



Comparative study for electrical transport characteristics of self-assembled monolayers formed by benzenethiol, cyclohexanethiol, and adamantanethiol



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ARTICLE INFO

Article history:

Received 17 June 2017

Received in revised form

8 August 2017

Accepted 16 August 2017

Available online 17 August 2017

Keywords:

Molecular electronics

Molecular device

Self-assembled monolayer

STM

Charge transport

ABSTRACT

We investigated the effect of molecular backbone structure on the electrical transport properties of self-assembled monolayer (SAM)-based molecular devices which were made with using three different molecules; benzenethiol (denoted as BT), cyclohexanethiol (CHT), and adamantanethiol (ADT). These molecules have similar ring-shaped backbone structures but different molecular orbital systems. The molecular devices were fabricated as a vertical metal-SAM-molecule structure by a conventional optical lithography-based microscale via-hole technique with employing PEDOT:PSS (poly(3,4-ethylenedioxythiophene)) stabilized with poly(4-styrenesulfonic acid) interlayer, which leads to a high device yield. We found that the current density of BT molecular devices was one order higher than that of CHT and ADT molecular devices due to the different molecular orbital systems. Also, we observed that the current densities of CHT and ADT devices were slightly different according to the statistical analysis because of the different structural uniformity of SAMs.

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1. Introduction

The goal of molecular electronics as a future candidate for semiconductor-based electronics approaching its scalable limit is to utilize an individual or ensemble of molecules as an active material for electronic device components such as diode, transistor, switch, and sensor [1–10]. In order to pursue this aim, many research groups have performed in-depth studies on the fundamental charge transport characteristics of various molecules especially in the form of self-assembled monolayers (SAMs), which is an essential prerequisite for this purpose [11–20]. For example, there have been several studies focusing on the effect of backbone structures of the molecules on the charge transport characteristics using some accessible molecules: σ -saturated molecules (e.g. alkanethiols) [21], π -conjugated aromatic molecules (e.g.

benzenethiols, or biphenylthiols) [22], and oligo(*p*-phenylene ethylene)s [23]. However, most of these studies have mainly been focused on the comparison between the molecules having completely different structural appearances, for example, π -conjugated oligoacene and σ -saturated alkanethiolate systems, in which their various intrinsic properties are obviously different [24]. On the other hand, this kind of comparison of the electrical characteristics with molecules that show similar molecular backbone structures but subtle differences in bonding properties may be helpful to gain a better understanding on the effect of backbone structures on the molecular charge transport mechanisms.

Here, we studied the structural and electrical properties of three different molecules: benzenethiol (denoted as BT) with a π -conjugated aromatic ring, cyclohexanethiol (CHT) with a σ -bonded flexible aliphatic ring, and adamantanethiol (ADT) with a σ -bonded rigid and spherical aliphatic ring. These molecules with the simple chemical structure can be the best model compounds for elucidating those issues compared with molecules containing a complicated structure. To this end, we fabricated a large number of

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ensemble molecular junctions as microscale via-hole structures using PEDOT:PSS (poly(3,4-ethylenedioxythiophene)) interlayer, which leads to the excellent device yield [25]. In particular, we examined how much the electrical transport properties are affected by the molecules containing π -conjugated aromatic ring and σ -bonded aliphatic ring as well as by the molecules containing two different σ -bonded aliphatic rings. We also examined whether the order and two-dimensional packing structure of SAMs with aliphatic cyclic ring (CHT and ADT) affected the electrical transport properties of SAM-based molecular electronic devices.

2. Experimental section

2.1. SAM preparation

The chemical structures of the molecules are shown in Fig. 1. BT, CHT, and ADT molecules were purchased (Tokyo Chemical Industry Co.) and used without further purification. The BT, CHT, and ADT SAMs were characterized using scanning tunneling microscopy (STM). For this, Au(111) substrates with atomically flat terraces in the range of 100–400 nm were prepared by thermally evaporating Au onto a freshly cleaved mica plate, as previously described [26]. Then, BT, CHT, and ADT SAMs were prepared by immersing the Au(111) substrates in a 1 mM ethanol solution of the corresponding molecules at room temperature for 24 h in a N₂-filled glove box. After SAM-deposited Au samples were taken from the solutions, they were thoroughly rinsed with pure ethanol to remove weakly adsorbed molecules. STM measurements were carried out under ambient conditions using a NanoScope E with a commercially available Pt/Ir tip (80:20). All STM images were obtained using the constant current mode. During the STM imaging, bias voltage ranging from 300 to 550 mV and tunneling current ranging from 200 to 500 pA were applied.

2.2. Electrical transport measurement

To characterize the electronic transport properties of BT, CHT, and ADT SAMs, we fabricated molecular devices employing a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (called as PEDOT:PSS) as an interlayer between the SAMs and top metal electrodes in the vertical M-SAM-M structure. Fig. 2 shows the schematic illustrations of device fabrication processes. We followed the similar fabrication process that has been widely used by several groups [27–30]. Briefly, the bottom electrodes (50 nm Au/5 nm Ti) were first deposited on a p++ SiO₂/Si substrate by an electron beam evaporator at a deposition rate of 0.2 Å/s. Patterned shadow mask was used for bottom electrode patterning. Then, photoresist (AZ 5214E) was spin-coated and conventional photolithography

process was performed. Bottom electrodes are squares with a side length of 20 or 40 μm . Then, SAMs were formed on the bottom electrodes by immersing the samples in 1 mM ethanol solutions of the corresponding molecules for 24 h at room temperature in a N₂-filled glove box. The samples were rinsed by using pure ethanol to eliminate physisorbed molecules on SAMs. The rinsed samples were dried for ~3 h in a vacuum desiccator. PEDOT:PSS (Clevios PH 1000) was spin-coated on the substrate and dried for ~3 h in the vacuum desiccator. As an interlayer, PEDOT:PSS prevents devices from the formation of filamentary conducting path during top electrode deposition. After the PEDOT:PSS deposition, we deposited Au top electrode (30 nm thick) using the electron beam evaporator at a deposition rate of 0.2 Å/s via patterned shadow masks. Finally, residual PEDOT:PSS was removed with a reactive ion etcher using O₂ gas (50 sccm, 100 W). Fig. 2(b) shows the optical, scanning electron microscopy (SEM), and cross-sectional transmission electron microscopy (TEM) images of fabricated molecular devices. Particularly, from the TEM image, we observed that penetration of gold through PEDOT:PSS interlayer had not occurred. The fabricated molecular devices were characterized using a semiconductor parameter analyzer (Model 4200 SCS, Keithley) for the electrical characterizations.

3. Results and discussion

Fig. 3 shows the high-resolution STM images of BT, CHT, and ADT SAMs formed on Au substrates. BT SAMs with a π -conjugated aromatic ring were mainly composed of the disordered phase with SAM-covered Au adatom islands (bright islands), as shown in Fig. 3(a). The formation mechanism of these Au adatom islands has been discussed in our review paper [31]. Many STM studies also showed the similar surface structure, so that the Au adatom islands can be considered as the intrinsic surface characteristics for BT SAMs. In contrast to BT SAMs, CHT and ADT SAMs with σ -bonded aliphatic cyclic rings had long-range ordered phases, as shown in Fig. 3(b) and (c). Molecular-scale STM imaging clearly revealed that CHT SAMs on Au(111) in the inset of Fig. 3(b) have a zig-zag bright and dark molecular row structure, which has also been visualized in our previous works [32–34] and others [35]. This unique packing structure is attributed to the existence of two energetically stable conformers, i.e., equatorial and axial conformers resulting from a conformation change of 6-membered aliphatic cyclic ring [32]. The packing structure for CHT SAMs is assigned as a $(5 \times 2\sqrt{3})R35^\circ$ superlattice and the average areal density for the CHT SAMs was calculated to be 36.09 Å²/molecule. The structural details were discussed in earlier papers [34]. CHT SAMs had a corrugated packing structure, whereas ADT SAMs with a bulky, spherical aliphatic ring backbone have a very uniform and hexagonal close-

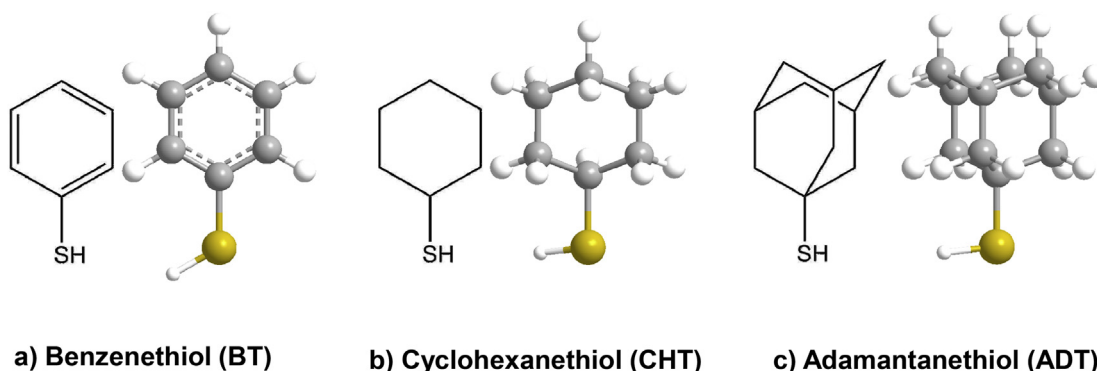


Fig. 1. Chemical structures of three molecules used in this study: (a) BT, (b) CHT, and (c) ADT.

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