not been obvious how to bring two metal surfaces supporting SAMs together to study these properties: contact between two solid metal surfaces supporting SAMs results in damage to the SAMs and in electrical shorting. Characterization and control of the topography of the contact region in these systems are not practical.

Metal−insulator−metal junctions incorporating Langmuir−Blodgett (LB) films have been fabricated since the 1970s to measure the electrical properties of these films; in these junctions, the second electrode (aluminum) was evaporated through a mask on top of the LB film, which was, in turn, supported on a metal electrode.[10] Mann and Kuhn used Hg, Al, Pb, and Au in contact with films of fatty acids physisorbed on Al to study conductivity through the organic films.[10b] A similar system has been used recently to measure the insulating properties of alkylsiloxane SAMs on the surface of doped silicon.[11] Since these systems have formed one electrode in the junction by evaporation of a metal on the LB film or SAM: the nature of the interaction of the highly reactive, condensing metal atoms and the organic molecules is an important subject for understanding the structure of these junctions but one that has not been studied in any detail. The methods of fabrication used in generating these metal−insulator−metal junctions frequently generate systems having electrical shorts and require the preparation and measurement of large numbers of samples to produce reliable data.

Metal−insulator−metal junctions have also been assembled by deposition of silver paint on top of a gold-SAM surface; a breakdown voltage of 2 V (0.4 GV/m) has been reported for an octadecanethiolate monolayer.[12] This system, although simple, is also not well characterized. The silver paint, which contains both a solvent and polymer, might contribute to the insulating characteristics of the system. More recently, Reed at al. have assembled a nanofabricated junction to measure electrical properties of SAMs (and molecules included in them) in which e-beam lithography defined a small contact area ($\sim$700 nm^2).[13] The second metal surface of the junction was formed by evaporation of titanium onto a SAM, followed by gold; the potential for reactivity of the titanium toward the organic components of the system introduces a substantial level of complexity into this system. In recent years, STM tips have been used extensively as the second metal surface to build tunnel junctions that can be considered metal−SAM−metal junctions.[14−16] With this system, several groups[13,14] have measured what were interpreted to be the electrical properties of single molecules of aromatic thiols and alkanethiols. Kubiak

et al. have built a junction that sandwiches a SAM of dithiol between an Au surface and colloidal Au particles.[15] STM imaging, in combination with electrical measurements, has been interpreted as having detected and characterized single aromatic molecules protruding from the alkanethiolate SAM.[15,16] These results were also interpreted in terms of a model involving electrical current passing through a single organic molecule, "a molecular wire". A third type of junction has also been demonstrated by Reed et al.: the tips of a fractured gold wire (a "break junction") have been used as two nanoelectrodes in a junction, and this system has also been used to study single aromatic dithiol molecules localized between these electrodes, separated by $\sim$1 nm.[17]

None of these methods for studying the electrical properties of SAM is ideal (nor, for that matter, is the method reported here). Several require complicated fabrication using sophisticated apparatus, and many of them generate information whose interpretation rests on assumptions. The probability of failure of even the simplest of them due to electrical shorting is high. It is therefore useful to have new methods that complement these existing ones. Ideally these methods should be simple enough to be readily accessible to chemists, especially those interested in combining synthesis and electrical measurement to generate structure−property relationships. In all systems involving macro- and microscopic (as opposed to nanoscopic) solid electrodes, defects or changes in topology in the metal surface seem to allow enough metal−metal contact, even when the metals are ostensibly covered by SAMs, to cause electrical shorting. Junctions connecting two liquid metals (that is, the Hg−SAM/SAM−Hg junction[1]) are limited in their compatibility with changes in the properties of the metal and in the SAMs they support[1] and have obvious limitations in their relevance to devices.

To develop a system that would be sufficiently simple and experimentally flexible to allow screening of the electrical properties of SAMs having a range of structures and properties, we required a stable and easily assembled metal−SAM/SAM−metal junction. The immediate application of this junction would be to provide an electrical "test-bed" for SAMs and a system with which to examine organic molecules and functional groups embedded in these SAMs. We have settled on the Hg−SAM/SAM−metal system for this work. The advantage to the use of mercury as one electrode is that it readily forms SAMs and that it is a liquid at room temperature. SAMs of alkanethiols on mercury have been well characterized structurally.[7,18,19] A liquid Hg surface supporting a SAM is compliant and can conform to the topography of a solid surface with which it is brought in contact; this ability to conform minimizes the effects of irregularities of the solid surface on the structure of the SAM and also minimizes the potential for shorting (Figure 1). This system also, of course, has ambiguities, for example: (i) mercury

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Monolayers Used as Organic Dielectrics

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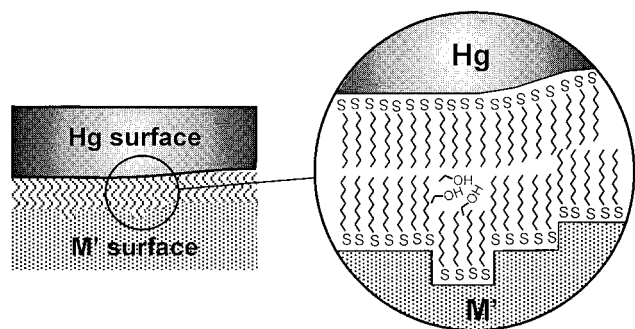
Figure 1. Schematic representation of the topography of the interface in the Hg−SAM/SAM−M′ junction. The liquid mercury−SAM surface comes into conformal contact with the M′−SAM surface. It is energetically unfavorable for it to conform to abrupt changes in the topography of M′. The ability of the Hg−SAM/SAM−M′ junction to come into uniformly atomic contact is not clear, and there are probably small pockets of solvent (here ethanol) left at the interface.

itself has a very high surface tension ($\gamma_{25\ °C} = 480$ mN/m),[20b] and it is energetically unfavorable for it to conform to abrupt changes in the topography of M′. Although the Hg−SAM surface will have a much lower surface tension than clean Hg, the ability of the Hg−SAM/SAM−M′ to come into uniformly atomic contact with a metal surface having steps and defects is not known. If the surfaces do not come into uniform atomic contact, there may be small pockets of solvent left at the interface between them (Figure 1). (ii) Mercury is volatile and adsorbs on and amalgamates with gold, silver, and copper.[20,21] The influence of the diffusion of mercury across the SAM bilayer is not known, nor is it necessarily obvious whether a small amount of diffusion/amalgamation would have a significant influence on electrical properties of the junction. (iii) Bringing a Hg−SAM system into contact with a solid surface may involve some local distortions in the SAM, with unknown influence on its properties. (iv) An applied electrical field charges the mercury and the other metal surface and causes them to attract one another; this attraction compresses the SAMs substantially (we estimate the pressure later in this paper), with unknown consequences for their structures. (v) Visual estimates, even with magnification, of the contact area may be inaccurate.

These ambiguities not withstanding, we believed that the development of a Hg−SAM/SAM−M′ junction would allow us (i) to study the electrical properties, especially the BDV, of the SAM/SAM junction on different metals; (ii) to exploit the possibility of changing the structure of the SAM with greater flexibility than would be possible with a Hg−SAM/SAM−Hg junction to infer structure−property relationships; (iii) to pattern the SAM on M′ (using soft lithography)[22] at the submicron scale; (iv) to study local variations in conductivity or BDV on a single wafer; and (v) to investigate the properties of heterogeneous SAMs.

Design of the New Junction. Scheme 1 shows the assembly of the Hg−SAM/SAM−M′ junction, where M′ is the surface of an evaporated film of pure metal (Ag, Au, Cu), or the surface of a heterogeneous metal system (Au/Hg). This last system (Au/Hg), described by Grunze et al.,[23] is formed by preparing a SAM

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Scheme 1. Illustration of the Assembly of the Hg−SAM/ SAM−M′ Junction and the System Used for the Measurement of Breakdown Voltages (BDVs)[a]
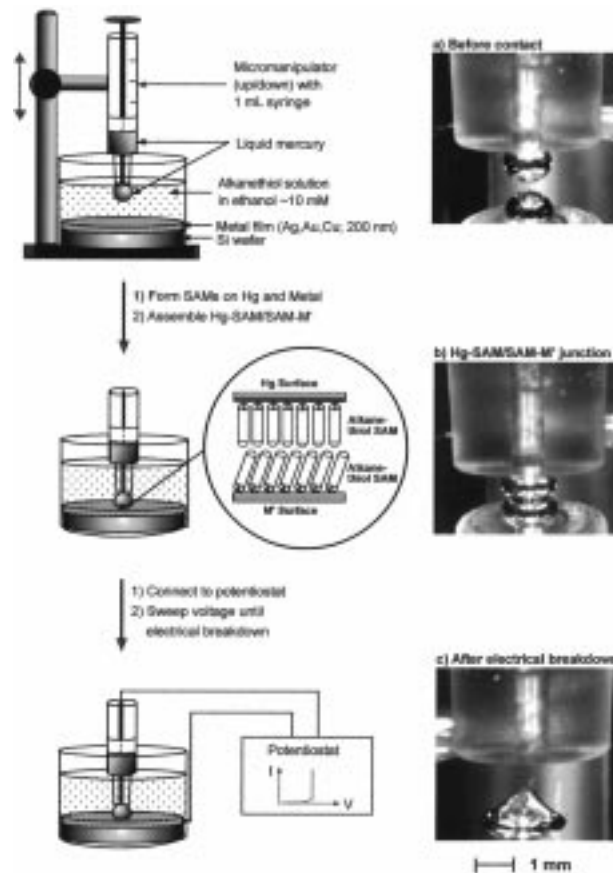
[a] The photographs illustrate the following: (a) the two metal surfaces, covered with a SAM of hexadecanethiol but not yet in contact; (b) the two metal−SAM surfaces after being brought in contact using a micromanipulator (the contact area was monitored by a video camera using a 50× objective); and (c) the two electrodes after electrical breakdown of the junction, an accompanying simultaneous mechanical breakdown of the mercury drop with amalgam formation. For the measurement of the BDV, the two halves of the junction are connected to the computer-controlled potentiostat in two-electrode mode. At the BDV of the junction, an abrupt rise of current in the current−voltage curve occurs and the drop of mercury spreads (within 0.1−100 s, depending on the length of the alkanethiol).

on gold by exposure of a film of gold to a solution of alkanethiol using conventional procedures, then exposing the Au−SAM surface to mercury vapor, and finally re-exposing the system to the solution of the alkanethiol. Although the details of the changes occurring during this process are still being elaborated, it generates a SAM with a higher lateral density of organic molecules than does gold itself, and the SAMs on Au/Hg have an average tilt angle θ_t of ~11° (close to that of silver, and in contrast to the value of θ_t ~30° for the analogous SAM on unmodified gold).

The structure of an alkanethiolate SAM depends on the metal that supports it. Table 1 summarizes the relevant structural parameters for SAMs on Ag, Au, Cu, and Hg surfaces: Hg forms a liquidlike SAM with a tilt angle of θ_t ~ 0°, while Ag and Cu form crystalline-like SAMs that are densely packed and that have small tilt angles, θ_t ~10°;[6] Au forms the least densely packed SAM, and has the largest tilt angle θ_t ~30°.[5]

To assemble the Hg−SAM/SAM−M′ junction (M′ = Ag, Au, Au/Hg, Cu), we used a Hg drop with a diameter of ~1 mm (5−10 μL), hanging from a microsyringe, and a freshly

Table 1. Selected Structural Parameters of Metal−Alkanethiolate Surfaces and Properties of the Underlying Metal

	metal supporting the SAM				
parameters	Ag	Au	Au/Hg	Cu	Hg
R-R spacing [Å]	4.5[5c]	5.0[4,5c]	*a*	4.7[6]	4.75[7e]
tilt angle, θ_t of SAM [deg]	11[5c]	33[4,5c]	∼11[23]	12[6]	0[18]
WF, ϕ [eV][b,c]	4.74	5.31	*a*	4.94	4.49
IP(I) [eV][b,d]	9.2	7.6	*a*	7.7	10.4
mp [°C][b]	962	1064	*a*	1083	−39

a The Au/Hg surface is hetergeneous. *b* These data were obtained from ref 21. *c* Electron work function derived from photoelectric measurements (crystallographic direction for single crystals of Ag, Au, Cu: <111>). *d* First ionization potential in the gas phase.

evaporated metal surface M′. SAMs were formed on Hg and on the solid metal surface M′ following established procedures.[4,7] The mercury−SAM surface was then brought into contact with the solid metal−SAM surface using a micromanipulator (Scheme 1). The SAMs isolate the two metal surfaces electrically and chemically and thereby prevent amalgamation: a clean Hg drop, brought into contact with a clean coinage metal surface, immediately wets and spreads and then amalgamates. The two electrodes of the junction were connected to a computer-controlled potentiostat (in two-electrode mode) for I−V measurements. The junction is easily assembled and disassembled by moving the Hg drop in and out of contact with the SAM-M′ surface using the micromanipulator. The contact areas can be controlled over a range between 0.01 and 1.0 mm² by changing the initial size of the Hg drop and by the pressure applied to the drop by the micromanipulator when the metal−SAM surfaces are in contact.

Results and Discussion

1. The Junction. A. Fabrication. The SAMs on the solid metal surfaces (Ag, Au, Au/Hg, Cu) were formed over ∼24 h by exposure to a solution of alkanethiol in ethanol (10 mM). The SAM on the Hg drop was formed in situ (∼5 min to a 10 mM solution of alkanethiol in ethanol). Every junction was assembled in the presence of a solvent containing alkanethiol (normally ∼10 mM). This procedure allowed the SAM to form on mercury and increased the stability of the junction.[24] We hypothesize that this stabilization reflects both the healing of defects caused by the motion of the liquid surface and the stabilization of the drop against vibration by viscous damping. The contact area of the Hg−SAM/SAM−Ag junction was calculated on the basis of capacitance measurements with the junction immersed in thiol-containing solvent (see below).[1] The performance of the junction was not sensitive to the speed at which the mercury drop was lowered (over a range from 0.1 to 1 mm/s), or to low levels of vibration in the room. We carried out preparations and measurements on a bench in the open laboratory, with no special precautions to avoid dust. Small particles in the interface should, however, be avoided because they can influence the breakdown voltage measurement (Table 2). The nature of the solvent influenced the characteristics of the junction (see the following discussions). Stable junctions are formed in more than 90% of attempts using alkanethiols longer than C10. Junctions formed with shorter alkanethiols (<C9) are more sensitive than those with longer ones and must be assembled more carefully.[25]

(24) A M′−SAM/Hg junction can also be formed but is less stable. We will report studies of this junction separately.

(25) Short-chain alkanethiols (C4−C6) form mechanically stable junctions but immediately breakdown when a small potential (10 mV) is applied.

Table 2. Influence of Several Parameters on the BDV of the Hg−DT/HDT−Ag Junction

parameter		BDV [V][a]
standard[b]		3.2 ± 0.5
solvent	acetonitrile	3.0 ± 1.0[c]
	ethanol	3.2 ± 0.5
	glycerol	5.5 ± 1.3[c,d]
	hexadecane	2.7 ± 0.6
	i-octane	2.6 ± 0.3
	perfluorononane	6.4 ± 1.1[c,d]
	water	2.5 ± 0.7[c]
electrolyte (1 mM in EtOH)	Bu₄NOH	1.6 ± 0.2
	F₃CCO₂H	1.2 ± 0.1
	LiClO₄	1.3 ± 0.2
	NaOH	1.7 ± 0.2
electrolyte (1 mM in water)	Bu₄NOH	1.4 ± 0.5
	LiClO₄	1.1 ± 0.3
measurement under	argon	3.1 ± 0.3
	darkness	3.2 ± 0.4
addition of powder in the interface of the junction before assembly	talcum powder	5 to >10[e,f]
	carbon black	0
preparation of the Ag-surface (evaporation method used)	thermal 100 nm	2.9 ± 0.2
	200 nm	3.2 ± 0.5
	400 nm	2.6 ± 0.3
	e-beam 200 nm	2.8 ± 0.5
concentration of HDT[g] in the preparation of the Ag-SAM	0.1 mM HDT, 2 d	3.3 ± 0.5
	1.0 mM HDT, 2 d	3.6 ± 0.5
	10 mM HDT, 2 d	3.2 ± 0.5
	10 mM HDT, 24 h	3.2 ± 0.5
concentration of HDT[g] in the preparation of the Hg-SAM	1.0 mM HDT, 5 min	2.5 ± 0.4
	1.0 mM HDT, 15 min	3.1 ± 0.5
	10 mM HDT, 5 min	3.2 ± 0.5
concentration of HDT[g] in the solvent surrounding the junction	1.0 mM HDT	3.2 ± 0.5
	10 mM HDT	3.2 ± 0.5
method of assembly[h]	with potential: 1V	3.0 ± 0.3
	without potential	3.2 ± 0.5
number of cycles from 0-2V at 100 mV/s before BDV measurement[i]	0	3.2 ± 0.3
	10	3.1 ± 0.5
	100	2.9 ± 0.4
time the junction was in assembled before measurement (min)	1	3.2 ± 0.5
	10	3.0 ± 0.6
	100	2.7 ± 0.4

a The experimental uncertainties are based on the differences between the maximum and minimum values of BDV obtained in five independent measurements on the same wafer. Thus, for example, "3.2 ± 0.5" reflects the fact that the maximum and minimum values of BDV differed by 1.0 V. *b* Unless otherwise indicated, the values were measured on a Hg−HDT/HDT−Ag junction (HDT = hexadecanethiol) having these parameters: 22 °C on a open laboratory bench, sweep rate 1 V/s, Hg positively biased in ethanol containing 10 mM hexadecanethiol, Hg surface (200 nm, thermally evaporated), Ag-HDT and Hg-HDT SAMs were formed in a 10 mM solution of hexadecanethiol in ethanol for 24 h (Ag) and 5 min (Hg). *c* This solvent does not dissolve substantial concentrations of hexadecanethiol (<1 mM), and the junction was less reproducible than junctions made in other solvents. *d* For this junction, a very low capacitance was measured (C < 0.1 nF, A = 0.5 mm²), suggesting a large distance between the two electrodes and the presence of a solvent layer in the interface (compare Figure 3). *e* The two surfaces are propped apart by the particles of the powder. *f* The breakdown voltage depends on the amount of talcum powder added. *g* HDT = hexadecanethiol; ethanolic solution. *h* The Hg−SAM surface was brought into contact with the HDT−Ag surface with and without a potential between the two surfaces. *i* The junction was cycled between 0 and 2 V for the indicated number of cycles.

The measurement of a breakdown voltage (BDV) can be repeated on the same metal surface several times by generating a fresh Hg−SAM drop and moving it laterally to a new spot on the solid metal surface: by using a 3″ wafer, it was possible to make ∼50 measurements of BDV in ∼8 h. To test if mercury diffusion across the junction influenced the BDV, we compared values obtained immediately after the mercury drop had been brought into contact with the SAM−Ag surface and after they had been in contact for 10 and 100 min: there were no significant differences between the values obtained (Table 2).
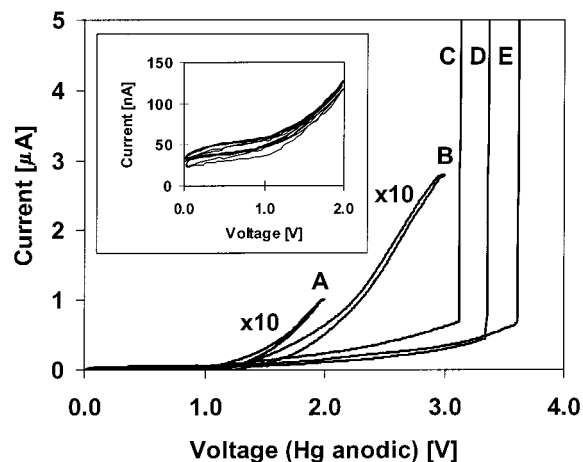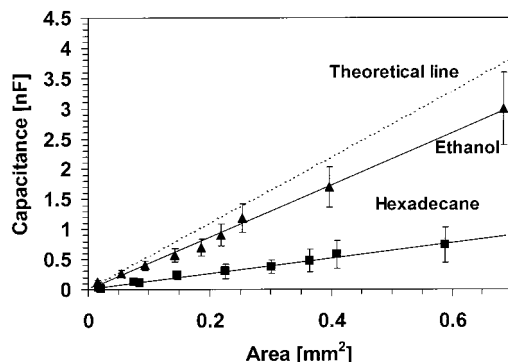
Figure 2. Representative I−V curves for the Hg−HDT/HDT−Ag junction. Curves A and B show I−V diagrams for the Hg−HDT/HDT−Ag junction at voltages below breakdown. The voltage was swept reversibly at a rate of 50 mV/s from 0 to 2 V for A and from 0 to 3 V for B (the current is amplified by a factor of 10). Curves C, D, and E show typical examples of breakdown voltage measurements (BDV = 3.1, 3.3, 3.6 V) for three different Hg−HDT/HDT−Ag junctions. The voltage was swept from 0−4 at a rate of 1 V/s. The inset shows every 10th cycle for I−V measurements from 0 to 2 V (note the different current scales). All measurements were performed with Hg positively biased in ethanol, containing hexadecanethiol (10 mM).

In addition, XPS did not reveal any Hg on the surface of a SAM on Ag that had been in contact with a SAM-coated drop of Hg for 1 h (with no applied potential) in a Hg−HDT/HDT−Ag junction.[26]

B. Measurement. Once assembled, the Hg−HDT/HDT−Ag (HDT = hexadecanethiol) junction was stable. The BDV of each junction was indicated by the abrupt/irreversible rise in current in the I−V diagram. Figure 2 shows I−V diagrams for the Hg−HDT/HDT−Ag junction obtained by sweeping the applied potential with the Hg electrode positively biased. We also examined the effect of sweeping the potential over voltage ranges in which the Hg electrode was negatively biased (see the Supporting Information). Since the junction incorporates two different metals, it is unsymmetrical; this asymmetry is reflected in different I−V curves when biased with different polarity, although the breakdown voltages of the junction were similar. A value of BDV = 3.2 ± 0.4 V was obtained when the mercury was positively biased, and a value of BDV = 2.6 ± 0.5 V was obtained when Hg was negatively biased.

The I−V curve for the negatively biased mercury showed that, below potentials of about −1 V, the junction underwent some irreversible transformation, as can be seen by the hysteresis and the substantially reduced value of the BDV when mercury was again biased as anode (see the Supporting Information). When the Hg was positively biased, we could not observe any significant hysteresis even at voltages close to the BDV. I−V measurements at voltages below breakdown could be repeated many times (>100, when the voltage was cycled from 0 to 2 V at 100 mV/s over an interval of 3 h) without change in the shape of I−V curves (inset in Figure 2) or in the value of BDV ultimately obtained (Table 2). When the voltage was cycled to

Figure 3. Plot of capacitance versus contact area for the Hg−HDT/HDT−Ag junction in ethanol and hexadecane, each containing 10 mM hexadecanethiol (HDT). The contact area was monitored by a video camera using a 50× objective, and the capacitance values were measured using a digital multimeter. The theoretical line was calculated under the assumption of a thin-film capacitor: $C/A = \epsilon_{SAM}\epsilon_o/d$ ($\epsilon_{SAM} = 2.5$, $\epsilon_o = 8.85 \times 10^{-12}$ C^2/Nm^2, $d = 40$ nm). The length of the bar indicating uncertainty is twice the difference between the mean and the extreme values.

voltages higher than 2 V, the lifetime of the junction decreased: on sweeping the voltage from 0 to 2.5 V the junction survived 5−10 cycles; from 0 to 3 V, 1−2 cycles.

C. Solvent Effects. The BDV measurements were performed with the Hg−HDT/HDT−Hg junction in contact with different solvents: acetonitrile, ethanol, glycerol, hexadecane, isooctane, perfluorononane, and water (Table 2). While the current depends on the conductivity of the solvent and other factors,[27] the values of BDV seem to be relatively independent of the solvent. For solvents such as acetonitrile, glycerol, perfluorononane, and water, which do not dissolve substantial concentrations of hexadecanethiol (<1 mM), variations in BDV are higher; this variability demonstrates again the need of an alkanethiol solution surrounding the junction in order to stabilize it.

We have measured the capacitance (C) values in ethanol and hexadecane for different contact areas (A) to determine the distance (d) between the two electrodes and to estimate the amount of the solvent entrapped between the two metal−SAM surfaces (Figure 3). The contact area was evaluated using a video camera with a 50× objective. These junctions show a linear relationship between capacitance and contact area, as one would expect for thin film capacitors.[1] The theoretical line has been calculated under the assumption of a Hg−HDT/HDT−Ag junction with no solvent in the interface $C/A = \epsilon\epsilon_o/d$ ($\epsilon_{SAM} = 2.5$, $\epsilon_0 = 8.85 \times 10^{-12}$ C^2/Nm^2, $d_{HDT/HDT} = 4.0$ nm). The capacitance values measured for the junction with a given area of contact between the Hg−SAM and SAM−Ag surfaces in ethanol are close to the theoretical value of capacitance. This observation, which is supported by the results obtained for the Hg−SAM/SAM−Hg junction,[1] suggests that there are no significant amounts of ethanol in the interface between the two SAMs. For hexadecane, however, the lower slope in the plot of capacitance versus distance suggests a larger distance between the two electrodes and the presence of a thin layer of solvent in the interface.[1,28] We have used ethanol as a solvent for all BDV

(26) A Hg−HDT/HDT−Ag junction was assembled and left for 1 h in contact. After disassembly of the junction, the contact area on the Ag−HDT surface was analyzed by XPS spectroscopy; no detectable levels of Hg were observed. In contrast a sample of Ag−HDT exposed to mercury vapor (in a closed chamber for 30 min), followed by successive washing with ethanol, showed significant levels of Hg on the Ag−HDT surface in the XPS spectrum.

(27) The absolute value of the current for the junction depends on the surrounding solvent and is higher in acetonitrile, water, and ethanol than in isooctane or hexadecane and perfluorononane. A larger separation of the two electrodes (cf. Figure 3) by an unpolar solvent can also be the cause for this observation.

(28) Another explanation for a slope lower than the theoretical slope in the capacitance vs contact area plot (Figure 3) might be that we have overestimated the contact area, based on the visual measurement of the contact diameter.
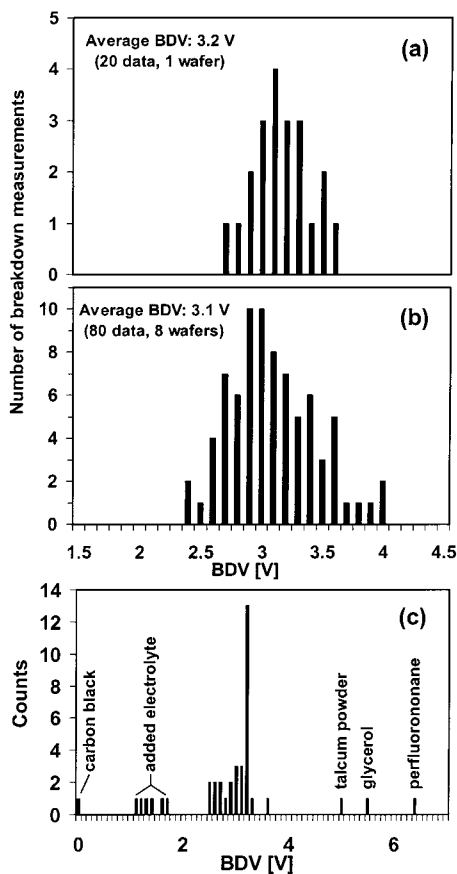
Figure 4. (a) The distribution of 20 BDV measurements taken on the same wafer, and (b) the distribution of 80 BDV measurements taken on 8 different wafers for the Hg−HDT/HDT−Ag junction, with Hg as the anode, in a 10 mM solution of hexadecanethiol in ethanol (sweep rate 1V/s). (c) Histogram for parameters reported in Table 2 illustrating the clustering of BDV values around 3.2 V for the Hg−HDT/HDT−Ag junction under a variety of conditions.

measurements because it does not affect the distance between the metal−SAM surfaces and forms the most stable and reproducible Hg−SAM/SAM−M′ junctions.

D. Reproducibility. Junctions suitable for studies in molecular electronics must be highly reproducible and well characterized. This section reports the effect of different assembling procedures, external parameters, and measurement conditions on the BDV value in the Hg−HDT/HDT−Ag junction (HDT = hexadecanethiol). The BDV measurements are consistent for the same SAM−metal sample (maximum deviation <15%) and less consistent for different SAM−metal samples (maximum deviation <30%) (Figure 4). The individual values of BDV approach a statistical distribution about the mean BDV for a given junction. Since each BDV is the average of only 5−10 measurements and the commonly used statistical tests require larger numbers of data than this, we have chosen to estimate the precision of the experiment as twice the difference between the maximum and average BDV. The I−V curves have been recorded below and up to the BDV. We can sweep the voltage many times without evidence of significant electrochemical processes (e.g., cathodic stripping of the SAM),[7] provided that (i) Hg is positively biased and (ii) the upper limit of the voltage range is ∼20% below the BDV. Provided that these limits are kept, only a small hysteresis is observed on repeated cycling (inset in Figure 2).

The influence of different parameters on the BDV value is summarized in Table 2. The value of BDV observed in different environments with this junction is generally insensitive to external conditions, although it is sensitive to the presence of electrolytes in aqueous and ethanolic solution.[29] No significant difference in the value of BDV was observed for measurements carried out under air and in oxygen-free solutions. BDVs were measured for the Hg−SAM/SAM−Ag junction between 0 and 50 °C in ethanol: the BDV values were indistinguishable (3.2 ± 0.6 V) over the whole temperature range. The thickness of the underlying metal and the type of evaporation (e-beam versus thermal evaporation) seemed to result in small, systematic variations in the value of BDV: thicker and therefore rougher surfaces show smaller values of BDV; thermally evaporated metal films show slightly higher BDVs, which might arise from a decreased roughness through thermal annealing.[30] During the thermal evaporation at a rate of 0.1 nm/s, the temperature usually increased to ∼100 °C in the evaporator, while during the e-beam evaporation the substrate temperature increased only slightly (∼50 °C).[31] The concentration of the alkanethiol solutions forming the SAM on each metal surface seemed to have only a small effect on the BDV values. To obtain densely packed metal−SAM surfaces within short time, we chose a 10 mM concentration of alkanethiol in ethanol in preparing SAMs.

The only values significantly deviating below the standard (3.2 V) are those obtained by the addition of carbon black (0 V) and electrolytes (1.1−1.7 V). The higher breakdown voltages in some solvents (glycerol, perfluorononane) and after the addition of talcum powder can be explained with a larger separation of the two electrodes as indicated by capacitance measurements.

There is a small influence of the sweep rate on the average breakdown voltage over the range 10−10000 mV/s: higher sweep rates show slightly higher values of BDV (∼0.2 V). The deviation in the BDV measurements is smallest at the highest sweep rates (>100 mV/s) (data shown in Supporting Information). We chose a sweep rate of 1 V/s for most measurements.[32]

2. Structure−Property Relationships. We have used the Hg−SAM/SAM−M′ junction to measure I−V curves and breakdown voltages (BDV) of (i) hexadecanethiol SAMs on different metals (Ag, Au, Cu, Hg, Au/Hg), (ii) alkanethiol SAMs of different length (C7, C8, C9, C10, C11, C12, C14, C16, C18, C22, C26) on silver, and (iii) SAMs on silver and gold of different structural types, including aromatic and functionalized thiols.

A. Dependence of the BDV on the Metal Surface. We measured the BDV of three alkanethiols (C9, C16, and C26) on five metals (Ag, Cu, Hg, Au/Hg, and Au) (Figure 5). The results are internally consistent within this series of experiments. We describe in detail the results obtained using HDT-SAMs, (hexadecanethiol, C16) since the metal−HDT surface is usually used as a standard for comparison in experiments involving SAMs.[4,5,7,18] We observed similar results with C9 and C26 although the shorter alkanethiols (<C10) yield less stable junctions, and longer alkanethiols (>C20) tend to precipitate

(29) The addition of electrolytes might enhance electrochemical processes on the metal surfaces, such as cathodic stripping of the thiol; compare ref 7a,e.

(30) Guo, L.-H.; Facci, J. S.; McLendon, G.; Mosher, R. *Langmuir* **1994**, *10*, 4588−4593.

(31) We also compared the breakdown voltages of Au−HDT surfaces obtained from e-beam-evaporated gold (Au$_{eb}$) with those from thermally evaporated gold (Au$_{th}$). The Au$_{eb}$−HDT surfaces showed an average breakdown voltage of 1.5 ± 0.2 V, whereas the value for the Au$_{th}$−HDT surface was significantly higher: 2.2 ± 0.5 V. We attribute this observation to the effect of thermal annealing on of the gold surface, generating larger grains and fewer pinholes in the Au−SAM surface.

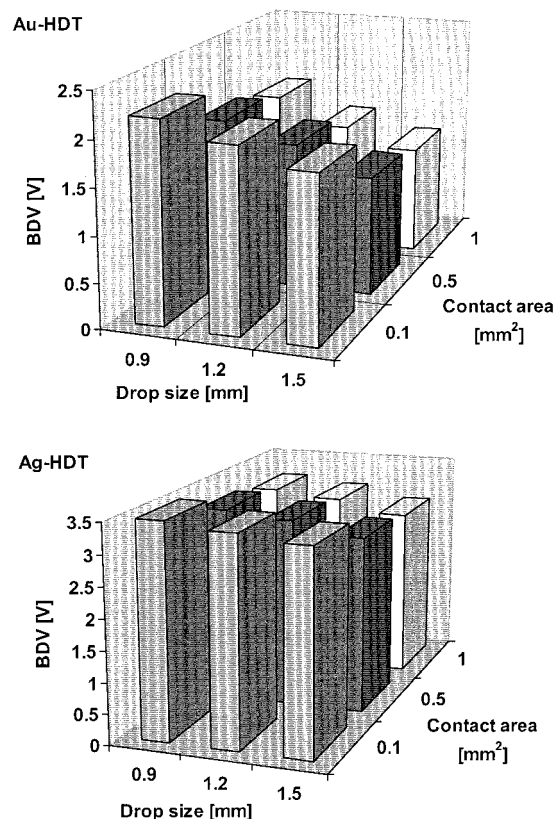(32) For shorter alkanethiols (<C10), a sweep rate of 100 mV/s was used.
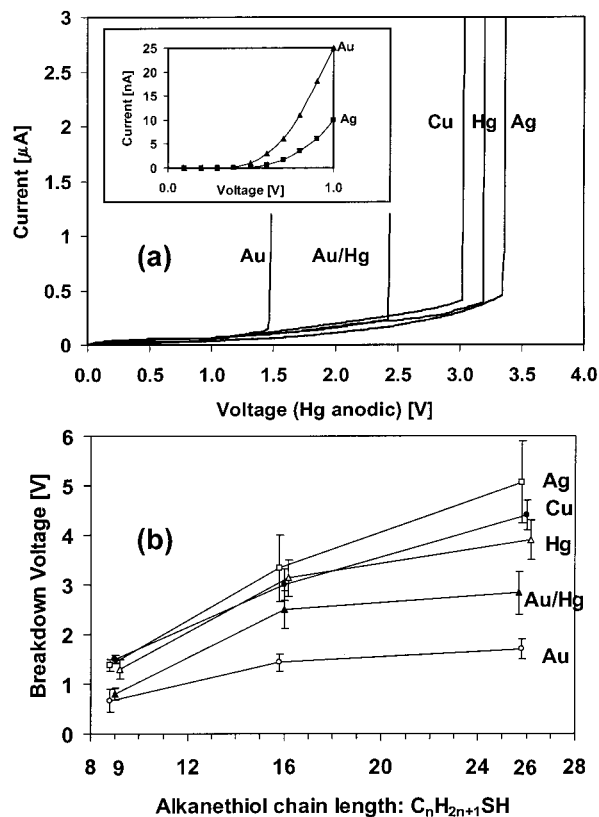
Figure 5. (a) Representative I−V curves for the electrical breakdown of hexadecanethiolate (HDT) SAMs in Hg−HDT/HDT−M′ junctions (M′ = Ag, Au, Ag/Hg, Cu, and Hg). The breakdown voltage of each junction (indicated by the abrupt rise of the current) was obtained by sweeping the voltage from 0 to 7 V at a rate of 1 V/s (all measurements were performed in a 10 mM solution of hexadecanethiol in ethanol). The inset shows the I−V curves of the Hg−HDT/HDT−M′ junctions (M′ = Ag, Au) from 0−1 V, using individual static potentials in 100 mV steps (note the difference of 10^3 between the scales of current). (b) Average breakdown voltages (lines) for different metals in the Hg−SAM/SAM−M′ junction: M′ = Ag (□), Cu (●), Hg (△), Au/Hg (▲), and Au (○) as a function of the alkanethiol chain length (C9, C16, and C26). The average breakdown voltages were obtained from five independent measurements for each M′−SAM combination. The length of the bar indicating uncertainty is twice the difference between the mean and the extreme values. The data for some of the metals were spread slightly horizontally to avoid overlap. The breakdown voltage of each junction was obtained by sweeping the voltage from 0 to 7 V at a rate of 1 V/s. All measurements were performed in a solution of ethanol containing hexadecanethiol (10 mM).

from their solutions in ethanol. Figure 5 shows representative I−V curves for Hg−HDT/HDT−M′ (M′ = Ag, Cu, Hg, Au/Hg, Au) junctions. There are four important inferences from these experiments. (i) The current increases with a nonlinear[33] dependence on voltage, as expected for a metal−insulator−metal junction,[34] up to the voltage at which the junction breaks down. (ii) For a given voltage, the current measured across a junction incorporating a Au−SAM electrode is higher than for a Ag−SAM electrode by a factor of ∼2.5 (insert of Figure 5a). (iii) At the same time that the junction breaks down electrically, the mercury drop merges with the underlying metal surface (Scheme 1). Thus, electrical breakdown results in disruption of

Figure 6. Dependence of the BDV on the contact area for Au−HDT (top) and Ag−HDT junctions (bottom). Two parameters, the Hg drop size (before contact) and the observed contact area (measured by videomicroscopy, using a 50× objective), were investigated for each junction.

the SAMs and contact of the mercury with M′. (iv) The values of BDV increase in the order Au < Hg ≈ Cu ≈ Ag. The BDV for the junction incorporating Ag−SAM as one component depends less on the contact area than that having Au−SAM (Figure 6). This observation is compatible with the hypothesis that the Au−SAM system has more defects than the Ag−SAM system[35] and that these defects contribute to electrical breakdown.

The BDV values depend on the SAM−metal combination in a way that correlates, at least generally, with the tilt angle and therefore the in-plane density of the SAM (Table 1).[4,5,36] For SAMs on Au, which exhibit the largest R−R distances and tilt angles, the value of BDV is lowest. Although the differences between SAMs on Ag, Cu, and Hg are not statistically significant, we believe that the SAMs that form on Ag seem to provide the best electrical insulation of the solid metal surface.[37]

The difference in BDV values between SAMs on Au and SAMs on Ag, Cu, and Hg surfaces, whatever its origin, cannot be due to surface morphology alone. We used evaporated films of Au, Ag, and Cu that were ∼200 nm thick: the peak-to-valley roughness of these surfaces seems, from many studies of them by AFM and STM,[5c,30,36] to be approximately 10−20% of their thickness, and the influence of the thickness on the BDV was relatively small (cf. Table 2). The surface of mercury is, however, smooth, and the surface of SAM−Hg also seems to

(33) Theoretically the dependence of the current on the voltage is determined by the mechanism of conductivity, which is different for different voltage regimes. The complexity of the junction does not allow us to study this relationship.

(34) Simon, J.; Andre, J.-J. *Molecular Semiconductors*; Springer: New York, 1985.

(35) Van Patten, P. G.; Noll, J. D.; Myrick, M. L. *J. Phys. Chem. B* **1997**, *101*, 7874−7875.

(36) Hutt, D. A.; Cooper, E.; Leggett, G. J. *Surf. Sci.* **1998**, *397*, 154−163.

(37) Silver provides a good surface for densely packed monolayers studied by various techniques; compare refs 5c, 6, 36.
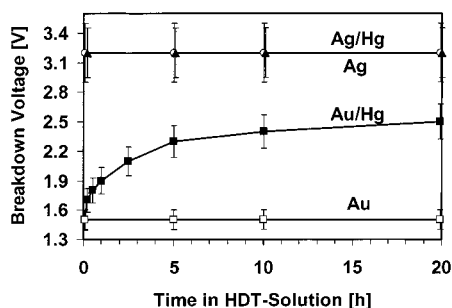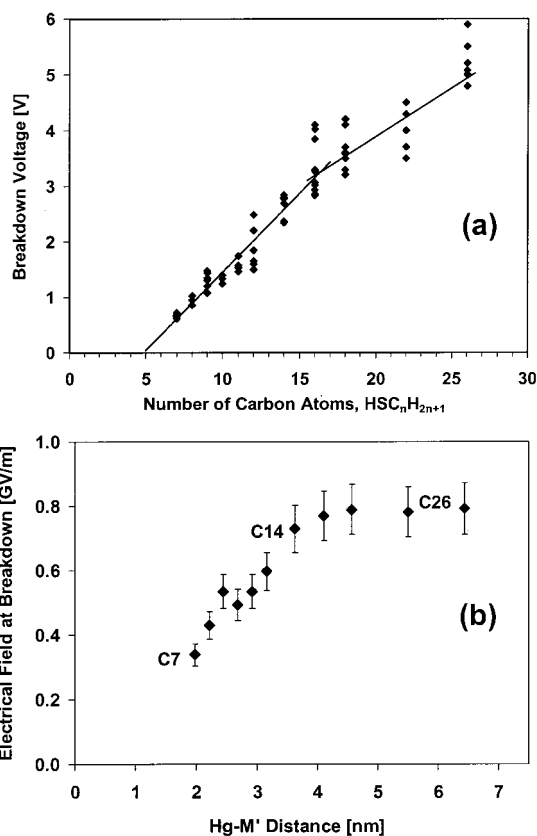
Figure 7. Evolution of the breakdown voltage with the time in which the planar metal surface was incubated with a 1 mM solution of hexadecanethiol (HDT) in ethanol before assembly of the junction: (a) Au−HDT surface (au, □), (b) Au-HDT surface treated with Hg vapor for 30 min (Au/Hg, ■), (c) Ag-HDT surface (Ag, ○), (d) Ag-HDT surface treated with Hg-vapor for 30 min (Ag/Hg, ▲). The sweep rate for the I−V curve was 100 mV/s, and three measurements were performed and averaged to determine each BDV. The length of the bar indicating uncertainty is twice the difference between the mean and the extreme values.

be smooth.[18] Since junctions based on Ag, Cu, and Hg are similar in BDV and that based on Au is different, it thus seems unlikely that surface morphology/topography alone determine the value of the BDVs.

SAMs derived from fluorinated alkanethiols on Au are incommensurate with the Au (111) lattice, probably because the cross-sectional diameter of the extended fluorinated alkanethiols (5.6 Å) is larger than that of alkanethiols (4.5 Å).[4,38] The fluorinated alkanethiols form SAMs on Au with a smaller tilt angle ($12° \pm 2°$) than alkanethiols and an interchain distance of 5.8 Å (compared to 5.0 Å for alkanethiols; cf. Table 1). We have compared the BDVs of HS−$(CH_2)_2(CF_2)_9CF_3$ and of C12 alkanethiol having the same carbon chain length supported on Au and Ag surfaces: on gold the fluorinated SAM has a BDV of 2.2 ± 0.4 V, almost twice the value of the hydrocarbon SAM with the same chain length (BDV = 1.3 ± 0.3 V); on silver the difference between the BDV values of fluorocarbon SAM (2.3 ± 0.3 V) and hydrocarbon SAM (1.9 ± 0.4 V) are not statistically significant. These results support other observations throughout this work in suggesting that dense packing and a value of θ_t close to $0°$ correlate with high values of BDV.

The role of the lateral density of the SAM in determining the BDV is further confirmed by BDV measurements using a Au/Hg−SAM and Ag/Hg−SAM surface as one of the electrodes. These surfaces are prepared by treating Ag−SAM and Au−SAM with Hg vapor and alkanethiol, according to the procedure of Grunze et al.[23] The BDV of Au/Hg−SAM increased from 1.5 to 2.5 V over a time span of 20 h after reimmersion in hexadecanethiol solution (Figure 7) (although it never reached the value of BDV characteristic of Ag−SAM). Grunze has established that conversion of Au−SAM to Au/Hg−SAM is accompanied by a decrease in θ_t and an increase in packing density. The BDV for the Ag−SAM system does not increase with this procedure. The treatment of Ag−SAM with Hg vapor and a solution of HDT has not been studied previously, but the lack of an effect is not surprising, since Ag−SAM is already highly ordered and densely packed. The effect on the BDV of the increased lateral density is substantial even if it does not reach the high value of Ag−SAM, probably because of the reported heterogeneous structure of the Au/Hg−SAMs.[23]

(38) Liu, G.; Fenter, P.; Chidsey, C. E. D.; Ogletree, D. F.; Eisenberger, P.; Salmeron, M. *J. Chem. Phys.* **1994**, *101*, 4301−4306.

Figure 8. (a) Dependence of the breakdown voltage on the alkanethiol chain length for the Hg−SAM/SAM−Ag junction. The BDV was measured for eleven *n*-alkanethiols (C7, C8, C9, C10, C11, C12, C14, C16, C18, C22, and C26)[25] using at least five independent junctions for each thiol on the same wafer. Inset: the best linear least-square fit to the data (with uniform weighting gives two different slopes): 0.28 V/CH₂ unit for short alkanethiols (C7-C14), and 0.17 V/CH₂ unit for long alkanethiols (C16-C26). The *x*-intercept (BDV = 0 V) occurs at ∼5 carbon atoms.[25] See Supporting Information for a tabulated presentation of the data in Figure 8a. (b) Plot of the electrical field (GV/m) at breakdown versus the estimated distance between the two metal surfaces for the Hg−SAM/SAM−Ag junction. The electrical field (E = BDV/d) values were calculated from the average breakdown voltages; the electrode distances (d) were determined according to the published thickness of alkanethiolate SAMs on the surfaces of Ag and Hg.[5a] The length of the bar indicating uncertainty is twice the difference between the mean and the extreme values.
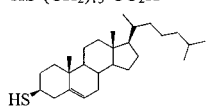
B. Dependence of the BDV on the thickness of the SAM. Figure 5b shows the values of BDV for different lengths of alkanethiolate SAMs (C9, C16, C26) on five different metals (Ag, Au, Au/Hg, Cu, and Hg). On each metal, the BDV of the SAM depends on the length of the thiol. We have also studied the dependence of the BDV on the thickness of the SAM, using the Hg−SAM/SAM−Ag junction, where the SAMs are formed from a series of alkanethiols (Figure 8a).[25] The BDV shows an approximately linear dependence on alkanethiol chain lengths from C7 to C16 (increasing by ∼0.3 V per CH₂ group), while for longer alkanethiols, from C16 to C26, it increases more slowly (∼0.2 V per CH₂). Figure 8b plots the electrical field (E = V/d) at the BDV versus the thickness (d) of the SAMs: E increases approximately linearly for shorter alkanethiols (C7−C14) and becomes constant after C14. Shorter alkanethiols are less ordered and less densely packed than longer ones;[5] SAMs from these alkanethiols are less stable (per unit of thickness) to electrical breakdown than are those formed from higher *n*-alkanethiols. After C14, the electrical strengths of the SAMs reach a value of 0.8 GV/m. The highest observed breakdown

Table 3. Average Breakdown Voltage of the Hg−SAM/SAM−M′ Junction for SAMs with Different Chemical Structure Au and Ag and Alkanethiolate SAMs with Similar Thickness

| entry	thiol (HS−R) used to form the SAMs	BDV [V][a]	
		Ag−SAM	Au−SAM
1	HS-(CH$_2$)$_2$(CF$_2$)$_9$CF$_3$[b]	2.3 ± 0.3	2.2 ± 0.4
	HS-(CH$_2$)$_{11}$CH$_3$	1.9 ± 0.4	1.3 ± 0.3
2	HS-H$_2$C-⬡-⬡	1.3 ± 0.3	0.7 ± 0.2
	HS-(CH$_2$)$_8$CH$_3$	1.3 ± 0.2	0.7 ± 0.3
3	HS-⬡-⬡	0.68 ± 0.3	ns[c]
	HS-(CH$_2$)$_7$CH$_3$	0.95 ± 0.1	nd[d]
4	HS-⬡⬡	0.65 ± 0.1	ns[c]
	HS-(CH$_2$)$_6$CH$_3$	0.67 ± 0.04	ns[c]
5	HS-⬡⬡	0.23 ± 0.08	ns[c]
	HS-(CH$_2$)$_5$CH$_3$	ns[c]	ns[c]
6	HS-(CH$_2$)$_{11}$(OC$_2$H$_4$)$_3$OMe	1.6 ± 0.2	nd[d]
	HS-(CH$_2$)$_{11}$(OC$_2$H$_4$)$_6$OMe	1.7 ± 0.3	nd[d]
	HS-(CH$_2$)$_{21}$CH$_3$[e]	4.0 ± 0.5	nd[d]
7	HS-(CH$_2$)$_{15}$-CO-PEI/ HS-(CH$_2$)$_{15}$-CO$_2$H[f,g]	3.0 ± 0.3	nd[d]
	HS-(CH$_2$)$_{15}$-CONHC$_{12}$H$_{25}$/ HS-(CH$_2$)$_{15}$-CO$_2$H[g]	5.7 ± 0.8	nd[d]
8	(cholesterol structure) HS-	ns[c]	ns[c]

[a] All measurements were performed with Hg positively biased, in a solution of ethanol, containing the thiol being examined (10 mM). The experimental uncertainties are based on the differences between the maximum and minimum values of BDV obtained in five independent measurements on the same wafer. [b] Major component in a mixture of fluorinated thiols (Tolumer B thiol).[51] [c] Junction is mechanically stable but immediately breaks down when a potential is applied (ns: not stable). [d] nd: not determined. [e] SAM with the same number of carbons (similar length). [f] PEI (polyethylene imine) cross-links the underlying carboxylic anhydride SAM; ref 41. [g] This surface was prepared from a surface presenting an interchain carboxylic anhydride [S(CH$_2$)$_{15}$CO-]$_2$O used by the procedure in ref 42, followed by reaction with the amine; this reaction sequence results in a SAM terminated in a 1:1 ratio of amide and carboxylic acid groups. The mercury surface was covered with a HDT-SAM.

voltage, 5.9 V (cf. Figure 8a), was recorded for the Hg−S(CH$_2$)$_{25}$CH$_3$/ CH$_3$(CH$_2$)$_{25}$S−Ag junction; this value corresponds to an electrical field of ~1 GV/m.

C. Dependence of the BDVs on the Chemical Structure of the SAMs. To extend the classes of compounds studied beyond the saturated aliphatics, we surveyed SAMs of different chemical structures (Table 3 and Figures 9, 10): (i) SAMs of several aromatic thiols, which are known to be densely packed, with R−R distances similar to those of alkanethiols.[39] (ii) Two SAMs derived from 11-(triethyleneglycol)-undecane-1-thiol and 11-(hexaethyleneglycol)-undecane-1-thiol; in these SAMs the oligoethyleneglycol groups are more flexible than hydrocarbon chains and not well packed.[40] (iii) Two SAMs, generated by reaction of an anhydride terminated C16 SAM with polyethylenimine (PEI)[41] and C12 alkylamine.[42] The length of the C12

(39) (a) Sabatani, E.; Cohen-Boulakai, J.; Bruening, M.; Rubinstein, I. *Langmuir* **1993**, *9*, 4−2981. (b) Chang, S.-C.; Chao, I.; Tao, Y.-T. *J. Am. Chem. Soc.* **1994**, *116*, 6792−6805.
(40) Pertsin, A. J.; Grunze, M.; *J. Phys. Chem.* **1998**, *102*, 4918−4926.
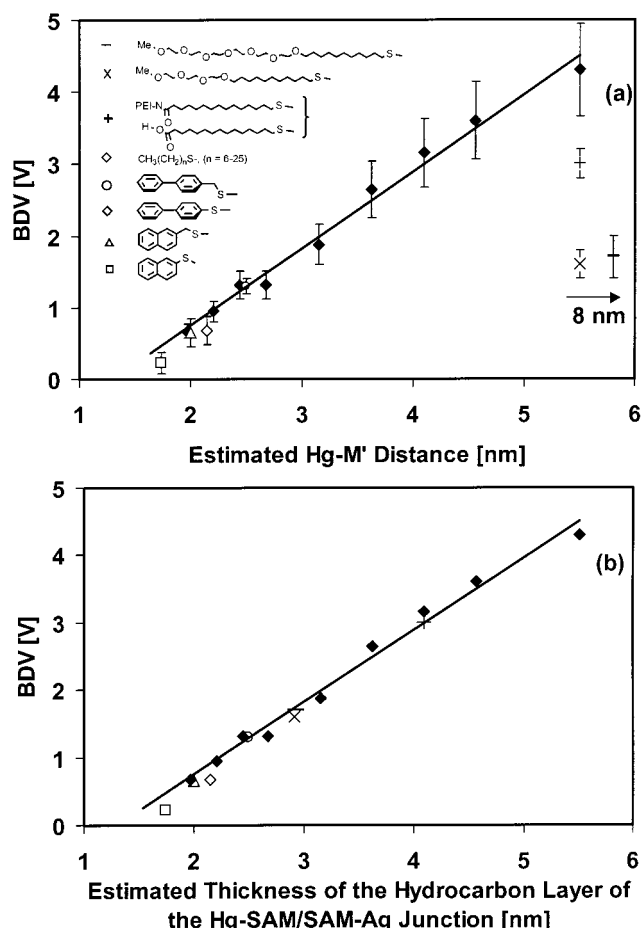
Figure 9. (a) Average values of BDV for SAMs of alkanethiols (◆), SAMs of aromatic thiols (open symbols), a SAM derived from triethyleneglycol-undecanethiol and hexaethyleneglycol-undecanethiol (× and −), and a SAM generated by cross-linking a C16 SAM terminated in interchain carboxylic anhydride with polyethylenimine (+) plotted against the distance of the two electrodes in the Hg−SAM/SAM−Ag junction (the length of the bar indicating uncertainty is twice the difference between the mean and the extreme values). (b) The same average values of BDV plotted against the thickness of the hydrocarbon layer composing each junction. The electrode distances were determined from the estimated thickness of alkanethiolate SAMs on the surfaces of Ag and Hg.[5a]

alkyl chain corresponds to the thickness of the cross-linking PEI (~1 nm). (iv) A SAM of thiocholesterol (a secondary thiol similar in length to C16 thiol).[43] In this case a mechanically stable junction was formed, that is, the SAM-covered Hg-drop did not fuse with the SAM-covered Ag surface when the two were brought in contact, but the junction immediately broke down after application of a potential as small as 10 mV.[25]

Figure 9 displays the data for SAMs of different structure in two plots: Figure 9a shows the BDV vs the estimated overall thickness of the SAM and attached groups; Figure 9b shows the BDV vs the thickness of the crystalline, heteroatom-free (aliphatic (CH$_2$)$_n$ or aromatic) layer. The thickness calculations are based on the number of carbon atoms and θ_t.[5a,39] Two observations emerge from these data (i) the BDV correlates with the thickness of the crystalline layer (CH$_2$)$_n$; there is, to first

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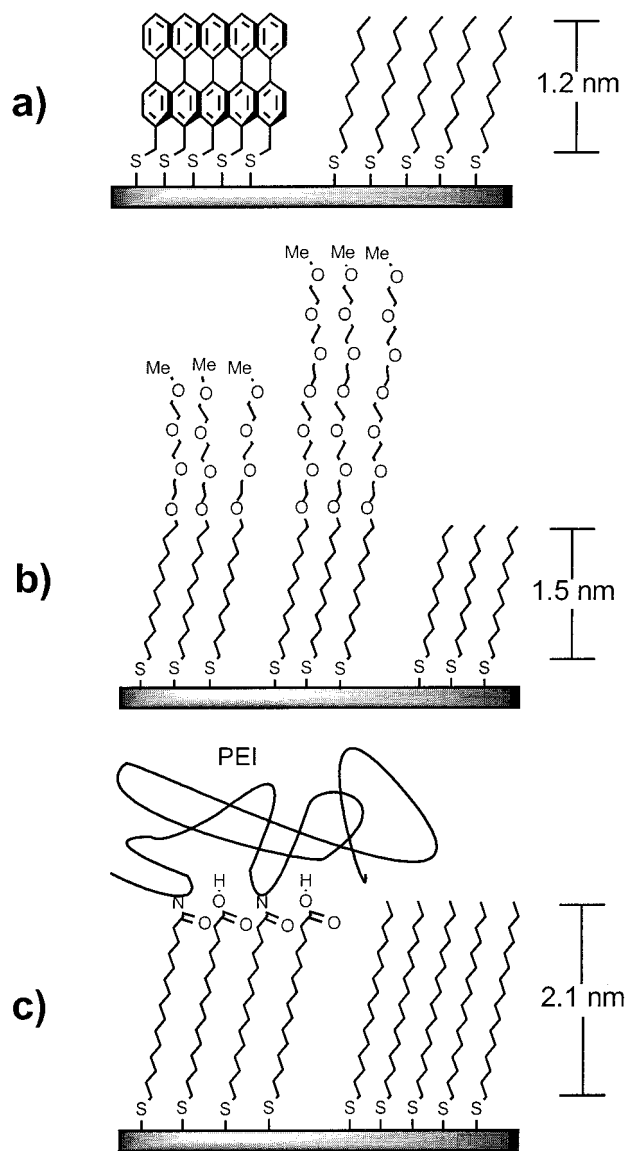
Figure 10. Schematic representations of the structures of SAMs from four types of thiols: an aromatic SAM, two oligoethyleneglycol-containing SAMs of different length, a SAM cross-linked by reaction of PEI with a SAM presenting interchain carboxylic anhydride, and the corresponding alkanethiol SAMs with a similar value of BDV. The scale bars indicate the thickness of the alkanethiolate SAM on M′ and the thickness of the corresponding hydrocarbon layer of functionalized SAMs on M′ (see Figure 9).

order, no contribution to the BDV value from the disordered part of the SAM (e.g., the SAM from oligoethylene glycol functionalized undecanthiol, PEI-cross-linked thiohexadecanoic acid, and thiocholesterol); and (ii) the BDV is independent of the chemical composition of the SAM (aliphatic or aromatic) once it is densely packed and depends only on the thickness of the SAM.

We were surprised that the BDV does not depend on whether the SAM contained aliphatic or aromatic moieties, but only on the thickness of the densely packed hydrocarbon portions of the SAM. This result can be interpreted in more detail only in connection with an understanding of the mechanism of breakdown of the junction. The mechanism of breakdown has been extensively studied for different dielectrics, such as organic insulators (e.g., polyethylene) and thin inorganic films. In thin-film organic dielectrics, such as Langmuir–Blodgett films,[44] two mechanisms seem to fit the experimental data for break-

down: electromechanical collapse (electrostriction) of the film[45] caused by electrical forces applied to the two metal surfaces, and an intrinsic space charge mechanism that results from electrical charges injected into, or extracted from, the insulator by the electrodes.[46-48] In the present case, a pure mechanical breakdown of the SAMs caused by electrostriction would explain the indifference of the BDV to the chemical nature of the SAM. The pressure in the junction Hg–HTD/HTD–Ag, applied to the SAMs by the metal electrodes at a potential of 2 V, can be calculated as ∼100 atm.[49] This pressure could, perhaps, cause a mechanical disruption of the SAM at the Hg surface and/or at the boundaries of the SAM on the solid surface. The abrupt increase of the current (Figures 2 and 5) with the simultaneous merging of the two metal surfaces (Scheme 1) indicates clearly that a mechanical rupture of both SAMs occurs at the BDV. When the flow of current across the junction is limited to ∼10 μA, the two surfaces can, however, be separated with the micromanipulator after the BD has occurred, and only a microscopic rupture of the junction is observed. This observation suggests that the mechanical rupture is a consequence, rather than a cause, of electrical breakdown.

These and other data suggest that electrostriction cannot be the only mechanism of breakdown. The most important of these other data is that the highest value for the electrical field at BD that we observe for alkanethiol SAMs on Ag is indistinguishable from that of thin polyethylene films: $E = 0.8$ GV/m (cf. Figure 8b). Since mechanical failure of polyethylene is certainly not involved in the breakdown of thick films of that material,[50] it seems that the (CH$_2$) region of the SAMs and the polyethylene share a common mechanism for electrical breakdown, and that this mechanism is neither an electrochemical process involving mobile ions nor a mechanical fracture under compression. In addition, the observation that the PEI-cross-linked SAM has the electrical stability expected for its (CH$_2$) region also argues for a mechanism of breakdown based on electrical failure: the PEI plausibly reinforces the SAM laterally against distortion under pressure[41] and would lead to a BDV value higher than that of the hydrocarbon portion if the breakdown was caused by electrostriction.

The presence of electrolytes, even in small concentrations (<1 mM), significantly lowers the BDV values (cf. Table 2). It is possible that small numbers of ions can be trapped in the interface between the two electrodes when it is formed; ionic migration or polarization on application of the potential might contribute to damage the SAMs and ultimately lead to break-down.

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(49) The Hg–HDT/HDT–M′ junction was treated as a parallel plate capacitor. This assumption is justified because the separation between the two metals is much smaller than the surface area in contact with the SAM. The force inside a thin-film capacitor is given as $F = Eq$ (E, electrical field; q, charge), the pressure is given as $P = F/A = Eq/A$. The electrical field is defined as $E = V/d$ (V, potential; d, distance between the two electrodes), the charge is defined as $q = CV$ (C, capacitance) and $C = \epsilon\epsilon_0 A/d$. Hence, the pressure between the two electrodes can be calculated from $P = (V/d)^2 \epsilon\epsilon_0$. At a potential of 2 V, the pressure is 10^7 Pascal or 100 atm ($\epsilon_{SAM} = 2.5$, $\epsilon_0 = 8.85 \times 10^{-12}$ C^2/Nm^2, $d = 40$ nm).

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Conclusions

The Junction. We have built a new type of electrical junction, the Hg−SAM/SAM−M′ junction, where the compliant surface of a Hg drop (and, we infer, of a mercury drop covered with a SAM) allows conformal, nondamaging contact with a second, rigid, SAM-covered metal surface. The dimension of the Hg drop and the pressure applied to the drop by the micromanipulator determine the contact area. The presence of an ethanolic solution of the thiol that forms the SAM in the volume surrounding the contact area makes the junction easy to assemble. This junction is stable to the small deformations of the Hg drop that result from the mechanical motion required to bring it into contact with the solid metal surfaces and from other small-amplitude vibrations. The junction provides a versatile system with which to study the electrical properties of SAMs (and especially the dependence of the electrical properties of these systems on the structures of the organic thiols and the organization of the SAMs). The most difficult part of this system (at least for most organic chemists) is the measurement of the current/voltage curves. These measurements require the ability to measure small (pA) currents and require a good programmable potentiostat and electrometer.[51]

We believe that the junction provides a good "test-bed" with which to examine organic and organometallic compounds being considered as components for molecular electronics. Its major advantage is that it allows a broad range of organic thiols to be incorporated into SAMs and tested. Since it does not require microfabrication, it can be used by most laboratories equipped to make SAMs. It is, thus, a useful system for physical-organic approaches to the study of electron transport through thin organic/organometallic films. The system also has several disadvantages. (i) It relies on liquid mercury: although the mercury offers a junction that is easily and flexibly assembled, it is toxic and volatile and is not a practical material for fabricating real devices. (ii) It cannot easily form contact regions with nanometer dimensions. Although it is easy to form small (1−100 μm) Hg drops, and although even smaller mercury surfaces could undoubtedly be formed by electrodeposition of Hg(0) onto small, lithographically patterned electrodes, the size of these systems would need to be reduced to dimensions that are difficult to manipulate before they would allow electrical measurements on single organic molecules embedded in the SAM. (iii) The system (in its present form) does not allow fabrication of junctions in which there is a continuous path of covalent bonds connecting one metal surface to the other.

Measurements of Breakdown Voltage. The maximum voltage sustained by the junction (BDV) has been measured from I−V curves using a simple potentiostat in two-electrode mode. By using the Hg−SAM/SAM−M′ junction where SAMs are formed by alkanethiols of different chain length on different metal surfaces (M′ = Ag, Au, Cu, Hg), we infer that the thickness of the ordered hydrocarbon layer is the major factor that determines the BDV and note that the value of the BDV correlates with the lateral density and tilt angle of the SAM. The value of the BDV is surprisingly indifferent to the detailed structure of the molecules making up the SAM. This observation implies that these SAMs are acting primarily as simple insulating dielectric layers. The BDV of alkanethiol SAMs on Au is lower by a factor of 2 than those on Ag but can be increased by (i)

Table 4. Electrical Strength of Insulating Materials and HDT SAM on Ag[52]

material	E [GV/m]	material	E [GV/m]
Teflon	25[a]	resins	0.3−0.8
OTS−SAM on Si	0.9−1.2[b]	paraffines	0.2−0.5
HDT-SAM on Ag	0.8[c]	Pyrex	0.17
polyethylene	0.6−0.8[d]	rubber	0.1
quartz	0.7	ceramics	0.05
ODT-SAM on Au	0.4[e]		

[a] Reported for 130 μm thick Teflon sheets (ref 52b). [b] Octadecyltrichlorosilane (OTS) grafted on a silicon wafer (ref 11a). [c] Measured for the Hg−HDT/HDT−Ag junction in ethanol (HDT = hexadecanethiol). [d] Different values are obtained for sheets of different molecular weight PE (ref 52a). [e] Octadecanethiolate SAM on Au (ref 12).

changing the structure of the monolayer (using for example a fluoroalkyl SAM) and (ii) increasing the lateral density of the SAM (using the Au/Hg system described by Grunze[32]). SAMs on Ag have not improved by any strategy we have tested.

The role of the organization of the SAM in determining its electrical strength emerges as a striking result. The electrical strength (the maximum sustainable electrical field) calculated for each alkanethiol SAM shows that HDT-SAM on Ag can sustain an electrical field equal to that of a polyethylene sheet, $E = 0.8$ GV/m; that is, a hexadecanethiol-derived SAM on Ag has an intrinsic electrical strength similar to that of bulk polyethylene. The comparison of intrinsic electric strength of SAMs with other common insulating materials shows that alkanethiol SAMs (>C14) on Ag have one of the highest electrical strengths presently known (Table 4).[52] We conclude that, on Ag surfaces, SAMs longer than C14 show an "intrinsic breakdown", that is, an electrical strength characteristic of the dielectric itself. The values of electrical resistance, recently reported,[1] and the electrical strength of these alkanthiolate SAMs make them excellent thin-film, nanometer-thick materials for dielectric applications.

Breakdown Voltages of SAMs of Different Chemical Structures. We see no evidence that SAMs incorporating simple aromatic groups differ fundamentally in their behavior from aliphatic SAMs. The observation that aliphatic and aromatic systems with similar thickness have similar values of BDV does not bear directly on the question of whether there is, in this system or in others, electron transport involving delocalized orbitals on the organic molecules (that is, some mechanism of transport that might involve the organic molecule acting as a "wire" with substantial conductivity rather than a low-conductivity medium through which electron transport occurs by tunneling).[53] Interpretation of BDV's in terms of conductivities is complicated by the fact that the interface between the two SAMs constitutes an insulating barrier, as do the two different metal−sulfur interfaces; the height and shape of these barriers all remain to be characterized. At this time, we cannot unambiguously define the mechanism of breakdown, but we have direct and indirect data suggesting an electronic component in the BD mechanism. The most important of these data is that the highest value of BDV that we observe is indistinguishable from that for thick (∼1 mm) films of polyethylene. Since mechanical failure of the polyethylene is almost certainly not involved in the breakdown of that material, nor are ionic

(51) The aggregate cost of equipment used for measurements of I−V curves is ∼$10 K. The minimum instrumental requirement to measure breakdown voltages is a digital multimeter and a tunable voltage source (both ∼$100). When the exact currents of the junction below breakdown are of interest, however, a more sophisticated device is required.

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processes involving ions in solution or solvent molecules, it seems that the $(CH_2)_n$ regions of the SAMs and the polyethylene share a common mechanism and probably one involving electronic current.

Experimental Section

Fabrication. All measurements were performed with a two-electrode junction: Hg−SAM/SAM−M′ (Ag, Au, Au/Hg, Cu). A hanging mercury drop electrode was used to generate one metal surface of the junction. A commercial Hamilton gastight 1 mL syringe, in which a tungsten wire was placed through the Teflon stamp to electrically connect the upper metal part of the stamp with mercury reservoir, was used (Scheme 1). Mercury (electronic grade, 99.9998%) was purchased from Alpha. *CAUTION: Mercury can cause CNS injury if inhaled or swallowed.* The size of the Hg droplet before touching the second surface was ∼1 mm in diameter. The second metal surface, Ag(111), Au(111), or Cu, was prepared on Si/SiO$_2$ using reported procedures.[54] The thin metal film (5 nm Cr and 200 nm of Ag, Au, or Cu) was freshly prepared by e-beam or thermal evaporation (Edwards Auto 306) of the metal onto a 3 in. silicon wafer (Silicon Sense, test grade). The evaporation chamber was vented with nitrogen, and the bare metal surfaces were transferred into the solution of thiol through air as soon after evaporation as possible (∼10 min). The Au/Hg−SAM surfaces were prepared according to the published procedure.[23] A freshly prepared Au−SAM surface (see above) was treated with mercury vapor for 30 min in a closed chamber, saturated with Hg vapor (under air). The surface was then reimmersed in a 10 mM HDT solution in ethanol for 24 h. The experimental setup used for the Hg−SAM/SAM−Hg junction was different and has been described previously.[1]

The self-assembled monolayers (SAMs) on gold and silver were formed from a 10 mM solution of the respective alkanethiol in EtOH over 24 h. The monolayers on the hanging mercury drop were formed on a fresh mercury surface, dipped in the alkanethiol solution for 5 min. The Hg−SAM/SAM−M′ junction was assembled by using a micromanipulator to bring the hanging mercury drop (Hg−SAM) in contact with the solid metal−SAM surface (Scheme 1). The contact areas were determined by video microscopy and capacitance measurements. For this purpose a video camera with a 50× objective was placed next to the junction, recording a side view of the system (Scheme 1).

Chemicals. Anhydrous ethanol (Pharmaco, 200 proof) was used to dissolve the respective alkanethiols. The unfunctionalized *n*-alkanethiols and 2-naphthalenethiol (all >95%) were purchased from Aldrich, Pfaltz & Bauer, and TCI and were used without further purification. Tolumer B thiol [HS−(CH$_2$)$_2$(CF$_2$)$_9$CF$_3$],[55] 11-triethyleneglycol-1-undecanethiol,[56] 4-biphenylthiol,[57] 4-methylene-biphenylthiol,[58] and 2-methylene-naphthalenethiol[58,59] were prepared according to the published proce-

dures (>98% purity by ^{1}H NMR spectroscopy). The interchain carboxylic anhydride [S(CH$_2$)$_{15}$CO-]$_2$O was prepared according to the published procedure,[42] followed by reaction with the amine; this reaction sequence results in a SAM terminated in a 1:1 ratio of amide and carboxylic acid groups. The reactions with the dodecylamine[42] and PEI[41] were performed as described previously.

Instrumentation and Measurements. The junction was connected to a computer-controlled potentiostat (Pine, Biopotentiostat AFCBP1, Grove City, PA) in the two-electrode mode, and the voltage was swept from 0 to 7 V at a rate of 0.1−1 V/s (as indicated in the text). The breakdown voltage of the junction was determined from the abrupt rise in the current/voltage diagram (Figure 2). All measurements were repeated at least five times on the same surface for each junction and 10 times for the Hg−HDT/HDT−M′ junctions. For better reproducibility and less sensitivity to vibration, all breakdown voltage measurements were performed with the junction immersed in a 10 mM solution of alkanethiol in ethanol. The current measurements at static potentials (inset in Figure 5a) were performed using a KEITHLEY 617 Programmable Electrometer. The capacitance measurements were performed by connecting the Hg−SAM/SAM−M′ junction to a MICRONTA digital multimeter (400 Hz sampling frequency). We carried out all preparations and measurements on a bench in the open laboratory, with no special precautions to avoid dust.

Supporting Information Available: Six (6) figures: I−V digrams for the Hg−HDT/HDT−Ag junction under different conditions; experimental distribution of BDV values; histogram of Table 2; dependence of BDV on sweep rate; plot of average BDV for different metals; relationship of BDV on R−R distance and tilt angle. Two (2) tables: average BDVs for Hg−SAM/SAM−M junctions; dependence of BDV on alkyl chain length (7p). This material is available free of charge via the Internet at http://pubs.acs.org.

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