Tip-Loading, Force-Dependent Tunneling Behavior in Alkanethiol Self-Assembled Monolayers Studied Through Conducting Atomic Force Microscopy

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Metal/self-assembled monolayer (SAM)/metal junctions are currently considered key elements in the ultimate miniaturization and integration of molecular electronic devices through the bottom-up strategy.[1,2] A full understanding of charge transport through SAMs is essential for actual device applications; however, such transport measurements are experimentally challenging, particularly due to the difficulty of making reliable electrical contacts to the nanometer-scale monolayers. To this end, the conducting atomic force microscopy (CAFM) method holds key advantages for easily-accessible junction formation, since no micro-fabrication process is required.[1] In addition, unlike scanning tunneling microscopy with a vacuum gap, CAFM provides a direct contact on a sample, so that a controlled tip-loading force can affect electronic properties in the molecules.

In this study, we report a tip-loading, force-dependent tunneling behavior in alkanethiol SAMs using CAFM. A variable tip-loading force applies to alkanethiol SAMs with a standard AFM feedback, and current(I)-voltage(V) characteristics are simultaneously measured while varying the loading forces. In particular, we observe how a tip-loading force in CAFM influences the transport properties of alkanethiol SAMs.

For our experiments, alkanethiols (from Sigma-Aldrich) of various molecular lengths, octanethiol ($CH_3(CH_2)_7SH$, denoted as C8 for the number of alkyl units), dodecanethiol ($CH_3(CH_2)_{11}SH$, C12), and hexadecanethiol ($CH_3(CH_2)_{15}SH$, C16) were used to form the active molecular components. The metal/molecule/metal junctions were formed by placing a Au/Cr-coated AFM tip in stationary-point contact with alkanethiol SAMs prepared on Au substrates under a controlled tip-loading force, as shown in Figure 1(a). All electrical measurements were carried out inside a nitrogen-filled AFM chamber. Experiment details are described in the supporting information.

Figure 2(a) shows the force-dependent $I(V)$ characteristics of C12 SAMs when the tip-loading force is varied from 1 to 30 nN. All data were obtained with the same tip in the same sample position. The current in the molecular junction increased with increasing tip-loading force. It is helpful to examine the current density of the molecular junction to demonstrate the force-dependent charge transport. An increase
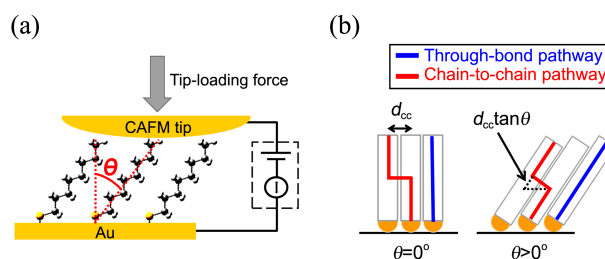

Figure 1. Schematics illustrating the (a) CAFM method and (b) tunneling pathways through alkanethiol SAMs.

in the junction current is often mistakenly thought to result from expansion of the tip-molecules in the contact area with increasing loading force. The current density should remain constant; however, if only the enlarged contact area contributes to the increase in current. The current density can then be calculated by estimating a contact junction area for a given loading force. The Johnson-Kendall-Roberts (JKR) mechanical contact model is typically used to evaluate the contact area (see the supporting information for a detailed method).[3]

Figure 2(b) shows that the current densities of C8, C12, and C16 are not constant, but instead gradually increase when additional loading force is applied. The error bars in this case were determined statistically from the associated measurements. The observation in Figure 2(b) implies that an increase in current is not simply due to an increase in the contact junction area, and thus a potential change in geometry of the molecules under the tip loads influence the electrical properties of the junctions. Several authors have suggested the existence of an ordered tilted-chain phase of alkanethiol SAMs on Au(111) within the loading effect applied by the tip. Most of the deformation under a tip-loading force leads to additional tilting of the molecules, even though gauche and other defect-related deformations might cause a small change in overall charge transfer.[4-6]

Molecular-tilt dependence on tunneling transport through alkanethiol SAMs is graphically illustrated in Figure 1(b). The blue lines indicate the through-bond tunneling pathway, whereas the red lines indicate the chain-to-chain tunneling pathway, including the intermolecular charge hopping. A
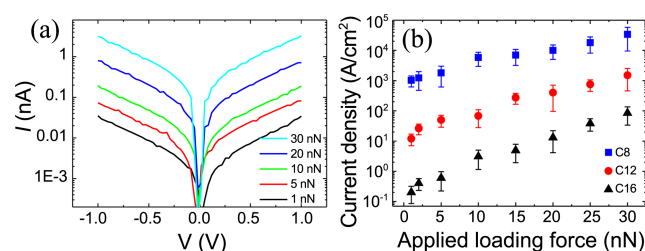
Figure 2. (a) Representative force-dependent current-voltage characteristics of C12 SAMs with varied tip-loading force from 1 to 30 nN. (b) A semilog plot of current densities at 1.0 V for C8, C12, and C16 SAMs as a function of applied tip-loading force. The error bars were obtained from repeated measurements at various positions of the samples. A contact junction area for a given loading force was estimated using the Johnson-Kendall-Roberts contact model described in the supporting information.

molecular tilt with angle θ results in a decrease in tunneling distance by $d_{cc} \tan \theta$ (where d_{cc} is the intermolecular distance), because the intermolecular charge transfer takes place through the shortest pathway between adjacent alkyl chains. Thus, the overall chain-to-chain tunneling distance becomes $d_m - d_{cc} \tan \theta + d_{cc}$ (where d_m is the molecular length). Therefore, a tilted configuration in alkanethiol SAMs under tip-loading effect enhances intermolecular charge transfer, because tunneling distance for the intermolecular pathways decreases with the tilt of alkanethiol molecules. Such an additional intermolecular tunneling process as the molecules tilt results in an increase in overall tunneling current.

We demonstrate that through-bond tunneling is the dominant transport mechanism in alkanethiol SAMs by investigating the dependence of current density on each tunneling distance for through-bond pathways (d_m) and chain-to-chain pathways ($d_m - d_{cc} \tan \theta + d_{cc}$). Figure 3 shows a semilog plot of current density versus tunneling distance. Data points for through-bond tunneling were obtained with alkanethiol SAMs of different chain lengths (C8, C12, and C16) at a constant tip-loading force of 1 nN, where tunneling distance corresponds to molecular lengths of alkanethiols (d_m). Data points for chain-to-chain tunneling were obtained with C8 SAMs during varying tip-loading forces (1 to 30 nN), where tunneling distance corresponds to $d_m - d_{cc} \tan \theta + d_{cc}$ (see the supporting information for estimating molecular tilt angle (θ) induced by tip-loading force). It can be observed in Figure 3 that the rate of current density increase for chain-to-chain pathways (the slope of linear fit, red line, is −0.48) is smaller than that for through-bond pathways (the slope of linear fit, blue line, is −0.92), meaning that more efficient tunneling pathways can be made in the direction of the σ-bonds in alkanethiol SAMs than through chain-to-chain pathways, which is consistent with previous results.[7]

In summary, the force-dependent tunneling transport in metal/alkanethiol/metal junctions was examined using CAFM. Tunneling current and current density through alkanethiol SAMs increased with increasing tip-loading force in CAFM, which suggests that a potential change in geometry of the
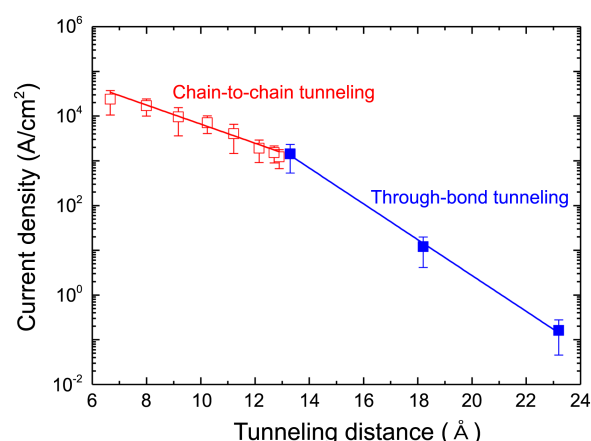

Figure 3. Semilog plots of current density versus tunneling distance for chain-to-chain tunneling data (red) obtained with alkanethiol monolayers of different chain lengths (C8, C12, and C16) at a constant tip-loading force of 1 nN, where tunneling distance corresponds to molecular lengths of alkanethiols (d_m), and through-bond tunneling data (blue) obtained with octanethiol during varying tip-loading forces (1 nN to 30 nN), where tunneling distance corresponds to $d_m - d_{cc} \tan \theta + d_{cc}$.

molecules under the tip loads influences the transport properties of alkanethiol SAMs. Enhanced intermolecular tunneling transport in the tilted molecular configuration under tip-loading effect is likely responsible for such an increase in tunneling current density. We also demonstrated that through-bond tunneling is a more efficient pathway in alkanethiol SAMs than are intermolecular chain-to-chain pathways, by demonstrating a dependence of current density on the associated tunneling distances.

Supporting Information. Experimental details; the method for estimating the contact radius and molecular tilt angle using the Johnson-Kendall-Roberts (JKR) contact model.

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