



Preparation of large-area molecular junctions with metallic conducting Langmuir–Blodgett films



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ABSTRACT

Metallic conducting Langmuir–Blodgett (LB) films were used as soft electrodes to fabricate molecular junctions with self-assembled monolayers (SAMs) of alkanethiols ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$) on an Au surface. Alkanethiols can form highly ordered, stable dielectric SAMs on metal surfaces over large areas. However, it is difficult to establish electrical contacts on such SAMs, which has limited their application. In this work, we used metallic conducting LB films composed of bis(ethylenedioxy)tetrathiafulvalene and stearic acid as a soft electrode onto alkanethiol SAMs (C_n -SAM, $n = 12, 14, 16, 18$) to prepare Au/SAM/metal junctions of relatively large size ($\sim 15.6 \times 10^3 \mu\text{m}^2$). The current density–voltage (J – V) characteristics across the junctions exhibited rectifying behavior with a ratio R of ~ 5 ($R = |J(V)|/|J(-V)|$ at ± 1 V). The lower transfer rate corresponding to the electron transport from Au to the LB films exhibited nonlinear J – V characteristics, while the higher transfer rate of electrons from the LB film to Au showed linear J – V characteristics. Kelvin probe force microscopy revealed that the work function of the metallic LB films was smaller than that of Au. The observed rectification behavior is probably caused by different electron transport mechanisms between the two current directions.

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1. Introduction

In the past decade, researchers have fabricated numerous functional organic molecules for use in molecular devices. Molecular devices are used in a wide range of fields from electronics to bionomics. In electronics, self-assembled monolayers (SAMs) are expected to be useful for developing molecular devices. This is because SAMs can readily form as a high density, well-ordered monolayer over relatively large areas. The simplest application of SAMs is as an ultrathin insulating layer by alkanethiol. Several research groups have investigated the electrical characteristics of alkanethiol SAMs by scanning probe microscope techniques, such as atomic force microscopy and scanning tunneling microscopy or in nanopore junctions [1–4]. They observed that the current density through SAMs depends on the length of the alkyl chain. Furthermore, nonlinear behavior was found in current density versus applied voltage (J – V) curves, which was attributed to tunneling [4,5].

Another application of SAMs is as molecular rectifiers, which allow a larger current to pass in one bias than in the other. Rectifiers are essential components for memory and logic elements in molecular electronics. The mechanism of molecular rectification, however, is poorly understood. The classical junction model for molecular rectification is metal–molecule–metal junctions with a molecule containing donor–acceptor moieties, which was predicted by Aviram and Ratner

[6] and fabricated by Metzger [7]. In this junction, the electron flow in the acceptor–donor direction is allowed by applying a low voltage, whereas the reverse electron flow requires a much higher voltage to overcome the larger gap between the highest occupied molecular orbital (HOMO) of the acceptor and the lowest unoccupied molecular orbital (LUMO) of the donor. Recently, other rectification mechanisms in different molecular systems have also been found. For example, several research groups produced junctions where two metal electrodes were linked through the SAM of alkyl chains functionalized by π -conjugated groups [8–10]. The HOMO of the π -conjugated group interacts strongly with the adjacent metallic state of one electrode, which increases the rate of electron tunneling from the HOMO to the other electrode but not in the reverse direction, resulting in rectification behavior.

Although many interesting electronic behaviors including rectification and tunneling have been observed for metal–molecule–metal junctions based on SAMs, actual application of these behaviors in electronic devices has not been achieved. The main drawback of SAM-based devices is that it is difficult to fabricate metal electrode contacts on SAMs. SAMs are quite fragile because they are extremely thin, thus defects or metal filaments easily form inside the film. As a result, common electrode fabrication processes such as vacuum deposition or sputtering of noble metals on SAMs cause short-circuiting. Accordingly, the contact of the metal top electrode has been a limiting step in device fabrication. A variety of techniques have been developed to avoid film disturbance, including scanning probe techniques

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[3], nanoscale holes [4], cold gold evaporation [11], Hg-drop electrodes [12], eutectic alloy contacts [13], and conductive polymer electrodes [14]. Although these techniques can establish electrical contact to SAMs without serious damage, many of them are only applicable for nanoscale area junctions and unsuitable for solid state devices. In this paper, we use metallic conducting Langmuir–Blodgett (LB) films as soft electrodes to form electrical contacts on SAMs. The LB technique allows films to be prepared gently, so it does not damage an underlying SAM. In addition, the electrode in thin film form is suitable for device fabrication because of an easiness to incorporate into practical device structure.

LB films composed of bis(ethylenedioxy)tetrathiafulvalene (BO, Fig. 1) and a fatty acid exhibit stable metallic behavior from room temperature down to 110 K. Macroscopic DC conductivity of up to 80 S/cm was observed at 300 K for this LB film [15]. Moreover, BO–fatty acid LB films are better suited for device fabrication than other conducting LB films because the metallic phase of this LB film is obtained after the film is transferred from the water surface; no additional treatment such as heating or counterion doping is required to obtain a metallic phase [16]. In this report, we built metal/SAM/metal junctions using BO–stearic acid (SA) LB films on alkanethiol SAMs with the composition $\text{CH}_3(\text{CH}_2)_n-1\text{S}$ (C_n -SAM) prepared on Au surfaces. The J - V characteristics were measured for the Au/C_n-SAM/BO–SA LB films junctions with different alkyl chain lengths of C_n -SAM ($n = 12, 14, 16, 18$). Kelvin probe force microscopy (KPFM) experiments were performed on both Au and BO–SA electrodes in order to investigate their electronic properties. An unusual rectifying behavior was observed in all J - V characteristics. Possible carrier transport mechanisms are discussed based on the experimental results.

2. Experimental details

2.1. Reagents and materials

Alkanethiols with different alkyl chain length, $\text{CH}_3(\text{CH}_2)_n-1\text{SH}$ ($n = 12, 14, 16, 18$), were purchased from Wako Chemicals (Japan). BO was synthesized according to the literature [17] and then characterized by ^1H nuclear magnetic resonance spectroscopy and mass spectrometry. Water was purified using a Millipore water purification system. Reagents of analytical grade were obtained from Aldrich and used as received without further purification.

2.2. Substrates

Junctions were prepared on Si substrates (20 mm × 10 mm). Using both photolithography and vacuum evaporation, we deposited circular Au electrodes (Au 1000 Å/Ti 100 Å) with a diameter of 500 μm connected by a thin contact line and a T-shaped Au pattern as the counter electrode on the Si substrate. An SiO_2 insulating layer (1000 Å) was formed on the substrate, then, by using the lithographically patterned membrane, pores with a diameter of 250 μm were etched through the SiO_2 layer by HF at the center of each Au circle and over the whole area of the counter electrode. This gave an Au electrode with its edges covered by a SiO_2 layer (Fig. 2).

We previously used substrates that did not have their edges covered by SiO_2 . However, samples prepared on such substrates exhibited a high proportion of short-circuiting of over 80%, which made experiments difficult. The present substrate possesses a flat, edgeless Au electrode, which helps to prevent short-circuiting. Using this substrate, devices

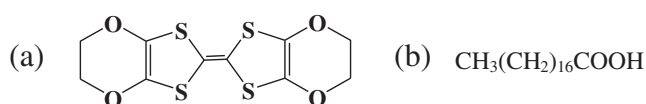


Fig. 1. Chemical structures of (a) BO and (b) stearic acid.

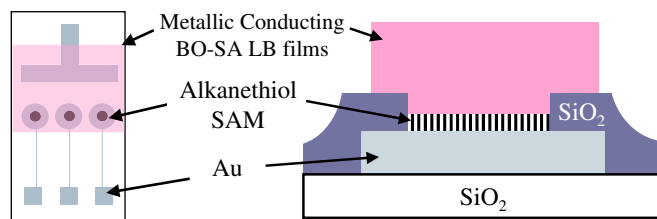


Fig. 2. Schematic diagram of an Au/SAM-C_n/BO–SA LB film junction.

less than 15% caused short-circuit. This significant decrease indicates that the side of the electrode has a strong tendency to induce pinholes or defects in SAMs.

2.3. Preparation of SAMs

The substrates were cleaned with piranha solution ($\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4 = 2:1$, v/v) for 1 min, rinsed thoroughly with deionized water, and dried under a N_2 stream. We prepared four kinds of alkanethiolate SAMs with different alkyl chain length: C_{12} , C_{14} , C_{16} , and C_{18} . SAMs were formed on the small circular Au electrodes by immersing the substrates in solutions of $\text{CH}_3(\text{CH}_2)_n-1\text{SH}$ ($n = 12, 14, 16, 18$) in ethanol (10 mM) for 24–48 h in a nitrogen-filled glove box. The samples were washed with ethanol and water, and then dried in N_2 steam. Note that the counter electrode was preserved as native Au surface without SAM layer.

2.4. Formation of conducting LB films

Oxygen-substituted tetrathiafulvalene (TTF) derivatives of BO tend to form metallic states through partial charge transfer between counter anions or acceptor molecules. We previously found that a mixture of BO and fatty acid spontaneously forms a conducting Langmuir film on the water surface [16]. The mechanism of film formation involved a chemical reaction between BO and the COOH group of the fatty acid, resulting in a partial charge transfer state of BO. The transferred BO–SA LB films exhibited metallic conduction above 110 K. Preparation of BO–SA LB films is very simple: molecules are spread on the surface of water and then transferred onto a substrate. Film preparation is described in detail below.

Solutions of BO and SA in chloroform (both 1.0 mM) were mixed to give a 1:1 molar ratio and then dispersed on the surface of ultrapure water ($\geq 18 \text{ M}\Omega \text{ cm}$). The dispersed molecules were left on the water surface for 10 min to allow chloroform to evaporate, and then they were compressed by a moving barrier to increase their surface pressure to 20 mN/m. Y-type film transfer (transfer on both up and down strokes) was then performed until 21 layers of BO–SA LB film were deposited on the substrate including both the SAM-covered circular hole and T-shaped counter electrode (Fig. 2). The BO–SA LB films established electrical contact between the two areas, forming a Au/C_n-SAM/BO–SA LB film junction on the surface of each circular hole.

2.5. Characterization

Electrical transport through the junctions was determined by measuring their J - V characteristics with an electrometer (Model 6517A Keithley, Ohio). After LB film formation, the samples were dried in an ambient atmosphere for 12 h and then under vacuum (10^{-1} Pa) for 24 h. Transport measurements were acquired under the same vacuum conditions. KPFM images were obtained by a Nano search microscope (SFT-3500SPM Shimadzu, Japan) at a scan speed of 1 Hz using a chromium and platinum-coated Si probe (EFM-20 NanoWorld, Switzerland) with a force constant of 2.8 N/m. Images were taken under ambient atmosphere.

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