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Statistical Representation of Intrinsic Electronic Tunneling Characteristics through Alkyl Self-Assembled Monolayers

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1. Introduction

The nature of electronic transport through the organic molecules sandwiched between metallic electrodes is of primary significance in building reliable molecular devices [1]. Since the transport characteristics in metal-molecule junctions are subject to stochastic fluctuation [2], statistical analysis and interpretation of data are necessary for an objective criterion to obtain the intrinsic characteristics of molecular devices.

Here we present a statistical method to investigate the electronic transport of molecular devices. For this, comprehensive temperature-variable current-voltage [$I(V,T)$] characterization has been performed with subsequent statistical analysis, using mass-fabricated molecular devices with nanometer-scale junction diameter. The $I(V,T)$ characterization can play a critical role in determining the transport mechanism which makes it possible, for example, to distinguish electronic tunneling transport from thermally activated conduction such as impurity-mediated transport [3]. A study based on the statistical approach would give impartiality in determining the intrinsic molecular transport properties.

2. Experiment

In this study, we used alkanethiol [$CH_3(CH_2)_{n-1}SH$] self-assembled monolayers (SAMs). Figure 1(a) shows the device structure, where alkanethiol SAMs are sandwiched between two metallic contacts through a nanowell [4,5]. The junction diameter is estimated to be ~50 nm from a scanning electron microscope (SEM) image.

3. Results and Discussion

We examined 6,745 devices fabricated as the nanowell structure shown in Fig. 1(a), employing alkanethiol SAMs of various molecular chain lengths. As a screening process for non-working devices, room temperature $I(V)$ measurements were executed before cooling in the cryogenic probe station. Of these devices examined, 482 devices (~7%) showed non-linear $I(V)$ characteristics and current in the nanoampere (nA) range, which corresponds to the general characteristics of metal-molecule-metal junctions under investigation. To investigate electronic transport properties from these candidate molecular devices, we performed temperature-variable current-voltage [$I(V,T)$] characterization.

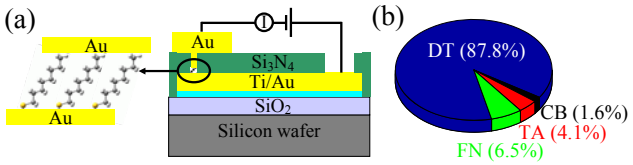

Fig. 1 (a) Schematic of the molecular device. (b) A pie chart summarizing the statistics of various transports observed: direct tunneling (DT), Fowler-Nordheim (FN) tunneling, thermal activation (TA), and Coulomb blockade (CB).

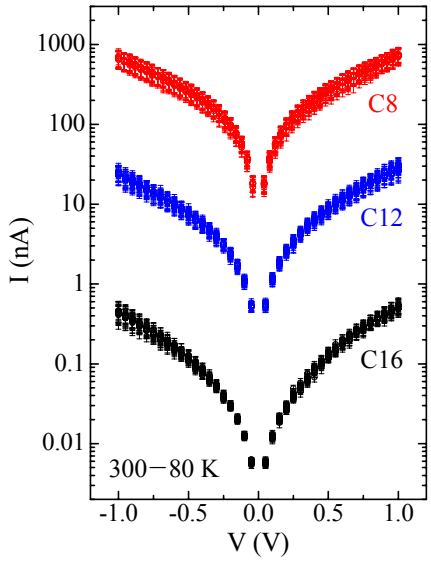

Fig. 2 The average of $I(V,T)$ characteristics for each alkanethiol SAM (C8, C12, and C16) as the representative data of 108 direct tunneling devices. 31 devices for C8, 42 devices for C12, and 35 devices for C16, respectively. The $I(V,T)$ data at temperature from 300 to 80 K with 20 K step are plotted on a semi-logarithmic scale.

Figure 1(b) summarizes the percentage of statistical distribution for which we observe each of the various transports based on the comprehensive $I(V,T)$ characterizations. We obtained a total of 123 $I(V,T)$ data in a complete temperature range of 300−80 K. Among them, 108 devices (87.8%) showed direct tunneling characteristics in ac-

cor dance with temperature-independent $I(V)$ characteristics and no transition on a plot of ln (I/V^2) versus $1/V$. Thus, as the most probable occurrence, the statistical assessment demonstrates that direct tunneling is indeed the dominant charge transport mechanism in the alkanethiol molecular devices. The dominance of direct tunneling in alkanethiol SAMs is in good agreement with previous reports [3-5] and can be reasonably anticipated due to their large highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) gap (~8 eV). However, as shown in Fig. 1(b), an uncontrolled device-to-device variation in transport mechanisms indicates the importance of a statistical study.

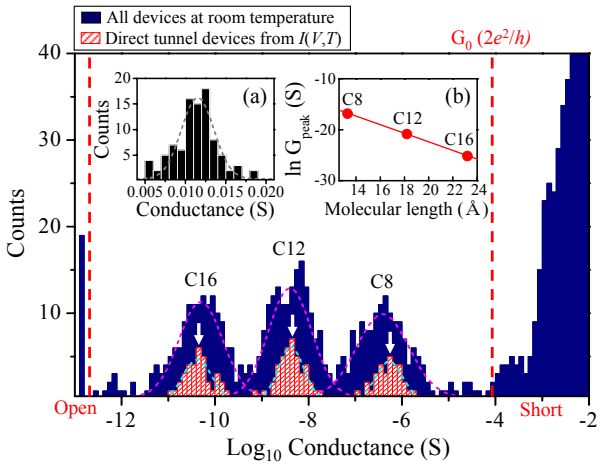

Fig. 3. Conductance histograms for all devices (filled columns) measured at room temperature and the direct tunneling devices (patterned columns) confirmed by $I(V,T)$ characterizations. The Gaussian curves (dashed lines) highlight the conductance peaks for each alkanethol. Inset (a) is a conductance histogram for the intentional short devices in the absence of molecules. Inset (b) shows a logarithmic plot of conductance peak values (marked by the arrows) versus molecular length.

Figure 2 shows the average of $I(V,T)$ characteristics for each of different length alkanethiol SAMs as the representative data of 108 direct tunneling devices [5]. The error bars on each data give the standard deviation upon the averaging. The devices exhibiting other parasitic conduction mechanisms are thoroughly excluded on the analyses so that the representative data would demonstrate the intrinsic molecular electronic properties responsible for dominating tunneling conduction mechanism.

Figure 3 shows histograms for the conductance measured at the ohmic region inside ±0.1 V, where filled columns represent the conductance histograms for all the fabricated 6,745 devices measured at room temperature and patterned columns represent those for 108 direct tunneling devices. Depending on the molecular length of alkanethiols (marked as C16, C12, and C8), the conductance values vary over orders of magnitude and appear to be distributed log-normally with well-defined conductance peaks highlighted by the Gaussian curves for each alkanethiol. Note that the log-normal distribution of the conductance values stems from a parameter that affects the conductance exponentially and is therefore likely due to a variation in tunneling distance [4]. This effect is not observed in the absence of molecules where the devices show linearly normal distribution in the histogram [see inset (a) in Fig. 3].

The peak positions in the conductance histograms of three different length alkanethiols for the direct tunneling devices (patterned columns) are identified by the arrows in Fig. 3, representing the most probable measured conductance value for the molecular device. To determine the decay coefficient (β) for the direct tunneling devices [3], the conductance values are plotted as a function of molecular length, as shown in inset (b) of Fig. 3. The conductance value exponentially depends on the molecular length, according to $G \sim \exp(-\beta d_m)$ (G is the conductance and d_m is the molecular length). Our data can be described by the above relationship, with $\beta = 0.86 \pm 0.02$ Å^{-1}, which is consistent with previous reports [3-6].

4. Conclusions

In conclusion, we reported a statistical method to study the intrinsic electronic transport of molecular devices. Our statistical analysis shows that direct tunneling is indeed the dominant conduction mechanism responsible for the intrinsic transport properties of alkanethiol molecular devices. The conductance histograms are well consistent with the tunneling characteristics and show log-normal distribution in conductance values, which is the result of a variation in tunneling distance. The statistical method can introduce an objective criterion for the examination of intrinsic electronic transport of molecular devices.

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