9th International Conference on Nano-Molecular Electronics

Fabrication of Metal–Insulator–Metal Junction with Metallic Conductive Langmuir–Blodgett Films

Kengo Mochizuki\textsuperscript{a}, Hitoshi Ohnuki\textsuperscript{a,*,b}, Keiichi Ikegami\textsuperscript{b}, Tatsuro Imakubo\textsuperscript{c}, Mitsuru Izumi\textsuperscript{a}

\textsuperscript{a}Tokyo University of Marine Science and Technology, 2-1-6 Etchujima, Koto-ku, Tokyo 135-8533, Japan
\textsuperscript{b}National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
\textsuperscript{c}Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

Abstract

The Langmuir–Blodgett (LB) technique can deposit a soft coating without damaging the substrate. Thus, the technique is appropriate for coating fragile materials such as nano-structures and biomaterials. We fabricated electrical contacts on a dodecanethiol self-assembled monolayer (C\textsubscript{12} SAM) using metallic conductive LB films of BEDO-TTF/stearic acid. We then prepared a metal–insulator–metal (MIM) junction, in which the C\textsubscript{12} SAM was sandwiched between the LB films and Au surface. The current–voltage characteristics across the MIM junction exhibited nonlinear behavior, which suggests that tunneling is the dominant conduction mechanism. The tunneling characteristic parameters calculated using the Simmons tunneling model were in agreement with previous reports. These results show that metallic conductive LB films can serve as a soft electrode for use with delicate materials.

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Keywords: Langmuir–Blodgett Films, self-assembled monolayer, TTF derivatives, metallic conductivity, tunneling

1. Introduction

Over the past few decades, the novel functionalities of molecular materials have been a resource for the development of new electronic devices. A wide variety of devices have been developed using this class of materials ranging from organic light-emitting diodes to biosensors. A common property of these materials is that they are fragile and have easily-damaged features. Thus, careful treatment is required in processing these materials. For fabrication of electronic devices, one of the most serious challenges is creating electrical contacts on these delicate materials. Ordinary methods of electrode fabrication, such as vacuum evaporation or sputtering, can cause irreversible damage to the samples, because of the severe environments and the high-energy flux heating that occur during these processes. Gentler methods of electrode fabrication are required. Electrode fabrication using the

\textsuperscript{*} Corresponding author. Tel.: +81-3-5245-7466; fax: +81-3-5245-7466.
E-mail address: ohnuki@kaiyodai.ac.jp.

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doi:10.1016/j.phpro.2011.05.026
Langmuir–Blodgett (LB) technique is advantageous, because of the characteristics of the soft-film formation process. In this study, we investigated application of metallic conducting LB films as soft electrodes for these delicate materials. To the best of our knowledge, this is the first attempt to use LB films as electrodes in molecular electronic devices.

LB films are conducting, which is a property that is indispensable for electrode materials. Several kinds of conducting LB films have been shown to have metallic behavior through Hall-effect measurements, EPR spectroscopy, and temperature dependent conductivity [1]. Among them, the LB films based on bis(ethylenedioxy)tetrathiafulvalene (Fig. 1, denoted as BO or BEDO-TTF) exhibited a very stable metallic behavior from room temperature down to 110 K [2, 3]. A macroscopic DC conductivity up to 80 S/cm was observed at 300K in this material. A feature of the LB films is that the metallic phase is obtained directly from BO and fatty-acid mixture through a spontaneous bilayer film formation on the water surface (Fig. 2) [4]. No additional treatments, such as counter-anion doping with iodine vapor, are required. Accordingly, the deposited LB film can be used as a soft electrode. This is quite advantageous for the fabrication of electrical contacts on delicate materials.

Self-assembly of molecules anchored to the surface of a conducting substrate is a useful method for the fabrication of molecular devices and biosensors [5, 6]. This is because self-assembled monolayers (SAMs) are very easy to implement using basic surface treatment processes. Also, the obtained film is robust to both mechanical and chemical stress, because of its covalent bond with the substrate. Previous research on charge transport through SAMs has shown that long alkyl-chain SAMs have excellent insulating properties [5]. In particular, metal-SAM-metal junctions can exhibit non-linear current–voltage characteristics. This indicates that electron transport through the SAM happens via a tunneling mechanism [7, 8]. However, the metal–insulator–metal (MIM) structures fabricated using a SAM often develop short circuits in the organic layer, because of metal diffusion through this layer. These short circuits can induce spurious effects in the electrical response. To overcome these problems, various methods of fabricating electrical contacts on the SAM have been investigated, such as scanning tunneling microscopy [8], conducting atomic force microscopy [9, 10], nanopores [7], and mercury-drop junctions [11]. These approaches are important for basic research. However, they are difficult to adapt for real device applications, because of the difficulty in handling and because the nano-scale fabrication area is too small. Recently, another approach was proposed, in which a thin conducting polymer layer is intercalated as a buffer layer between the SAM and the evaporated-metal electrode [12, 13].

In this paper, we employed metallic conducting LB films as soft electrodes to build a MIM junction. In our design, metallic LB films serve as electrical contacts for the SAM surface from an isolated electrode. Dodecanethiol (CH3(CH2)11SH, denoted as C12) SAM has well-studied tunneling behavior. Therefore, it is a good candidate to serve as a SAM insulating layer to evaluate the performance of the LB film soft electrodes. Unlike previous works [7-10], we have prepared relatively large-area MIM junctions (0.20 mm2). In these junctions, the C12 SAM is sandwiched between an Au surface and the metallic LB film, which is composed of BO and stearic acid (denoted as SA). The current density versus voltage (J–V) characteristics of the devices were investigated under the vacuum.
2. Experimental

The MIM devices were processed on 20 × 10 mm glass substrates (Corning Eagle 2000, Corning, NY, USA). We patterned Au (Au 2000 Å/Cr 50 Å) in small circles (0.5 mm diameter) with a thin contact line to a large counter electrode. We deposited the Au on the substrate using an electron beam evaporator under vacuum (10⁻⁵ Pa) and a shadow mask (Fig. 3). The substrates were cleaned with piranha solution (H₂O₂ - H₂SO₄ 2:1 v/v) for 5 min, rinsed thoroughly with deionized water, and dried under a N₂ stream. The C12 SAM was then formed on the small circles. The devices were dipped into a 5 mM solution of C12 (Sigma-Aldrich, St. Louis, MO, USA) in ethanol for 24 h inside a nitrogen-filled glove box, washed with ethanol and the pure water, and dried in N₂ steam.

The soft electrode LB films were prepared using the vertical dipping method. The chloroform solutions of BO (0.97 mM) and SA (10.2 mM) were mixed at a 1:1 molar ratio before they were spread on the ultrapure water surface (≥ 18 MΩ cm). The Y-type film transfers (transfer on both upstroke and downstroke) were performed at a fixed surface pressure of 20 mN/m. Then, 21 BO/SA LB film layers were deposited on the device, including both C12 SAM deposited on the small circles and the large counter electrodes. Using these processes, the MIM structure was fabricated on the substrate (Fig. 3). The prepared MIM samples were dried in air for 24 h, and then for 12 h in vacuum (5 × 10⁻¹ Pa). Current versus voltage characteristics were measured under vacuum at room temperature.

3. Results and discussions

The J–V characteristics of the MIM junction with the C12 SAM are shown in Fig. 4. The obtained curves were analogous to those of previous reports [7, 12, 14]. The J–V trace is linear in a low-bias region (±0.3 V), then it produces a sigmoidal shape in high-bias region. This behavior suggests that tunneling is the dominant conduction mechanism in the MIM junction. To identify what components gave rise to this non-linear behavior, we compared
J–V characteristics for the samples with and without a C12 SAM. Figure 5 shows J–V characteristics for the metal–metal (MM, BO/SA LB films-Au) junction, which lacks a C12 SAM layer. The J–V trace without C12 SAM exhibits ohmic features, which follows a straight line for high current densities and is obviously different from that of the sample with C12 SAM. The difference between the two samples indicates that the C12 SAM layer gave rise to the non-linear behavior observed in the MIM junction.

To investigate the existence of tunneling conduction in the MIM system, we used the Simmons model to fit our data. This model expresses the tunneling current density through a barrier in the tunneling regime, \( V < \Phi_B / e \), as

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

where \( m \) is the electron mass, \( d \) is the barrier width, \( \Phi_B \) is the barrier height, \( V \) is the applied bias, and \( \hbar \) \((=2\pi\hbar)\) is Planck's constant. \( \alpha \) is a unitless adjustable parameter that was introduced to modify the simple rectangular barrier model [11] or to account for an effective mass [16]. In our MIM structure that uses BO/SA LB films, we fixed the barrier width to be 37.2 Å, which corresponds to the sum of the C12 SAM (18.2 Å) [7] and SA layer (19 Å) thicknesses [3]. Because the hydrophobic part of the LB films have a strong tendency to be deposited on the hydrophobic surface (hydrophobic interaction) [1], the SA part of the bilayer film floating on the water surface will be first deposited to the hydrophobic C12 SAM surface by the LB transfer process, then the interfacial structure shown in Fig. 6 will be built. Employing the above equation and adjusting the two parameters, \( \Phi_B \) and \( \alpha \), a nonlinear least-squares fitting was performed on our data. It was found that the best fitting parameters were \( \Phi_B = 1.53 \) eV and \( \alpha = 0.67 \) (Fig. 4). These estimated parameters of both barrier height and \( \alpha \) agree well with previously reported values of \( \Phi_B = 1.39 \) eV, \( \alpha = 0.73 \) from the experiments using conducting polymer buffer layers [8], and \( \Phi_B = 1.42 \) eV, \( \alpha = 0.65 \) from the measurements employing Au electrode through nanopores [7]. Furthermore, the tunneling decay constant \( \beta \) at zero voltage calculated from the parameters was 0.85 Å⁻¹ for our device, which is also close to the values of 0.89 Å⁻¹ or 0.79 Å⁻¹ in the literatures [8, 7]. In order to identify the tunneling process, further measurements such as temperature dependence of J–V profile or the current dependence of SAM’s alkyl-chain length are required [7]. However, the present good agreement in the characteristic parameters indicates the viability of the MIM device based on conducting LB films. Thus, these results indicate that the simple BO/SA LB-film coating process is a feasible electrical-contact-fabrication method for devices based on delicate materials.

4. Conclusion

To demonstrate the viability of metallic conducting LB film soft electrodes, we fabricated MIM junctions. These devices used a C12 SAM that was sandwiched between an Au surface and a metallic conducting of
BEDO-TTF/stearic acid LB films. A non-linear sigmoidal J–V profile across the junction was observed. This implies that tunneling is the dominant conduction mechanism. The calculated parameters of tunneling characteristics are consistent with previous reports. These results show that metallic conducting BEDO-TTF/stearic acid LB films can serve as soft electrodes.

5. Acknowledgments

The financial support from MEXT KAKENHI (Grant-in-Aid for Science and Research (B), 21360006) is gratefully acknowledged. We would like to thank the staff of the Nanoprocessing Partnership Program (AIST, Japan) for their help in substrate preparation.

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