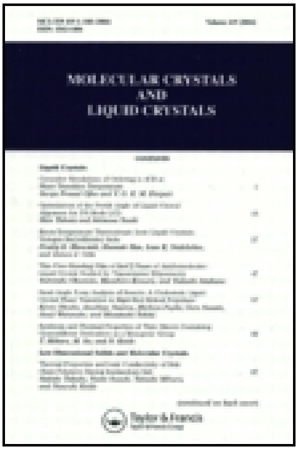

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Structures and Electrical Properties of Self-Assembled Monolayers of Alkanethiol and Alkanedithiol

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Structures and Electrical Properties of Self-Assembled Monolayers of Alkanethiol and Alkanedithiol

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Clearly resolved STM image of SAMs were obtained and molecule structures and conduction mechanisms are discussed.

Keywords: self-assembled monolayers; alkanethiol, alkanedithiol, scanning tunneling microscopy; dipole moment

INTRODUCTION

There have been increasing interests for self-assembled monolayers (SAMs) of thiol molecules on gold substrates, since it was revealed that molecules with thiol groups spontaneously assemble on gold from their solution or vapor and form densely packed monolayer films[1]. In addition, dithiol molecules are recently proposed as one of the most suitable molecules for designing molecular-based single-electron tunneling (SET) devices[2-4]. Such interesting ideas have been proposed, however, detailed molecular arrangements on gold substrate and/or electric characteristics have not been elucidated in nanometer scale yet. In this study, UHV-STM was used to investigate the packing structures and electrical properties of such SAMs and the obtained I-V characteristics are discussed in connection with the molecular structures with dipole moments.

EXPERIMENTAL SECTION

We prepared the gold substrate with the surface of (111) orientation by vacuum evaporation of gold onto mica. SAMs of octanethiol ($CH_3(CH_2)_7SH$) and octanedithiol ($HS(CH_2)_8SH$) were deposited by dipping the substrates in their dilute solution of ethanol or dichloromethane for about 24 hours at room temperature. The UHV-STM (ultrahigh vacuum scanning tunneling microscope) employed for this study was Unisoku USM-801 (Osaka, Japan). The STM image was obtained under high resistance tunneling condition at room temperature and in constant height mode, which provided high resolution. The I-V curves was measured by applying triangular voltage signals while the voltage applied to the Z-axis of the piezo scanner was held constant.

RESULTS AND DISCUSSION

Structures of SAMs

Structures of SAMs were examined with UHV-STM and several morphologies were obtained. In addition to the already known structures, the molecularly resolved STM images showed the unique packing structures for both SAMs. Figure 1(a) shows an image of the $(4\sqrt{3} \times 2\sqrt{3})R30°$ structure of octanethiol SAMs. We can clearly see three different brightness for methyl head groups, revealing the existence of three different sites in unit-cell, although this structure is usually found to contain two kinds of molecules[5-6].

On the other hand, Fig. 1(b) shows an STM image of octanedithiol SAMs. The image consists of equally spaced stripes of about 1.3 nm, which is nearly the same as the length of octanedithiol molecule. Thus, this result indicates that the molecules are lying parallel to the substrates. In addition, the FFT analysis exhibits three-fold symmetry, showing that molecules are epitaxially deposited on the gold(111) surface. While the observed structures of dithiol SAMs show the parallel arrangement, it may be changed by elevating temperature of the substrate during the deposition.

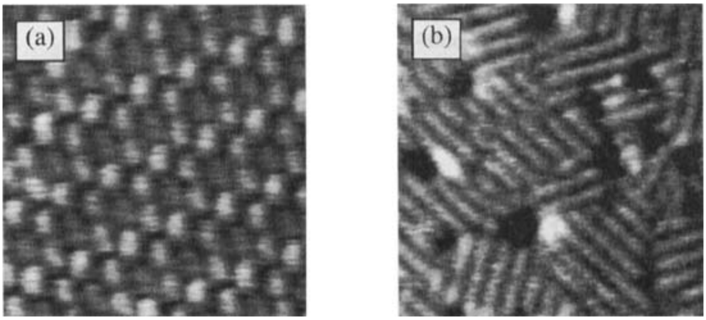

FIGURE 1 STM images of octanethiol SAMs (Vt = 0.6 V, It = 17 pA, 4.6 nm x 4.6 nm) (a), and of octanedithiol SAMs (Vt = -0.6 V, It = 18 pA, 22.5 nm x 22.5 nm) (b)

Electrical Properties of SAMs

We also measured the current voltage characteristics (I-V curves) of the SAMs using STM tip of UHV-STM. Figure 2 shows I-V curves of SAMs obtained with STM. As shown in Fig. 2(a), I-V curves of octanethiol SAMs exhibits asymmetric characteristics and non-linear behavior, while that of octanedithiol SAMs revealed symmetric characteristics and non-linear behavior, as shown in Fig. 2(b).

Here we discuss the asymmetric I-V characteristics observed for octanethiol SAMs. Evans and Ulman[7] measured the surface potential of SAMs and found increasing positive surface potential with chain length. The reported surface potential of ocatanethiol SAMs was about 0.55 V. Thus, SAMs of alkanethiol molecules may be considered as being composed of a sheet of negative charges close to the substrate and that of positive charges on the hydrocarbon (a dipole sheet structure). There may also exists the potential barrier at the interface of the gold substrates and the sulfur atoms of the molecule. Based on these suggestions, the schematic diagram of the conduction mechanism for octanethiol SAMs is shown in Figure 3(a). When the negative bias voltage is applied to the STM tip, a dipole sheet may become a barrier, reducing the current compared with the case when the positive bias is applied. Actually, the I-V curves obtained here and shown in Fig. 2(a) reveals that there is a shoulder point (indicated by the arrow) when the negative applied voltage become larger than 1.0 V, probably reflecting the barrier height by the dipole moment. Thus, this idea explains qualitatively the observed asymmetric I-V curve, but further detailed discussion including another mechanisms are certainly necessary. In contrast, the octanedithol SAMs have

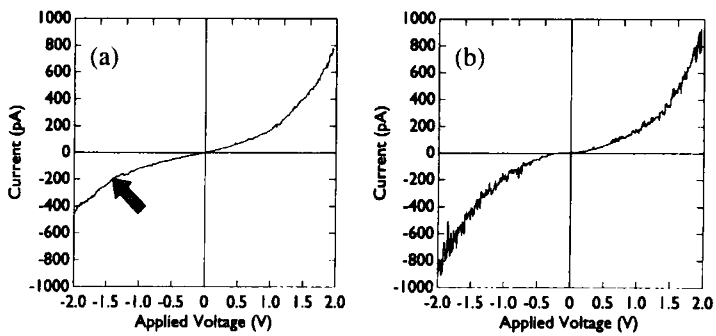

FIGURE 2 I-V curve of octanethiol SAMs (Vt = 0.6 V, It = 50 pA) (a), and of octanedithiol SAMs (Vt = 0.6 V, It = 50 pA) (b)

no net dipole moment and the molecules are lying with its axis parallel to the surface as shown in Fig. 3(b), so that it is judged reasonable that the observed I-V curves showed no dependence on the bias polarity.

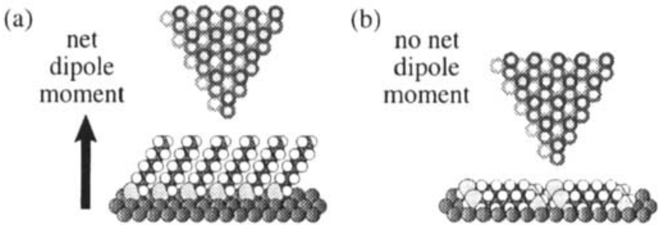

FIGURE 3 The schematic diagrams of the conduction mechanism of octanethiol SAMs (a), and of octanedithiol SAMs (b)

CONCLUSIONS

Clearly resolved STM images showed new morphological features, namely the existence of three different kinds of molecules in the $(4\sqrt{3} \times 2\sqrt{3})R30°$ structure in octanethiol SAMs and the molecular packing structures of octanedithiol SAMs, where the molecules are lying on the substrates with their axes parallel to the gold surface. Also I-V characteristics measured for both SAMs revealed that the existence of sheet dipole moment gives the effect on the asymmetry characteristics in the I-V curves of the ocatanethiol SAMs.

Acknowledgments

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