Mechanical and charge transport properties of alkanethiol self-assembled monolayers on Au (111) surface: The Role of Molecular Tilt

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ABSTRACT: The relationship between charge transport and mechanical properties of alkanethiol self-assembled monolayers (SAM) on Au(111) films has been investigated using an atomic force microscope with a conductive tip. Molecular tilts induced by the pressure applied by the tip cause step-wise increases in film conductivity. A decay constant $\beta = 0.57 \pm 0.03$ $\mathring{A}^{-1}$ was found for the current passing through the film as a function of tip-substrate separation due to this molecular tilt. This is significantly smaller than the value of ~1 $\mathring{A}^{-1}$ found when the separation is changed by changing the length of the alkanethiol molecules. Calculations indicate that for isolated dithiol molecules S-bonded to hollow sites, the junction conductance does not vary significantly as a function of molecular tilt. The impact of S-Au bonding on SAM conductance is discussed.

1. Introduction

The use of molecules as building blocks of electronic devices is potentially promising for technological applications and an important focus of fundamental research [1-4]. Examples of applications include organic light emitting diodes (OLEDs), organic charge transport media in solar cells [5,6] and single molecule / single electron devices [7-11]. Important topics in need of a fundamental understanding include: a) the mechanism of charge transfer from the electrodes to the molecules; b) transport through the molecules; c) transport across molecules; d) influence of the nature of molecule-electrode contact. Self-assembled films (SAM) formed by long chain alkylthiol molecules have been extensively studied because they form ordered structures on a number of metallic (Au, Ag, Cu etc.) and semiconductor surfaces (InP) [12], and because their internal and surface properties can be controlled by introduction of double bonds, and groups with delocalized orbitals inside the chain, as well as various terminal functional groups.

Molecules with alkane chains are insulators and electron transport occurs by tunneling mechanisms

[13-15]. When such molecules are placed between electrodes the junction resistance changes exponentially: $R = R_0 \exp(\beta s)$, with electrode separation s, where R_0 is the contact resistance and β a decay parameter. In most experiments the separation s is the length of the alkyl chain. However, length alone is not the only important parameter. Conformation and molecular orientation relative to the electrodes is also important. Other factors need be considered as well, including energy positions of the highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO), electrode work function and nature of the bonding to the electrodes [13-25]. These properties can be influenced by external forces that may cause molecular deformation and conformation changes. It is therefore relevant to study the relationship between mechanical and electronic properties of molecules.

In an AFM study of alkanethiol islands on gold, Barrena et al. [26] reported discrete changes in molecular film thickness and friction upon increasing tip pressure due to tilts of the alkane chain in the molecule. Mercury drop expansion experiments by Slowinsky et al. have shown a dependence of the current through the alkanethiol monolayers on surface concentration, prompting the authors to suggest the existence of additional pathways for charge transfer like chain-to-chain tunneling [20,21]. Wold et al. studied the junction resistance as a function of load using AFM. The resistance was found to decrease with increasing load with two distinct power law scaling regimes [23]. Song et al. examined the dependence of the tunneling current through Au-alkanethiol-Au junctions on the tip-loading force. It is found the two-pathway model proposed by Slowinsky et al. [20,21] can reasonably fit the results, leading the authors to conclude that the tilt configuration of alkanethiol SAMs enhances the intermolecular charge transfer [27].

In this paper we present a study of the effect of molecular conformation (tilting) on the tunneling characteristics of Au – SAM junctions as well as the results of state-of-the-art calculations of the tunneling current as a function of tilt angle of model, isolated dithiol molecules.

2. Experimental

The experiments were carried out with films of hexadecanethiol ($C_{16}H_{33}SH$), or C16 for short, self-assembled on Au(111). The alkanethiol molecules (~92% purity) were purchased from Aldrich and used as received. Gold substrates were in the form of thin films (~150 nm) prepared by evaporation on mica or glass and flame annealed in air. The resulting surface consists of grains with terraces of (111) orientation up to 500 nm in size separated by monatomic steps.

The experiments were performed on complete monolayers of the molecules and also on islands of molecules covering only a fraction of the surface [26]. In the first case the film was produced by immersing the substrate in 1 mM ethanolic solution of C16 for about 24 hours, followed by rinsing with absolute ethanol and drying in a stream of nitrogen to remove weakly bound molecules. Incomplete monolayers in the form of islands were prepared by immersing the substrate in a 5μM ethanolic solution of C16 for approximately 60 seconds, followed by rinsing as before. Samples consisting of islands facilitate the determination of the thickness of the molecular film relative to the surrounding exposed gold substrate.

To avoid capillary condensation effects on the current measurements the measurements were performed in a UHV chamber with 1.0×10^{-10} Torr base pressure using a commercial RHK microscope [28]. Cantilevers with spring constant of 2.5 or 1.1 N/m coated with approximately 50 nm of conductive TiN were used. The normal force was kept constant during imaging while current and friction force were simultaneously recorded [29].

3. Results

Figure 1 shows topography, friction and current images obtained simultaneously for a full monolayer

of C16. The topographic image reveals the commonly found structure of the gold film substrate, composed of triangular-shaped terraces separated by atomic steps. The current is low and uniform except at the step edges, presumably because the alkylthiol molecules are not well organized at these locations such that the tip can get closer to the Au surface. Lattice resolved images of the film (inset in the figure) reveal a $(\sqrt{3}x\sqrt{3})$-R30^o periodicity of the molecules relative to the gold substrate.

Current-voltage (I-V) characteristics were measured on this sample for loads varying between -20 and 120 nN. The traces are sigmoidal in shape over a $\pm$2 V range, with an approximately linear region between -0.5 and +0.5V, as shown in figure 1d. We checked by subsequent imaging that no nano-scale size damage was caused to the film in this voltage range [30]. All I-V traces acquired at different loads showed similar shapes, although the absolute currents were strongly dependent on the tip condition, radius and applied load. The shapes could be fit reasonably well with the Simmons model [13,31], shown by the curve in Fig. 1d. The fit was obtained using a tunneling barrier height of 2.05eV and an asymmetry parameter α=0.67. Above 120 nN, the current-voltage plot changes from sigmoid to linear over the entire range with a high slope of 40 nS. The fact that the conductance is much smaller than that of a single atom Au-Au contact (G_0=77μS) suggests there might be a nonmetallic layer such as oxide or carboneous species at the tip-sample junction which leads to the lower conductance than Au-Au contact.

The emphasis of this paper however is not on the shape of the I-V curves, which contain information on the electronic molecular orbitals, but rather on the dependence of I on the geometrical conformation of the molecules as it changes due to pressure. To that effect we measured the current as a function of applied load at a fixed voltage of 1 V. The results (Fig. 1e) show that the current changes in a step-wise manner. A step-wise response of the SAM film to pressure has been observed previously in other properties such as film height and friction. These changes were shown to correspond to the molecules adopting specific values of their tilt angle relative to the surface, and explained as the result of interlocking of methylene groups in neighboring alkyl chains [26].

As shown in previous publications, the values of the load where the changes occur are a strong

function of the tip radius [32, 33] and degree of perfection of the film, which is determined by defect concentration. These conditions can vary considerably in different experiments [34].

Since it is difficult to measure film height changes in complete SAM monolayers we performed measurements on samples with a partial coverage of C16. The surface of these samples consists of islands of molecules separated by either bare gold or gold covered with flat-lying molecules. The images in fig. 2 show topography (a), friction (b), and current (c), of a region containing islands. On top of the islands current and friction are low while in the gap between the islands both current and friction are high. Fig. 2(d) shows two topographic profiles across an island edge at loads of 45 nN to 135 nN. At low loads the film thickness is uniform and decreases abruptly over the edge, with a sharpness determined by the tip radius. At high loads however the film thickness decreases stepwise or gradually towards the edge, in agreement with previous findings of alkylsilanes on mica and alkylthiols on gold [26, 35]. The decrease in height near the edges at high load reflects the increasingly large tilt angle of the molecules in these locations. We had shown previously that defects, such as vacancies and domain boundaries are necessary to accommodate the lateral expansion of the film as it is compressed. Due to the island growth process around an initial nucleus the concentration of such defects increases from the center toward the edges. In the present work we exploit the gradual variation of height at the island edges to simultaneously measure thickness, current and friction force at a fixed load as in the example of figure 2d.

In experiments with complete monolayers, where the load needs to be varied to produce increasingly large molecular tilt angles, the tip-surface contact area increases due to elastic deformations and must be taken into account by normalizing the current by the contact area. This area was calculated using classical models of contact mechanics, specifically the Johnson-Kendall-Roberts model [36]. We used a value for the radius of our tip of 100 ± 20 nm (obtained from SEM micrographs), and the following elastic constants of the materials: TiN Young's modulus $E_1=600$ GPa, Poisson ratio $\nu_1=0.25$, Au Young's modulus $E_2=78$ GPa, Poisson ratio $\nu_1=0.35$. The adhesion force was determined experimentally

from the critical pull-off force Lc = -20nN.

The results for both islands and monolayers are shown in the semilog plot of junction resistance (R) per unit area versus film thickness of Fig. 3. In the case of complete monolayers the data in Fig. 1(e) were converted to current versus electrode separation by assigning each step in the current to a specific molecular tilt angle, following the sequence established in previous experiments [26]. As can be seen ln(R) increases approximately linearly with tip-surface separation, with an average slope $\beta = 0.57 \pm 0.03$ $\mathring{A}^{-1}$. Previously reported measurements and calculations of β obtained by changing the alkyl chain length, give a value close to 1 $\mathring{A}^{-1}$ [14, 20, 21, 23].

4. Discusssion

4.1. The two-path model

Since the molecular length is the same for all electrode separations in our experiments, one would expect ideally a value of β equal to zero if electron transport were determined purely by tunneling along the alkane chain and no other changes were occurring. Potential changes to consider include distortions of the S-Au binding configuration, and displacement of gold atoms, including formation of metal filaments as proposed by some authors [37].

To explain the intermediate value of β, halfway between 0 and 1, Slowinski et al. [21] proposed a two-pathway conductance model involving tunneling along the length of the alkyl chain (β_1, through-bond), and chain-to-chain coupling (β_2). Indeed by using the same decay constants as Slowinski et al. [21] ($\beta_1 = 0.91$ $\mathring{A}^{-1}$ and $\beta_2 = 1.31$ $\mathring{A}^{-1}$) together with the geometrical changes predicted by the molecular tilts we could obtain a reasonable fit to our data (not shown in the figure), within the scatter of the data in figure 3. In the following however, rather than elaborating on the value of the two-path model, we analyze in some detail the influence of molecular tilt on the S-Au bonding and its influence on the

tunneling.

4.2. Influence of S-Au bonding on tunneling

The nature of the S-Au bonding is crucial because conductance at low biases occurs through S-Au states with energies inside the molecular HOMO-LUMO gap [38]. The conductance of alkanedithiol-Au junctions has been studied extensively using density functional theory (DFT)-based transport calculations [38-40]. By varying the alkyl chain length for a fixed molecular tilt angle a value for β was obtained in good agreement with experiment [38]. However, the calculated conductance is typically larger than the measured value [38-40]. Furthermore, the conductance has been predicted to vary significantly – by about an order of magnitude – depending on the thiol binding site and atomic environment in the junction [40].

The lack of agreement with experimental conductance values as well as the significant impact of junction structure on conductance makes direct comparison between theory and experiment difficult. Moreover, the atomic details of the contact geometry of alkanethiol self-assembled monolayers on Au(111) are controversial [41-43], with the most common model involving S binding to Au at hollow sites [44]. The S-Au contact geometry under mechanical stress is also unknown.

To understand the effect of the S-Au binding structure and alkyl chain tilt angle we performed DFT conductance calculations on a simplified junction consisting of a single butane-dithiol molecule in a large supercell bonded to the hollow site of flat Au(111) surfaces by S-Au bonds at either end of the molecule. The supercell contains 16 Au atoms per layer, and the conductance is calculated with a 4 x 4 $k_{//}$-mesh. Other technical details follow those in previous work [45]. The molecular tilt angle is varied from 0° to 78°, and the atomic positions are fully relaxed for each angle. (Here, the tilt angle is defined as the angle between the molecular backbone and the surface normal.) The relaxed nearest S-Au distances are respectively 2.5, 2.5, 2.8 Å for the 0° case, 2.5, 2.5, 3.1 Å for 30° and 40°, 2.5, 2.5, 3.2 Å for 55°, and 2.5, 2.7, 3.5 for 78°. It is clear, especially for the tilted geometries, that S at the hollow site

relaxes to an off-centered position relative to the three-fold site, approaching a bridge site. This result is consistent with previous total energy calculations of CH_3S on Au(111) [46-49]. The low-bias conductance is then calculated with a scattering-state approach [50] using the Landauer formula. We find that for the single butane-dithiol molecule bonded to Au(111) at a hollow site, the calculated conductance varies by only a factor of 2 (0.01-0.02 G_0) for tilt angles 0°-55°. The minimal variation in conductance with tilt angle is consistent with the fact that the local bonding geometry at the contacts does not change significantly with angle up to roughly 55°. However, we find that as we tilt the molecule further, which decreases the distance between the molecular backbone and the Au electrodes, the calculated conductance increases. Specifically, for tilt angles of 66° and 78° (larger than that obtained in experiment), we obtain 0.08 and 0.36 G_0 for the conductance, respectively. In all cases, the calculated conductance results from tunneling *through the molecule* rather than through space: Removing the molecule [51] results in a calculated conductance of 10^{-5} G_0 for a Au lead-lead separation of 6 Å (corresponding to a tilt of 78°). Through-space tunneling between leads is thus more than three orders of magnitude less than through-molecule tunneling at this separation. Our results are consistent with previously-reported plane wave DFT calculations [52], which also concluded that tunneling through alkanethiols occurs predominantly through the molecule, and that the molecular density of states at E_F does not change significantly with tilt angle for bonding to flat Au(111) surfaces.

While the calculated conductance through alkanedithiol-Au junctions does not change significantly with molecular tilt for a fixed hollow binding site, it is possible that the hollow site is in fact not the preferred contact geometry. Previous studies have suggested other energetically-competitive configurations involving S bonded to Au adatoms [41], subsurface Au sites [53], or to a more complex adlayer [43].

In experiments with close-packed SAMs it is very likely that changes in binding site occur with molecular tilt. Indeed, steric considerations imply that upon tilting, there must be an increase of S-S distance from the initial $\sqrt{3}$ separation if the ideal van der Waals separation between adjacent molecules

is to be maintained. Our previous experimental findings of step-wise change in tilting angle with load fully support this [26,34,35]. For example, a simple calculation indicates that for the first tilt angle away from the initial 35° (43°) the S-S distance has increased by 0.9 Å. The energy required to increase the S-S separation and create intermediate metastable bonding configurations originates with the tip load. Since changes in binding site with tilt are expected, and since such variations can result in order-of-magnitude changes in conductance [40], it is quite possible that the observed trends in conductance with tilting to variations are due purely to changes in S-Au binding.

5. Summary and conclusions

In conclusion, a correlation between charge transport and molecular tilt changes caused by pressure has been found in alkanethiol molecules self-assembled on Au(111) films using AFM. The junction I-V characteristics are sensitive to the load applied by the tip, which causes film thickness and current to change in a step-wise manner. We found that the tunneling decay constant β through molecules of fixed chain length is significantly smaller than that for the case where the distance between electrodes is changed by using alkanethiol molecules of different lengths.

While an empirical model where electrons can tunnel through both the alkyl chain and across neighboring molecules can explain the conductance data by proper choice of decay constants, we examined an alternative model where the changes in conductance with tilt angle of the molecule due to the applied load are instead related to changes in the S-Au coupling. State-of-the-art scattering DFT calculations predict that for isolated di-butylthiol molecules bonded to hollow sites, the tunneling conductance changes at most by a factor of two with molecular tilt up to 55°, while the binding of S to the Au atoms changes only by small amounts. This change in conductance value is much lower than that observed experimentally.

We therefore propose that more important changes in S-Au binding structure occur due to the steric

forces acting between close packed molecules under pressure, which displace the S from hollow sites to bridge sites and possibly others. Such changes can produce much larger changes in the tunneling characteristics, as previous calculations have shown. Our study shows that an understanding of the effect of bonding structure in the electronic properties of molecules and the influence of external forces is fundamental for the development of molecular electronics.
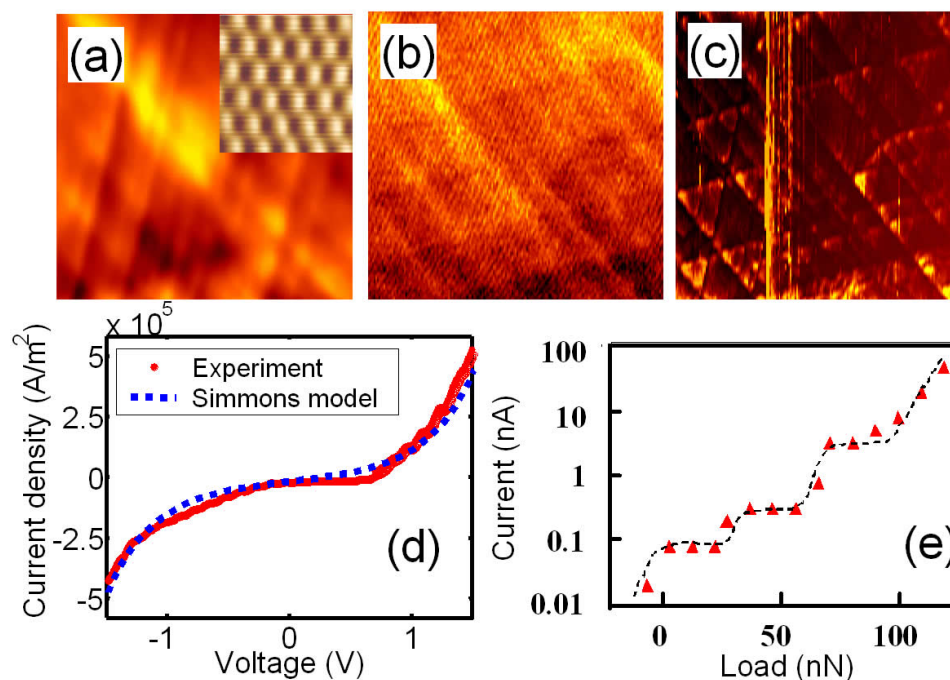
Acknowledgment

Figure 1(a) 200nm × 200nm topographic image (load = 48nN) of a C16 monolayer on Au(111). Inset is a high resolution image (2.5 × 2.5 nm) showing the (√3 × √3)R30° molecular periodicity. (b) Friction force image. (c) Current image (sample bias 1.5V). Higher current is observed at the step edges where the SAM film opens up allowing for a closer tip-surface interaction. (d) Comparison of IV curve at 8nN to the Simmons model. (e) Semilog plot of the current at 1V bias as a function of applied load. The plateaus are associated with discrete tilt angle of the molecules.
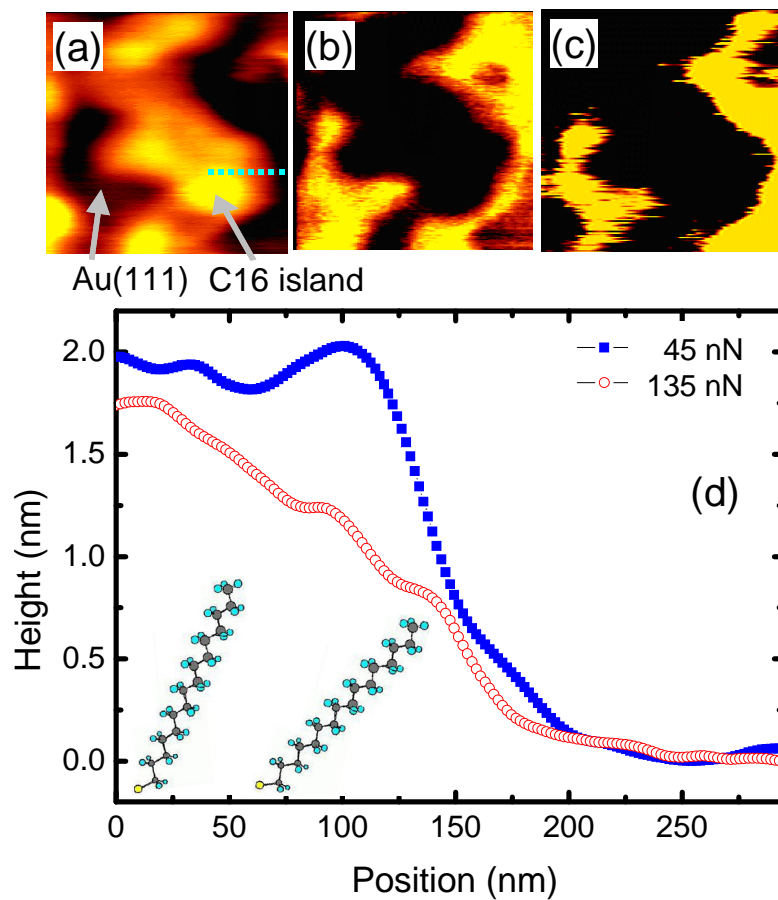
Figure 2(a) 600nm × 600nm topography image of a gold sample partially covered with C16 alkanethiols. (b) Friction force image. (c) Current image (bias: 1.5V) taken simultaneously with topographical image. (d) Height profiles from the center to the edge of the island at normal loads of 45nN and 135nN.
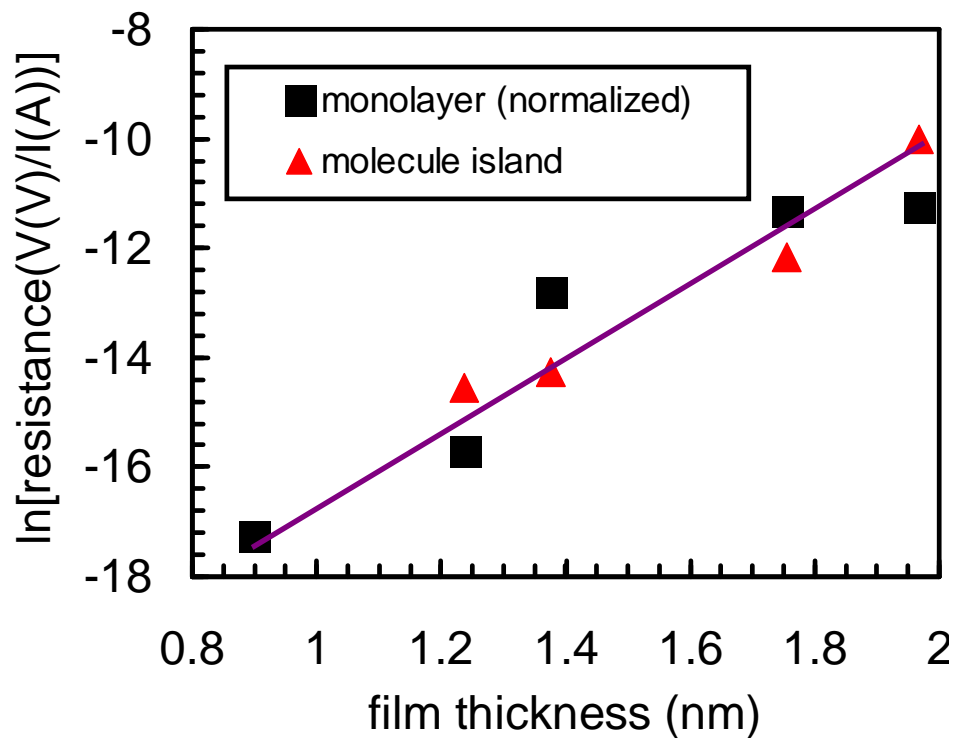
Figure 3 Semilog plot of the junction resistance per unit area versus distance between electrodes. Square symbols are experimental data for complete monolayers after the normalization by the contact area. Triangular symbols are experimental data on the C16 island sample. The line is a linear fit to the data, which gives $\beta = 0.57$ Å^{-1}.

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