Suppression of Charge Carrier Tunneling through Organic Self-Assembled Monolayers

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Self-assembled monolayers of long chain alkanes deposited on silicon wafers using an optimally designed procedure exhibit very large energy barriers (~4.5 eV) to carrier tunneling. The dc conductivity is found to be $\sim 4.6 \times 10^{-15}$ S/cm, close to that of bulk polyethylene, and independent of monolayer thickness. This demonstrates that the tunneling contribution to the overall conductivity can be made negligible when the organic structure is densely packed and highly ordered. Distinctly higher conductivity values are observed with disordered monolayers. [S0031-9007(96)00387-0]

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The design of nanoscale devices requires the wellcontrolled fabrication of very thin layers (less than few nm) of various materials with well-controlled architecture. In this downsizing approach, inorganic materials are most popular; however, they have limitations. For instance, when the thickness of a silicon dioxide insulating barrier is reduced below 3-4 nm, high tunneling currents start to appear, which preclude their use in reliable devices. It has been suggested long ago that organic materials could be useful substitutes in this domain, because of their low intrinsic electrical conductivity, and their possibility of forming monolayers and multilayers of nanometer thickness [1]. The pioneering measurements on monolayers of long chain fatty acids [2] have shown that their charge transfer characteristic was dominated by carrier tunneling. Charge transport in organic molecules is also a key feature to the development of molecular electronics. In this Letter, we demonstrate that tunneling can be avoided by controlling the layer organization and packing density within the organic layer. We show the amazing, and spectacular, result that the low electric field dc conductivity of optimally prepared self-assembled organic monolayers (SAMs) is independent of film thickness, and comparable to the conductivity of bulk material counterparts, even though our films are only 1.9–2.6 nm thick. We demonstrate that the interfacial tunneling energy barrier heights are indeed large enough to justify a negligible contribution of tunneling. The determination of the HOMO-LUMO gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of our SAMs of alkyl chains agrees with tight-binding calculations for all trans hydrocarbon chains, and we thus demonstrate that we have achieved nearly perfect, defect free, insulating monolayers. On the contrary, we measure much lower values of the tunneling barrier heights and much higher dc conductivities when the experiments are repeated on deliberately disordered monolayers.

SAMs of *n*-alkyltrichlorosilane molecules $[CH_3(CH_2)_{n-1}SiCl_3]$ with various chain lengths, n = 12,

16, and 18 (and referenced as C₁₂, C₁₆, and C₁₈), have been deposited on naturally oxidized silicon wafers using the Zisman-Sagiv method of retraction from solution [3]. Two key points must be followed in order to obtain a densely packed monolayer with highly ordered aliphatic chains [4]. First, the temperature of the deposition should be maintained below a critical value T_c which depends on the chain length. Second, the solid substrate should be prehydrated with a nanometer-thin layer of water. The rest of the procedure is standard: The cleaned substrates (by combining dry ultraviolet/ozone and wet H_2SO_4/H_2O_2 processes [4]) were dipped in a freshly prepared mixture of hexadecane/CCl₄ (70:30) and $10^{-3}M$ of *n*-alkyltrichlorosilane for 90 min. The critical surface tension γ_c of the silane-treated surface was found to be $\gamma_c = 20.5 \pm 0.5 \text{ mN/m}$, consistent with a top layer of methyl groups, as it should be if the silane molecules are densely packed. Ellipsometry shows that the films were composed of a single monolayer with thickness [5] $d = 2.65, 2.1, \text{ and } 1.83 (\pm 0.25) \text{ nm for the}$ C₁₈, C₁₆, and C₁₂ chains, respectively, in good agreement with the formula $d(C_n) = 0.126(n - 1) + 0.478 \text{ nm}$ valid for hydrocarbon chains oriented perpendicularly to the solid substrate and extended in their all-trans conformation [6]. The high chain packing order within the monolayer is best revealed by the infrared peak positions corresponding to symmetric d^+ and antisymmetric d^{-} stretching of the methylene groups. They are at 2849-2850 and 2916-2917 cm⁻¹, respectively, close to the values measured on alkane crystals but far below the positions for liquid alkanes which are at 2856 and 2928 cm^{-1} , respectively [4]. Electrical measurements (current density-voltage, J-V, characteristics) were performed on metal/insulator/silicon (MIS) structures obtained by evaporating aluminum (100 μ m \times 100 μ m, 10 to 100 nm thick) counterelectrodes directly onto the SAMs under ultrahigh vacuum (10^{-8} Torr) . To cause the least damage to the organic layers, a low deposition rate (8 Å/s) was selected. The silicon wafer was *n* type

highly doped (degenerated, $\rho \sim 3 \times 10^{-3} \Omega$ cm). The native oxide thickness was found to be 1.0 ± 0.2 nm, as measured by x-ray photoelectron spectroscopy (XPS), taking a value of 3.8 ± 0.4 nm for the electron escape depth in SiO₂ and comparing the Si_{2p} peak intensities for SiO₂ and pure silicon [7]. It was also checked by XPS that the cleaning process does not affect the oxide layer, which is therefore always present, with the same thickness, as a sublayer below the SAM. Photoconductivity experiments [8] were also performed by illuminating the structure through an optically transparent, 10 nm thick, aluminum electrode with monochromatic light (using a 150 W Xe lamp and a monochromator working in the 0.2–0.8 µm wavelength range, ~1.5–6 eV).

Extremely low J values of 10^{-11} to 10^{-8} A/cm² are obtained for C₁₈, C₁₆, and C₁₂ samples (Fig. 1, curves A). Measurements performed over a period of a few days to one year after the device fabrication showed no significant long term instabilities (Fig. 1), in contrast to earlier experiments on Langmuir-Blodgett monolayers [9]. Also indicated are the J values measured in the absence of the SAM: In curve B, the top electrode has been directly evaporated on the native oxide layer, whereas in curve C, the SAM has been first deposited as usual, then voluntarily removed by extensive UV-ozone photochemical cleaning before evaporating the aluminum electrode. In both cases, J takes values as large as 10^{-1} – 10^{2} A/cm², establishing that the data of curves A are controlled by the SAM itself and not by the native oxide sublayer. Usual tunneling theory in the MIS device predicts a lin-

10³ В 10² Without SAM 10¹ С Current density (A/cm²) 10⁰ 10⁻¹ 10⁻² 10⁻⁸ 10⁻⁹ C18 10⁻¹⁰ C16 C12 10⁻¹¹ -1,0 -0,5 0,0 0,5 1,0 Gate voltage (V)

FIG. 1. Curve *A*: current density (absolute value) versus voltage characteristics for C₁₈, C₁₆, and C₁₂ SAMs prepared according to the procedure described in Ref. [4] and measured after a few days. Solid curve is for a C₁₆ SAM measured one year after fabrication (stored in ambient air). Curves *B*: same as *A* but for a structure where the aluminum has been directly deposited on the native oxide of the silicon substrate. Curve *C*: same as *A* but after deliberately removing the SAMs from the substrate by UV-ozone irradiation. All measurements at 295 K. Typical error bars (including data dispersion over more than 50 samples) are indicated for the C₁₆ (similar for C₁₈ and C₁₂).

ear J-V dependence in a low electric field limit (here observed for |V| < 100-150 mV [10] allowing the determination of a conductivity, $\sigma = d(\delta J / \delta V)_{V \to 0}$, which is expected to be exponentially dependent on the film thickness [11]. Thus, σ values have been plotted in Fig. 2 as a function of the SAM thicknesses. The fact that they all fall on a horizontal line, with an average conductivity value $\sigma \sim 4.6 \times 10^{-15} \pm 3 \times 10^{-15}$ S/cm, is particularly striking. First, it disproves the possibility of direct electron tunneling through these ultrathin SAMs. Second, our σ value for a $\sim 2 \text{ nm}$ thick SAM is four decades lower than that previously reported for hydrocarbon-based monolayers of similar thickness deposited on aluminum substrate instead of silicon [2]. Our σ values are on the low side of those published for much thicker multilayers of similar alkyl chains $(2 \times 10^{-15} - 10^{-14} \text{ S/cm})$ [2]; they are also only 10 times larger than the bulk polyethylene value 2×10^{-16} S/cm [12]. Therefore, the conduction in a ~ 2 nm thick monolayer appears to be on a par with that of bulk organic materials.

Photoconductivity experiments at variable excitation wavelengths allow measurements of the tunneling energy barrier heights at both interfaces with metal and silicon [8]. Typical curves are shown in Fig. 3(a) [Fig. 3(b)] for C₁₈ SAMs with positive (negative) bias applied on the aluminum electrode. In the first case [Fig. 3(a)], the photocurrent is due to electrons injected from the conduction band (CB) of the silicon into the LUMO of the organic SAM over the energy barrier height Δ_e . Above the photoinjection threshold, linear variations are expected when plotting the cube root of the photoresponse (the



FIG. 2. Low field dc conductivity ($\sigma = d \,\delta J/\delta V$ at $V \rightarrow 0$) versus calculated monolayer thickness (see [6]) *d* for C₁₂, C₁₆, and C₁₈ SAMs. The hatched area contains the data measured on deliberately disordered SAMs. The dot-dashed line indicates the calculated tunnel conductivity, using an energy barrier of $\Delta = 4.3 \text{ eV}$ (from photoconductivity data of Fig. 3), $\sigma_0 = 92 \text{ S/cm}$, and $\beta = 1.018 \text{ eV}^{-1/2} \text{ Å}^{-1}$ as derived from Ref. [2]. The σ_0 value is an average obtained by fitting the thickness dependence of all the conductivity data in Ref. [2].



FIG. 3. Photocurrent response versus incident photon energy for the C₁₈ SAMs (Al gate) in the positive (a) and negative (b) bias mode (range $\pm 100-500$ mV). The squares correspond to a highly ordered SAM prepared below the critical temperature T_C , while the circles are for a disordered SAM prepared above T_C . The energy band diagrams for the metal/SAM/silicon structure are also represented (see text for more details). All measurements at 295 K.

photocurrent normalized to the incident photon flux) [8]. In the second case [Fig. 3(b)], the photocurrent is due either to electrons injected from the Fermi level (E_{fm}) of the metal, provided the photon energy is higher than Δ_m , or to holes injected from the degenerated silicon, provided the photon energy is higher than $\Delta_h + E_G$, E_G being the silicon band gap. In that case, above threshold, a linear variation is expected when plotting the square root of the photo response [8]. The values of these different thresholds can be derived from the intercepts of the extrapolated photoresponse with the photon energy x axis. In Fig. 3(a), we obtain $\Delta_e =$ 4.1 ± 0.15 eV. Similarly, in Fig. 3(b), two successive kinds are observed at 4.3 ± 0.15 and 5.1 ± 0.15 eV. From the known electron affinities of the Al ($\Phi_m =$ 4.3 eV) and Si electrodes (4.05 eV) [13], we know that Δ_m and Δ_e must differ by about 0.25 eV, and thus the lowest threshold of 4.3 eV can be unambiguously

attributed to Δ_m and the 5.1 eV threshold to $\Delta_h + E_G$, and then Δ_h is 4 ± 0.15 eV. The measured values for the C₁₆ and C₁₂ SAMs fall in the same range, within the error bars. These values readily explain our observation of a dc conductivity independent of the hydrocarbon chain length. The tunneling conductivity $\sigma_t = \sigma_0 \exp(-\beta \sqrt{\Delta d})$, calculated using the above Δ values and taking the same parameters σ_0 and β as in Ref. [2], is always smaller than the conductivity experimentally measured here (see Fig. 2, dot-dashed line).

The HOMO-LUMO gap of the SAM of alkyl chains is equal to $\Delta_e + \Delta_h + E_G$. Using the above results, one obtains a value in the range of 9.2 to 9.9 eV (± 0.3 eV) for all C₁₂, C₁₆, and C₁₈ SAMs. For all-trans alkane chains, semiempirical calculations in the tight-binding approximation predict (at $\pm 1 \text{ eV}$) ~ 11 and $\sim 12 \text{ eV}$ for C_{18} and C_{10} , respectively [14]. The agreement with our experimental results is rather good. That leads to the important conclusion that we have experimentally achieved a highly insulating character for these SAMs as theoretically predicted. Moreover, our values measured on SAMs are also in good agreement with those measured by photoconduction in bulk polyethylene ($\sim 8.8 \text{ eV}$) [15]. We have carefully checked that this result is independent of the nature of the metal electrode. For gold, $\Phi_m =$ 5.1 eV, and we have indeed observed that Δ_m is shifted accordingly to 4.7–4.9 (±0.15) eV, while Δ_e and Δ_h are not affected. Similarly, since the SAM is deposited on top of a ~ 1 nm thick SiO₂ oxide layer, it is legitimate to ask to which extent our electrical measurements are affected by this inorganic layer. Literature quotes the Al/SiO₂ interface barrier to be quite low, around 3.2 eV for thicknesses above 3 nm [13], and even smaller for thinner layers [16]. Such values are negligible when compared to the tunneling barrier heights measured in the present experiments. Similarly, the resistivity of the SiO₂ layer (10⁹ to 10¹¹ Ω cm for 2.9 to 3.5 nm thick stateof-the-art oxides [17], and even smaller for a 1 nm thick oxide) introduced in series with the organic layer is 5 to 6 orders of magnitude smaller than the resistivity of the present SAMs.

Finally, we have investigated the influence of molecular disorder on the insulating properties of the SAM by repeating the experiments on C₁₂ monolayers voluntarily prepared at temperatures higher than the critical temperature (at 10 °C while T_C is ~7.5 °C) of optimum deposition. In such samples, the surface coverage is only 90% to 95% of the close packing state and the hydrocarbon chains no longer are in their extended all-trans conformation, but rather exhibit gauche defects [4]. Figure 2 (hatched area) shows the measured conductivities for such liquidlike alkane monolayers. The data points are scattered over a wide range between 10^{-14} to 10^{-10} S/cm, with a large number of samples exhibiting conductivity

up to 4 orders of magnitude higher than the conductivity for the corresponding "high quality" C12 SAMs. The photocurrent curves are shifted towards smaller values of the energy barriers heights; Δ_m and Δ_h have dropped to \sim 3 and \sim 3.8 eV, respectively [Fig. 3(b), circles]. Therefore, there is a clear correlation between the structural quality of the deposited monolayer and its electrical transport properties. At this stage, it is difficult to quantify the amount of disorder induced by the temperature increase during the self-assembly of the monolayer. In particular, we cannot clearly relate our results to a specific type of defect among those investigated so far [18]. We surmise that the extra free volume between the chains in disordered SAMs allows the incorporation of metal atoms in the monolayers during the counterelectrode evaporation, resulting in a smaller effective barrier height and thus in larger leakage currents [19].

On the whole, we have shown that organic monolayers prepared by the self-assembly method have tunneling barrier heights which are close to the theoretical limit. As a consequence, the conductivity by direct electron tunneling is totally suppressed even though the self-assembled monolayers are only ~ 2 nm thick. We believe that the present experiments offer the first quantitative justification of the old intuition that organic monolayers can constitute exceptional insulators at a nanometer scale, once a good control of their molecular architecture has been achieved. These insulating performances can presently be matched only with inorganic oxide layers which are at least 2 times thicker [17]. This enables us to foresee their widespread application in future nanoscale inorganic and organic devices.

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- [1] A. Ulman, Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly (Academic Press, San Diego, 1991).
- [2] B. Mann and H. Kuhn, J. Appl. Phys. 42, 4398 (1971);
 E. E. Polymeropoulos and J. Sagiv, J. Chem. Phys. 69, 1836 (1978);
 E. E. Polymeropoulos, J. Appl. Phys. 48, 2404 (1977).
- [3] W. Zisman, Adv. Chem. Ser. 43, 1 (1964); R. Maoz and J. Sagiv, J. Colloid Interface Sci. 100, 465 (1984).
- [4] J.-B. Brzoska, N. Shahidzadeh, and F. Rondelez, Nature

(London) **360**, 719 (1992); A.N. Parikh, D.L. Allara, I.B. Azouz, and F. Rondelez, J. Phys. Chem. **98**, 7577 (1994); J.-B. Brzoska, I. Ben Azouz, and F. Rondelez, Langmuir **10**, 4367 (1994); D.L. Allara, A.N. Parikh, and F. Rondelez, Langmuir **11**, 2357 (1995).

- [5] In the calculation of the SAM thickness, we have used a value of 1.50 for the SAM refractive index at 633 nm for the close packed SAMs (see Refs. [1,4]). The optical functions of the oxidized substrate have been independently determined by measuring a bare wafer cleaned rigorously by the same surface cleaning process.
- [6] S. R. Wasserman, Y. T. Tao, and G. M. Whitesides, Langmuir 5, 1074 (1989).
- [7] R. Saoudi, G. Hollinger, A. Gagnaire, P. Ferret, and M. Pitival, J. Phys. III (France) 3, 1479 (1993).
- [8] R. J. Powell, J. Appl. Phys. 41, 2424 (1970).
- [9] R.H. Tredgold and C.S. Winter, J. Phys. D 14, L185 (1981).
- [10] J.G. Simmons, J. Appl. Phys. 34, 1793 (1964).
- [11] The crossover of the curves at higher field may be due to the onset of the field-assisted transport mechanism in the thinnest SAMs (C₁₂), resulting in more complicated voltage dependence: $\ln(J)$ versus V, $\ln(J/V^2)$ versus 1/Vrelationships in case of tunneling (medium and high field regimes, respectively). Note that a $\ln(J)$ versus $V^{1/4}$ relationship has been frequently reported in organic monolayers and multilayers: G.G. Roberts, P.S. Vincett, and W.A. Barlow, J. Phys. C **11**, 2077 (1978); R.H. Tredgold, A.J. Vickers, and R.A. Allen, J. Phys. D **17**, L5 (1984). A detailed discussion of the exact *J-V* relationship is beyond the scope of this Letter.
- [12] *Polymer Handbook* edited by J. Brandrup and E.H. Immergut (Wiley, New York, 1975).
- [13] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981); E. R. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York, 1982).
- [14] C. Delerue and G. Allan (private communication). In these calculations, the tight-binding parameters of Robertson were chosen for the C-C and C-H interactions: J. Robertson, Philos. Mag. B 66, 615 (1992).
- [15] K. J. Less and E. G. Wilson, J. Phys. C 6, 3110 (1973).
- [16] S. Horiguchi and H. Yoshino, J. Appl. Phys. 58, 1597 (1985).
- [17] C. Boulas, J.V. Davidovits, F. Rondelez, and D. Vuillaume, Microelectron. Eng. 28, 217 (1995).
- [18] I. R. Peterson, J. Chim. Phys. 85, 997 (1988).
- [19] Our results contradict those by Haran *et al.* [A. Haran, D. H. Waldeck, R. Naaman, E. Moons, and D. Cahen, Science **263**, 948 (1994)], who showed that the current decreased in disordered SAMs. They induced the disorder by heating the SAMs. In our case, after heating our below T_C SAMs (in the same condition as Haran *et al.*: 495 K in vacuum for 15 min), we did not observe any change in the measured conductivity. However, the experiments were not performed strictly in the same way, in Haran's work an electrolyte is used as the counterelectrode. We suspect that the conductivity decrease in Haran's work may be due to removal of water from the organic layer.