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Charge Transport of Alkanethiol Self-Assembled Monolayers in Micro-Via Hole Devices

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In this paper we fabricated 13440 microscale via hole structure devices using different length of alkanethiol self-assembled monolayers and characterized their electronic transport properties. Statistically averaged transport parameters such as current density, transport barrier height, effective electron mass, and transport decay coefficient were obtained from the great number of these devices. The yield of working microdevices was found as 1.5%. Temperature variable current-voltage characteristics for alkanethiol micro-via hole devices showed typical tunneling behavior when properly fabricated.

Keywords: Molecular Electronics, Device Yield, Metal-Molecule-Metal Junction, Alkanethiols.

1. INTRODUCTION

Due to the merits such as the use of functional molecules as a nanoscale building-block in miniaturized electronic devices for low cost, high-density, and less heat problem process, molecular electronics is currently undergoing a rapid development.[1–18] There has been extensive efforts to understand the charge transport in organic molecular layers. Probing the electrical characteristics of molecules by sandwiching them between metal electrodes is a main tool to study the molecular charge transport. Alkanethiol has been investigated extensively due to its robust formation as self-assembled monolayers (SAMs) on Au surface.[3] Scanning tunneling microscopy,[4,5] conducting atomic force microscopy,[6–9] mercury-drop junctions,[10,11] cross-wire junctions,[12] electrochemical methods,[13,14] break junctions,[15] nanopores,[16] and nanowell[17] have been used to study charge transport through alkanethiol SAMs.[18] The charge transport through alkanethiol SAMs is expected to be tunneling because the Fermi levels of the contacts lie within the large HOMO-LUMO gap (~8 eV) of these short (1–2.5 nm) alkanethiol molecules.[19] However, there has been little systematic work on device yield and statistically average transport parameters.

In this study, charge transport through alkanethiol SAMs in micro-via hole structure and the yield of mass-fabricated molecular devices (13440 devices) are investigated. Also, statistically averaged transport parameters such as current density, transport barrier height, effective electron mass, and transport decay coefficient were obtained from the great number of these devices.

2. EXPERIMENTAL DETAILS

The microscale alkanethiol metal-molecule-metal (M-M-M) junction devices were fabricated on a *p*-type (100) Si substrate which is covered with thermally grown 3000 Å thick SiO_2. As schematically shown in Figure 1, the conventional optical lithography method was used to pattern bottom electrodes that was made with Au (1000 Å)/Ti (50 Å) by an electron beam evaporator. And then, the patterned bottom electrodes were deposited by SiO_2 layer (700 Å thick) using plasma enhanced chemical vapour deposition (PECVD). Then, reactive ion etching (RIE) was performed to make micro-via holes of 2 μm diameter through SiO_2 layer to expose Au surfaces. Three different ~5 mM alkanethiol solutions were prepared by adding ~10 μL alkanethiols into ~10 mL anhydrous ethanol (Aldrich Chem. Co). The chips were left in the solution for 24–48 h for the alkanethiol self-assembled monolayer (SAM) to assemble on the Au surfaces exposed by RIE in a nitrogen-filled glove box with an oxygen of less than ~10 ppm. Alkanethiol molecules (Aldrich Chem. Co.) of different molecular lengths: octanethiol ($CH_3(CH_2)_7SH$, denoted as C8, for the number of alkyl unit), dodecanethiol ($CH_3(CH_2)_{11}SH$, C12), and hexadecanethiol ($CH_3(CH_2)_{15}SH$, C16) were used to

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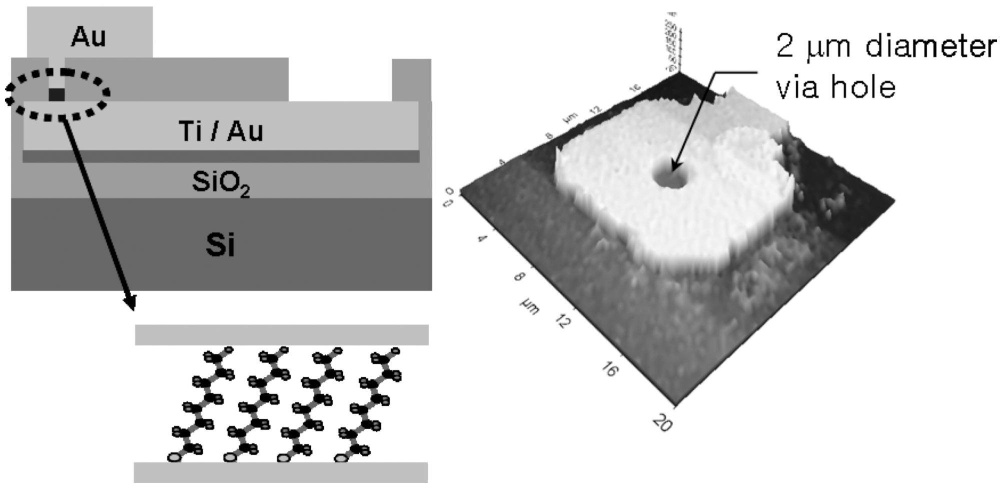

Fig. 1. Schematic of a micro-via hole structure and an AFM image of a single device. The typical junction is $\sim 2\ \mu$m in diameter.

form the active molecular component. Alkanethiol SAMs were formed on exposed Au surfaces, and the top Au electrode to form M-M-M junctions was made by thermal evaporation. The evaporation was done with a shadow mask on the chips with a liquid nitrogen cooled cold stage in order to avoid thermal damage to the active molecular component under the pressure of $\sim 10^{-6}$ torr.[19] With the same reason, the deposition rate of top Au electrode was kept very low, typically at ~ 0.1 Å/s and the total Au thickness was ~ 500 Å. Figure 1 shows the schematic of a microscale M-M-M junction device and AFM image of a single device with 2 μm diameter via hole for the junction area. Room temperature current–voltage (I–V) characteristics of as-fabricated molecular devices were carried out using a HP4155A semiconductor parameter analyzer. As-fabricated chips were packaged and loaded into a cryostat (Janis. Co). Sample temperature was varied from 300 to 77 K by flowing liquid nitrogen in the sample holder for temperature variable I–V measurement.

3. RESULTS AND DISCUSSION

Before describing our data, it is useful to briefly review the tunneling behaviour through alkanethiol M-M-M systems using widely used tunneling Simmons model.[20,21] The temperature independent tunneling current density J through an alkanethiol barrier is described as following.

$$J = \left(\frac{e}{4\pi^2\hbar d^2}\right)\left\{\left(\Phi_B - \frac{eV}{2}\right)\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\times\alpha\left(\Phi_B - \frac{eV}{2}\right)^{1/2}d\right] - \left(\Phi_B + \frac{eV}{2}\right)\times\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\alpha\left(\Phi_B + \frac{eV}{2}\right)^{1/2}d\right]\right\} \quad (1)$$

where m is the electron mass, d is the barrier width, Φ_B is the barrier height, V is the applied bias, and α is a unit

Table I. Summary of the number of devices and percentage.

# of fabricated device	Fab. failure	Short	Open	Working Devices – 201		
				C8	C12	C16
13440	392	11744	1103	84	57	60
100%	2.9%	87.4%	8.2%		1.5%	

Note: Short, open, and working devices were defined by I–V shapes and current levels (see text).

less adjustable parameter that may be used to differentiate between potential barrier shapes, or to describe effective electron mass.

To understand charge transport through alkanethiol in microscale M-M-M junction, 13440 individual micro-via hole devices of alkanethiol SAMs as schematically shown in Figure 1 were electrically characterized by a semiconductor parameter analyzer. Table I summarizes the specific status of as-fabricated devices and device yield of micro-via hole devices. Among 13440 fabricated devices, 11744 devices showed electrical short. The electrical short was defined when devices showed short-circuit ohmic I–V characteristics or current was larger than 10 mA at 1 V. There have been many reports about electrical short of molecular devices, and the main reasons of the electrical short of micro-via hole device are top Au contacts punching through the thin molecular layer and touching the bottom Au electrodes. This punching-through may occur via the defect sites of molecular layer such as grain boundaries of SAM, vacancies, and others. Fabrication failure (392 devices) and electrical open (1103 devices) mainly occurred because of mistakes in the fabrication process, for example, metal lift-off, lithography, and RIE. The electrical open was defined when devices showed open-circuit I–V characteristics or current was less than 1 nA at 1 V. And working devices were defined when devices showed a tunneling-like I–V behavior and current was between short and open device ranges. Among 201 working devices, C8, C12, and C16 working devices were 84, 57, and 60

Table II. Summary of statistically average transport parameters of alkanethiol SAMs in this study.

Alkanethiol	J at 1 V A/cm^2	Φ_B (eV)	α	β (Å^{-1})
C8	78000 ± 46000	1.29 ± 0.49	0.76 ± 0.09	0.87 ± 0.16
C12	2000 ± 400	1.26 ± 0.08	0.72 ± 0.04	0.83 ± 0.04
C16	5.2 ± 4.7	2.67 ± 0.28	0.52 ± 0.04	0.87 ± 0.05

devices, respectively. Thus, the device yield of micro-via hole device was found as ~1.5%.

Based on the measured I–V data of C8, C12, and C16 SAM, the Φ_B and α values were determined by finding a curve of optimum fit for the Simmons equation with the experimental data.[20, 22] The molecular lengths used in this work are 13.3, 18.2, and 23.2 Å for C8, C12, and C16, respectively, which were determined by adding an Au-thiol bond length to the length of molecule.[19] Table II summarizes the electrical parameters of Φ_B, α, β, and current density (J) at 1 V for octanethiol (C8), dodecanethiol (C12), and hexadecanethiol (C16) microdevices. Each parameter in Table II was obtained from the average and standard deviation of the individual fitting results from all working 201 microdevices.

To understand the length-dependent tunneling behaviors of C8, C12, and C16 SAMs in the M-M-M junction, we selected and characterized the representative micro-via hole devices. Figure 2 shows I–V characteristics of C8, C12, and C16 microdevices. The optimum fitting was performed on the experimental data of C8, C12, and C16 and found to be $\{\Phi_B = 1.01 \pm 0.01$ eV and $\alpha = 0.82 \pm 0.01\}$, $\{\Phi_B = 1.20 \pm 0.04$ eV and $\alpha = 0.74 \pm 0.02\}$, and $\{\Phi_B = 2.13 \pm 0.06$ eV and $\alpha = 0.54 \pm 0.01\}$, respectively. The increase of current flow through shorter alkanethiol in M-M-M junction imply the length-dependent charge transport through alkanethiols and is due to the difference of tunneling probability dependent on the molecular lengths. Figure 3 shows a semilog plot of tunneling current

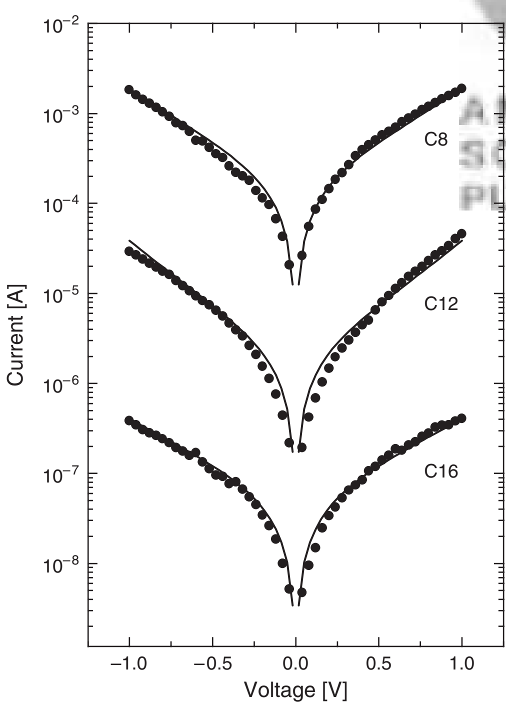

Fig. 2. Comparison of representative I–V characteristics of three different alkanethiol SAMs micro-via hole devices. Symbols are experimental data and lines are fitting curves with Simmons equation.

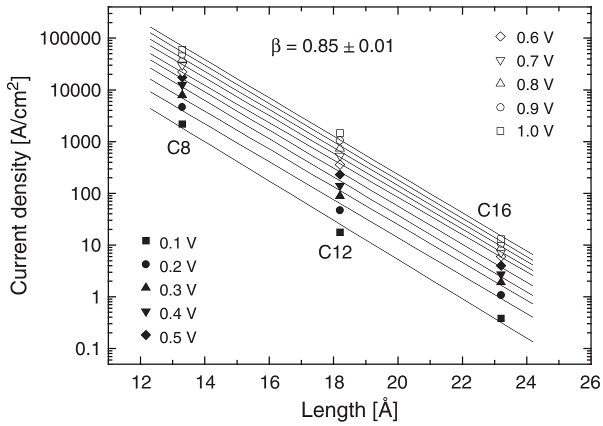

Fig. 3. Semilog plot of tunneling current densities of three different alkanethiol SAMs versus molecular length. The lines through the data points are exponential fittings.

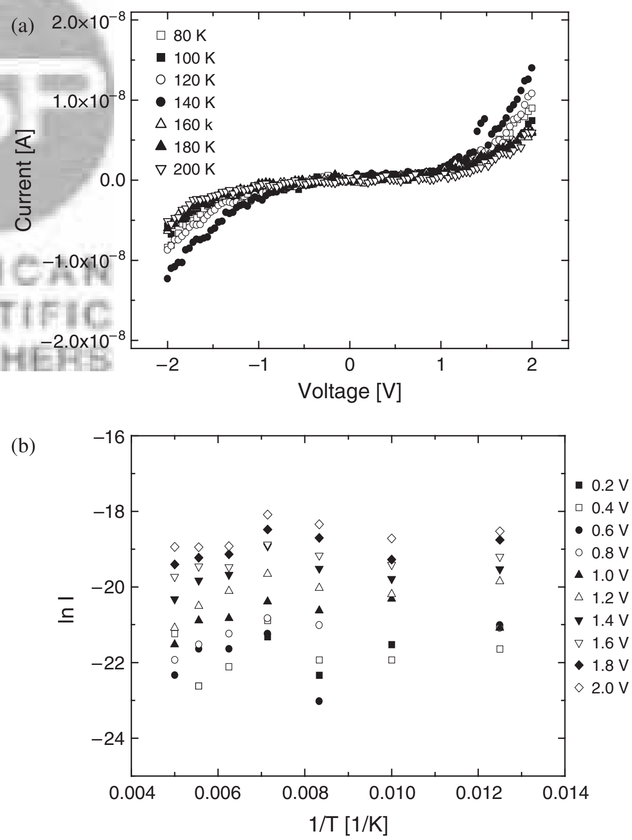

Fig. 4. (a) Temperature-variable I–V characteristics of dodecanethiol. I–V data at temperature from 200 K to 80 K with 20 K step are plotted. (b) Arrhenius plot generated from the I–V data in Figure 4(a) at voltages from 0.2 to 2.0 V with 0.2 V step.

densities at various voltages as a function of the molecular length for these alkanethiols. The tunneling current densities show exponential dependence on molecular lengths. The low-bias decay coefficient (β) value, 0.85 ± 0.01 Å^{-1}, was calculated from the average and standard deviation of the slope at each bias from Figure 3. This averaged β value agrees with the previously reported β results for alkanethiols, which ranges from ~0.7 to ~1.2 Å^{-1}.[22] To characterize the conduction mechanism of alkanethiol in M-M-M junction, temperature-variable measurement was carried out. Figure 4(a) shows a temperature variable I–V characteristic of dodecanethiol (C12) in the temperature range of 200–80 K. In spite of a little fluctuation in the I–V curves, there is not significant temperature dependence in the I–V characteristics observed. An Arrhenius plot [$\ln(I)$ versus $1/T$] is shown in Figure 4(b). It shows little temperature dependence in the slop of $\ln(I)$ versus $1/T$ at different voltages. These results suggest the conduction mechanism through alkanethiol microdevices is tunneling.[19]

4. SUMMARY AND CONCLUSIONS

13440 individual microvia hole metal-molecule-metal junction devices of alkanethiol SAMs were fabricated. Among these fabricated devices, 201 working devices were found. Thus, the yield of micro-via hole devices was about 1.5%. The transport parameters were determined by statistical averages from these working devices, and representative device showed temperature-independent tunneling behaviors.

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References and Notes

1. M. A. Reed and T. Lee, Molecular electronics, American Scientific Publishers, Stevenson Ranch (**2003**).
2. A. Nitzan and M. A. Ratner, *Science* 300, 1384 (**2003**).
3. A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-assembly, Academic Press, Boston (**1991**).
4. B. Xu and N. J. Tao, *Science* 301, 1221 (**2003**).
5. L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, *J. Phys. Chem. B* 103, 8122 (**1999**).
6. D. J. Wold and C. D. Frisbie, *J. Am. Chem. Soc.* 123, 5549 (**2001**).
7. D. J. Wold, R. Haag, M. A. Rampi, and C. D. Frisbie, *J. Phys. Chem. B* 106, 2813 (**2002**).
8. X. D. Cui, X. Zarate, J. Tomfohr, O. F. Sankey, A. Primak, A. L. Moore, T. A. Moore, D. Gust, G. Harris, and S. M. Lindsay, *Nanotechnology* 13, 5 (**2002**).
9. X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, L. A. Nagahara, and S. M. Lindsay, *J. Phys. Chem. B* 106, 8609 (**2002**).
10. M. A. Rampi and G. M. Whitesides, *Chem. Phys.* 208, 373 (**2002**).
11. K. Slowinski, H. K. J. Fong, and M. Majda, *J. Am. Chem. Soc.* 121, 7257 (**1999**).
12. J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang, T. L. Schull, J. Naciri, M. H, Moore, and R. J. Shashidhar, *J. Am. Chem. Soc.* 124, 10654 (**2002**).
13. J. F. Smalley, S. W. Feldberg, C. E. D. Chidsey, M. R. Limford, M. D. Newton, and Y. Liu, *J. Phys. Chem* 99, 13141 (**1995**).
14. K. Weber, L. Hockett, and S. Creager, *J. Phys. Chem. B* 101, 8286 (**1997**).
15. J. Reichert, H. B. Weber, M. Mayer, and H. von Lohneysen, *Appl. Phys. Lett.* 82, 4137 (**2003**).
16. W. Wang, T. Lee, I, Kretzschmar, and M. A. Reed, *Nano lett.* 4, 643 (**2004**).
17. N. Majumdar, N. Gergel, D. Routenberg, J. C. Bean, L. R. Harriott, B. Li, L. Pu, Y. Yao, and J. M. Tour, *J. Vac. Sci. Technol. B* 23, 1417 (**2005**).
18. B. A. Mantooth and P. S. Weiss, *Proc. IEEE* 87, 652 (**2003**) and references therein.
19. W. Wang, T. Lee, and M. A. Reed, *Phys. Rev. B* 68, 035416 (**2003**).
20. J. G. Simmons, *J. Appl. Phys.* 34, 1793 (**1963**).
21. R. Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* 123, 5075 (**2001**).
22. T. Lee, W. Wang, J. F. Klemic, J. J. Zhang, J. Su, M. A. Reed, *J. Phys. Chem. B* 108, 8742 (**2004**).

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