

## Effective Insulating Properties of Autooxidized Monolayers Using Organic Ditellurides

Tohru Nakamura,<sup>\*,†</sup> Satoshi Yasuda,<sup>†</sup> Takayuki Miyamae,<sup>†</sup> Hisakazu Nozoye,<sup>†</sup> Nobuhiko Kobayashi,<sup>†</sup> Hiroshi Kondoh,<sup>\*,‡</sup> Ikuyo Nakai,<sup>‡</sup> Toshiaki Ohta,<sup>‡</sup> Daisuke Yoshimura,<sup>§</sup> and Mutsuyoshi Matsumoto<sup>†</sup>

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5-2, 1-1 Higashi 1-Chome, Tsukuba 305-8565, Japan, Department of Chemistry, The University of Tokyo, Hongo, Tokyo 113-0033, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received July 12, 2002

It is particularly important that the properties of nanoelectronic interconnect between organic molecules and the metallic or semiconductive interfaces are controlled as a conductor or an insulator for the fabrication of molecular electronics. For example, interfaces with resistive and dielectric properties are crucial to fabricate nanodevices such as thin film transistors. Chalcogenide groups are the simplest as junctions because chalcogens are able to directly connect the organic moiety and the inorganic surfaces with two covalent bonds. Along this line, we started to study previously unknown films of heavy chalcogenide analogues with a view to tuning the electrical properties of organic molecular devices because heavy chalcogens (Se, Te) possess different characters as compared with lighter chalcogens (O, S). We report here that dialkyl ditellurides adsorb on Au(111) surfaces by wet deposition to form highly resistive autooxidized monolayers (AMs) under air. The theoretical calculations suggested effective conducting properties of telluride systems.<sup>1</sup> However, obtained conductivities of Te systems under ambient conditions are different from that of the calculations.

We select ditellurides such as dibutyl and dioctyl ditelluride ( $R_2Te_2$ :  $R = Bu$  ( $n-C_4H_9$ ),  $Oc$  ( $n-C_8H_{17}$ )) to form thin films because tellurol, which is a thiol analogue, is generally unstable under ambient conditions.<sup>2</sup> Dialkyl ( $Bu$  and  $Oc$ ) disulfides and diselenides were prepared as a control to compare with the ditellurides so that the contact resistances on the same alkyl group would be similar in the conductivity measurements. Dichalcogenide films were prepared under air unless otherwise stated. Conductive AFM (c-AFM) measurements were performed by using a modified SPA 300HV of Seiko Instruments Inc. with a 1 nA/V amplifier under the vacuum conditions of  $3 \times 10^{-7}$ – $2 \times 10^{-6}$  Torr to reduce the effect of water molecules. Detailed syntheses of compounds and experimental procedures are described in the Supporting Information.

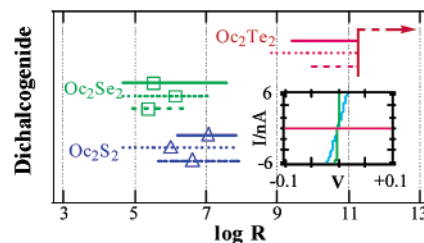
Figure 1 shows the logarithmic plot of conductivity obtained by current–voltage ( $I$ – $V$ ) measurements.  $I$ – $V$  characteristics are known to depend strongly on the tip conditions, for example, tip radius, tip shape, material, and contamination, especially in the case of noncovalent bonding systems.<sup>3</sup> To confirm the reproducibility, we prepared three different osmium-coated gold tips (tip No 1, 2, and 3) and three films each of dioctyl dichalcogenide ( $Oc_2S_2$ ,  $Oc_2Se_2$ ,  $Oc_2Te_2$ , nine samples in total). Each identical tip was used for the  $I$ – $V$  measurements of a series of films of three different dioctyl dichalcogenides. Good reproducibility was found even when the sequence of the  $I$ – $V$  measurements of the three films was changed.

\* To whom correspondence should be addressed. E-mail: tohru.nakamura@aist.go.jp or kondoh@chem.s.u-tokyo.ac.jp.

<sup>†</sup> Nanotechnology Research Institute, AIST.

<sup>‡</sup> The University of Tokyo.

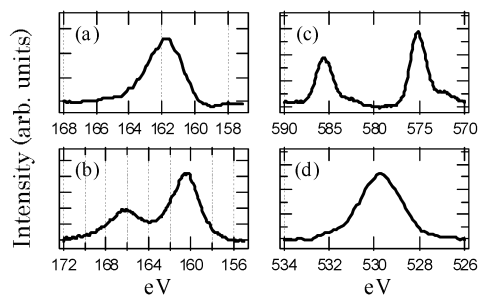
<sup>§</sup> Institute for Molecular Science.



**Figure 1.** Logarithm of resistances  $R$  (ohm) measured by c-AFM for each dioctyl dichalcogenide (blue,  $Oc_2S_2$ ; green,  $Oc_2Se_2$ ; red,  $Oc_2Te_2$ ). Each line shows the range of  $\log R$  obtained by  $I$ – $V$  measurements. Solid lines show the range of  $\log R$  of dioctyl dichalcogenides measured using tip 1, dotted lines using tip 2, and dashed lines using tip 3. The markers show the average overall values of  $\log R$  for each tip: triangle,  $Oc_2S_2$ ; square,  $Oc_2Se_2$ . The average overall values of  $\log R$ : 6.77 ( $Oc_2S_2$ ), 5.74 ( $Oc_2Se_2$ ). The standard deviation for each sample: 0.78 ( $Oc_2S_2$ ), 0.83 ( $Oc_2Se_2$ ). The averaged  $\log R$  and the standard deviation for  $Oc_2Te_2$ -derived films cannot be determined because some of the resistances surpass the limit for  $I$ – $V$  measurements. Inset: typical  $I$ – $V$ s for dichalcogenide films (blue,  $Oc_2S_2$ ; green,  $Oc_2Se_2$ ; red,  $Oc_2Te_2$ ).

It is evident that  $Oc_2Te_2$ -derived thin films have effective insulating properties when compared with disulfide and diselenide films. The same tendency was observed for butyl dichalcogenide films. The average resistances of the self-assembled monolayers (SAMs) of octanethiol were similar to that of dioctyl disulfide and were below  $10^{-4}$ – $10^{-5}$  times the values of ditellurides. The obtained results indicate that ditelluride can be used as a material to form effective insulating thin films. It is likely that a selenide junction is a more effective conductor than a sulfide junction from the results of the averages (Figure 1), although the variations in the measured resistances are large. The methodology employed by Cui et al. may enable us to discuss this point more precisely.<sup>3b</sup> The study along this line is now underway. These results are in contrast to the high conductive efficiency of telluride system shown by the calculation of a 1,4-(bis(chalcogeno)benzene) systems.<sup>1</sup> We consider that this discrepancy is caused by the chemical effect of the tellurium junction or the formation of multilayer systems of ditelluride. AFM and photoemission spectroscopy were employed to clarify this point.

Contact AFM observations were performed to estimate the thickness of ditelluride-derived films. A smooth surface was observed for each ditelluride-derived sample. After removing the materials of  $Oc_2Te_2$ -derived films by using contact AFM tips, the cross section observed showed that the thickness of the films was ca. 0.5 nm, suggesting the formation of monolayer-like structures. Next, X-ray photoelectron spectroscopy (XPS) measurements were carried out for dichalcogenide samples. Figure 2 shows the core level XPS of the chalcogen for each octyl sample on Au(111). The peak of S 2p in Figure 2a for dioctyl disulfide is positioned at 161.8 eV, which is in good agreement with that of the sulfur–gold



**Figure 2.** XPS core level spectra on Au(111). (a) S 2p for dioctyl disulfide. (b) Se 3p for dioctyl diselenide. (c) Te 3d for dioctyl ditelluride. (d) O 1s for dioctyl ditelluride.

covalent bond.<sup>4</sup> Se  $3p_{1/2}$  and  $3p_{3/2}$  peaks are evident at 166.2 and 160.3 eV, respectively, in Figure 2b. The existence of a selenide group in the dioctyl diselenide films is confirmed because the positions of the peaks are in good agreement with those of selenide SAMs on gold.<sup>5</sup> On the other hand, the peaks for Te  $3d_{3/2}$  and  $3d_{5/2}$  are evident at 585.6 and 575.2 eV, respectively (Figure 2c), suggesting the existence of Te-oxide associated species because these peaks are located near the  $\text{TeO}_x$  peaks. The existence of oxygen is also detected for ditelluride samples as shown in Figure 2d, but not for disulfide and diselenide films, indicating the existence of Te–O species. The C 1s peak was also observed at 284 eV for all of the films.

Elementary analyses of the dichalcogenide films were carried out to lead to the intensity ratio of 0.8:1.3:1.0 for Te, Se, S on the surface, respectively, after the normalization of the factors such as the intensity of X-ray and atomic subshell photoionization cross sections. Because it is well known that disulfides form SAMs, the results suggest that dioctyl heavy dichalcogenides ( $\text{Oc}_2\text{Te}_2$  and  $\text{Oc}_2\text{Se}_2$ ) also form monolayers on the surface. This is consistent with contact AFM measurements. The intensity ratio of oxygen to tellurium was ca. 2.0. These results suggest that dioctyl ditellurides are oxidized on the surface to provide monolayers of octyltellurinic acid- or tellurone-like species on the surface. These results obtained by AFM and XPS described above led us to consider that the oxidized species of ditelluride remarkably enhance the resistive property of the  $\text{OcTe}$ -oxide monolayers.

Oxidation of the ditelluride on Au(111) was studied using ultraviolet photoelectron spectroscopic (UPS) measurements. In this case, ditelluride monolayers were prepared under a dry nitrogen-purged glovebox and were stored carefully in nitrogen-bubbled ethanol to investigate the oxidation process of ditelluride on the surfaces. The valence UPS spectra of ditelluride SAMs before the oxidation showed basically the same spectra for those of disulfide and diselenide SAMs. At an incident photon energy of 80 eV,  $\text{Te}_{4d}$  emissions of ditelluride SAMs were found at 40.0 and 41.5 eV relative to the Fermi level, corresponding to telluride before oxidation on the surface. The other peaks appeared at 43.5 and 44.6 eV after immersion in water for 5 min. These concomitant peaks are consistent with the oxidation state of telluride. These results clearly indicate that dioctyl ditelluride forms telluride-containing monolayer films, which are readily oxidized by oxygen species under ambient conditions, presumably by hydrogen oxide rather than oxygen gas to give alkyl Te-oxide monolayers.

Theoretical analyses about our results are performed using molecular orbital calculations at the B3PW91/LANL2DZ level.<sup>6</sup> The decreasing order of HOMO–LUMO gaps of  $\text{OcX–Au}$  ( $X = \text{S}, \text{Se}, \text{TeO}_2$ ) is calculated as  $X = \text{TeO}_2, \text{S}, \text{Se}$ , which tends to correspond to the order of the resistance. Therefore, the calculations are also consistent with the experimental results.

We consider at present that high resistance of ditelluride AMs is due to the oxidized form of ditelluride. This will lead to an increase of the HOMO–LUMO energy gap that is relevant to the density of state (DOS) and/or a change of the interface dipole that is relevant to the work function and the shift of DOS. We are currently investigating the detailed mechanism of the effective insulating properties of ditelluride AMs by using surface analyses and a theoretical approach.

To improve electric devices, it is important to make thin films by low-cost procedures. Although some papers reported the particles and/or thick films of tellurium and/or tellurium oxide prepared by expensive procedures such as vacuum deposition and photolysis,<sup>7</sup> organic ditelluride systems have an advantage of easy preparation, that is, a low-cost procedure for the formation of smooth AMs with the peculiarities of Te-oxide.

In summary, AFM, XPS, and UPS measurements revealed for the first time that ditelluride AMs having high resistances easily form on the surfaces due to the autooxidation of ditelluride in contrast to the case of the lighter dichalcogenides. The ditelluride AMs could be applied to the selective fabrication of effective resists and/or new imaging systems using the feature of tellurium oxide in small device circuits. These types of materials (AMs) would be useful to support and develop nanotechnology.

**Acknowledgment.** The authors are grateful for the “Dynamic Nanotech Research Promotion Program (grant-in-aid N° DNR001)” in the Nanotechnology Research Institute. The XPS experiments were performed under the approval of the Photon Factory Program Advisory Committee (PF PAC No. 01S003). Part of this work (UPS) was performed as a Joint Research Program of UVSOR, Institute for Molecular Science. T.N. thanks Dr K. Yase for the usage of the Os-coater.

**Supporting Information Available:** Compounds, instruments, and histograms for I–V measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Ventra, M. D.; Lang, N. D. *Phys. Rev. B* **2001**, *65*, 045402.
- (2) Jensen, K. A.; Kjaer, A. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, p 5.
- (3) (a) Wold, D. J.; Frisbie, C. D. *J. Am. Chem. Soc.* **2001**, *123*, 5549. (b) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571. (c) Sakaguchi, H.; Hirai, A.; Iwata, F.; Sasaki, A.; Nagamura, T. *Appl. Phys. Lett.* **2001**, *79*, 3708. (d) Cui, X. D.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Primak, A.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Nanotechnology* **2002**, *13*, 5.
- (4) Castner, D. G.; Hinds, K.; Grainger, D. W. *Langmuir* **1996**, *12*, 5083.
- (5) For our preliminary XPS study about SAMs of organic heavy chalcogenides, see: (a) Nakamura, T.; Kimura, R.; Matsui, F.; Kondoh, H.; Ohta, T.; Sakai, H.; Abe, M.; Matsumoto, M. *Langmuir* **2000**, *16*, 4213. (b) Kondoh, H.; Nakai, I.; Nambu, A.; Ohta, T.; Nakamura, T.; Kimura, R.; Matsumoto, M. *Chem. Phys. Lett.* **2001**, *350*, 466.
- (6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (7) (a) Dutton, R. W.; Muller, R. S. *Thin Solid Films* **1972**, *11*, 229. (b) Lakshminarayan, N.; Radhakrishnan, M.; Balasubramanian, C. *J. Mater. Sci.* **1982**, *17*, 1623. (c) Irvine, S. J. C.; Mullin, J. B.; Robbins, D. J.; Glasper, J. L. *J. Electrochem. Soc.* **1985**, *132*, 968. (d) Ouchi, A.; Yamamoto, K.; Koga, Y.; Pola, J. *J. Mater. Chem.* **1999**, *9*, 563. (e) Pola, J.; Ouchi, A. *J. Org. Chem.* **2000**, *65*, 2759.

JA0276671