



Stability of rectification of iron porphyrin molecular junctions



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H I G H L I G H T S

- Studied rectification of Fe-Porphyrin molecule with two deposition techniques: drop-dry method and 60 s deposition method.
- Observed stable rectification from drop-dry deposition of Fe-Porphyrin on Au substrate.
- Discussed possible mechanisms of the stability of rectification.

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We report rectification from porphyrin molecules ligated to an iron atom. Current-voltage (IV) curves were measured from the molecules using a conductive atomic force microscope (AFM). Molecules were deposited on a substrate from template-stripped gold from 1 μM iron porphyrin solution by either a drop-dry or 60 s deposition method. The measured IV curves from the drop-dry samples were stable. Statistical analysis of the IV curves showed that the distribution of the threshold voltages (0.543 V - 0.588 V) and rectification ratios (34–42) from the drop-dry samples are confined to a smaller range than the threshold voltages (0.2 V - 0.7 V) and rectification ratios (2.5–162) from the 60 s samples. The fluctuations in the IV curve from the 60 s deposition samples can be explained by local joule heating. The roughness of the topography was analyzed to understand the difference in IV measurements between the two types of samples. The stability of the rectification from the drop-dry samples is attributed to good thermal contact between the AFM tip and the molecules on the substrate.

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1. Introduction

Since Aviram and Ratner proposed the first single molecular rectifier [1] in 1974, a molecular diode has been realized by using a Langmuir–Blodgett (LB) film [2,3] and a self-assembled monolayer [4]. The rectification of the LB film and the monolayer was characterized by placing the film or the monolayer between two electrodes to measure the current versus voltage (IV) [2–4]. Similarly, the characterization can be carried out electrochemically by placing the film or monolayer of molecules on a working electrode, and measuring a voltammogram with an electrochemical potentiostat [5]. In both scenarios, the characterization reflected the property of a large number of molecules due to the macro-size dimensions of the electrodes used for the measurement. Recently, the rectification of molecules has been investigated with scanning tunneling microscopy (STM) by positioning molecules between a substrate and

an STM tip [6–8]. Due to its nano-scale size of the tip, the STM measured the rectification from a few molecules to a single molecule with a molecular break junction technique [6]. From these measurements the IV curves showed instability induced by local joule heating and electromigration. Also, the irreproducibility of the measurement was observed because the electrical transport properties of the molecules depended on the contact between the molecule and the electrode and this contact changed with each IV curve measured. In order to realize molecular electronics that use molecules as active components, such as storage elements [9] in a circuit, the instability and irreproducibility observed in IV curves must be addressed.

In this study we have experimentally investigated rectification by conductive atomic force microscopy from porphyrin molecules ligated to an iron atom (FeP). We observed stable rectification from molecules deposited by drying drops of 1 μM FeP solution on a substrate prepared from template-stripped gold from silicon. This investigation may provide insight into the role that surface roughness at the molecule–electrode interface contributes to device stability and the design of future molecular electronic devices.

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2. Materials and methods

The gold substrate was prepared using a template-stripped method [10]. A gold (Au) film of 200 nm was deposited on a silicon (110) wafer by electron beam evaporation. The Au (99.999% purchased from International Advanced Materials) was evaporated at a rate of ~ 1 nm/s. A two component adhesive EPO-TEK 377 (purchased from Epoxy Technology) was applied to the surface of the Au film and a glass slide was attached to the epoxy layer. This sample was cured at 150 °C in an oven for one hour. After curing, the Au film was peeled from the silicon wafer. Atomic force microscopy was completed to determine the flatness of the template-stripped Au surface. The surface was analyzed using average values of the root mean square (RMS). The average RMS value was determined to be $0.160 \text{ nm} \pm 0.039 \text{ nm}$ from 364 selected areas of $0.25 \text{ } \mu\text{m} \times 0.25 \text{ } \mu\text{m}$. The same measurement was also performed for gold on mica and gold evaporated on silicon from 50 selected areas of $0.25 \text{ } \mu\text{m} \times 0.25 \text{ } \mu\text{m}$ and the average RMS values were $1.09 \text{ nm} \pm 0.38 \text{ nm}$ and $1.13 \text{ nm} \pm 0.08 \text{ nm}$, respectively. Based on these values the template-stripped gold substrate is much flatter than gold on mica and gold evaporated on silicon without using the template-stripped method. In order to obtain a fresh Au surface, the Au film was peeled from the silicon wafer just before depositing molecules onto the surface.

Iron porphyrin [Fe(III) 5,15-di[4-(s-acetylthio)phenyl]-10,20-diphenyl porphine acetate] (hereafter denoted FeP) was purchased from Frontier Scientific Porphyrin Products Division. The molar concentration of $1 \text{ } \mu\text{M}$ FeP in toluene solution was prepared by diluting a 1 mM FeP toluene solution.

Two methods were used to deposit the molecules: a drop-dry method and a 60 s deposition method. For the drop-dry method, three drops of $10 \text{ } \mu\text{L}$ from a $1 \text{ } \mu\text{M}$ FeP toluene solution were transferred to the center of a $1 \text{ cm} \times 1 \text{ cm}$ Au substrate using a $10 \text{ } \mu\text{L}$ pipette. After several minutes, the toluene evaporated and molecules remained on the substrate. For the 60 s deposition method, the substrate was submerged in a $1 \text{ } \mu\text{M}$ FeP toluene solution for 60 s. After the sample was removed from the solution, the substrate was rinsed with toluene several times before it was blow-dried with nitrogen. The sample as prepared is denoted hereafter as the 60 s sample. For both methods, the FeP molecules were deposited on template-stripped Au substrate from silicon.

3. Experimental

The current-voltage (IV) measurements were performed with a PSIA (Park Systems Corporation) XE-120 Atomic Force Microscope (AFM) in current-AFM mode using an external current preamplifier with variable gain. The topography of the samples was obtained with the AFM in contact mode. A gold coated AFM tip (HQ: NSC18/Cr-Au) purchased from MikroMasch with a force constant of 2.8 nN/m and an approximate radius of 35 nm was used for both IV measurements and topography scans. A force of 3 nN was applied to the molecules of FeP. The system was allowed at least 20 minutes to become stable before IV curves were measured. The IV was completed using a bias range from -1 V to 1 V . The current measured from the FeP molecules was amplified with a current preamplifier (FEMTO DLPCA-200) purchased from PSIA and measured using data acquisition. Measurements were completed at different locations on the surface of the sample. As a control experiment the IV measurement was also performed on a bare gold substrate not exposed to toluene and a gold substrate after submersion in toluene.

4. Results and discussions

For the measurements the samples were biased through the substrate instead of the tip; the tip is virtual ground in this experiment. The rectification behavior was observed in the negative current and voltage direction. When the tip was biased as reported in previous work [12] the rectification was observed in the positive voltage regime. For the purpose of convention the current and voltage values of the original plot was inverted.

The IV curve from the drop-dry sample was observed to be stable, reproducible, and in the current range of micro-ampere. In order to demonstrate the stability and reproducibility of the IV

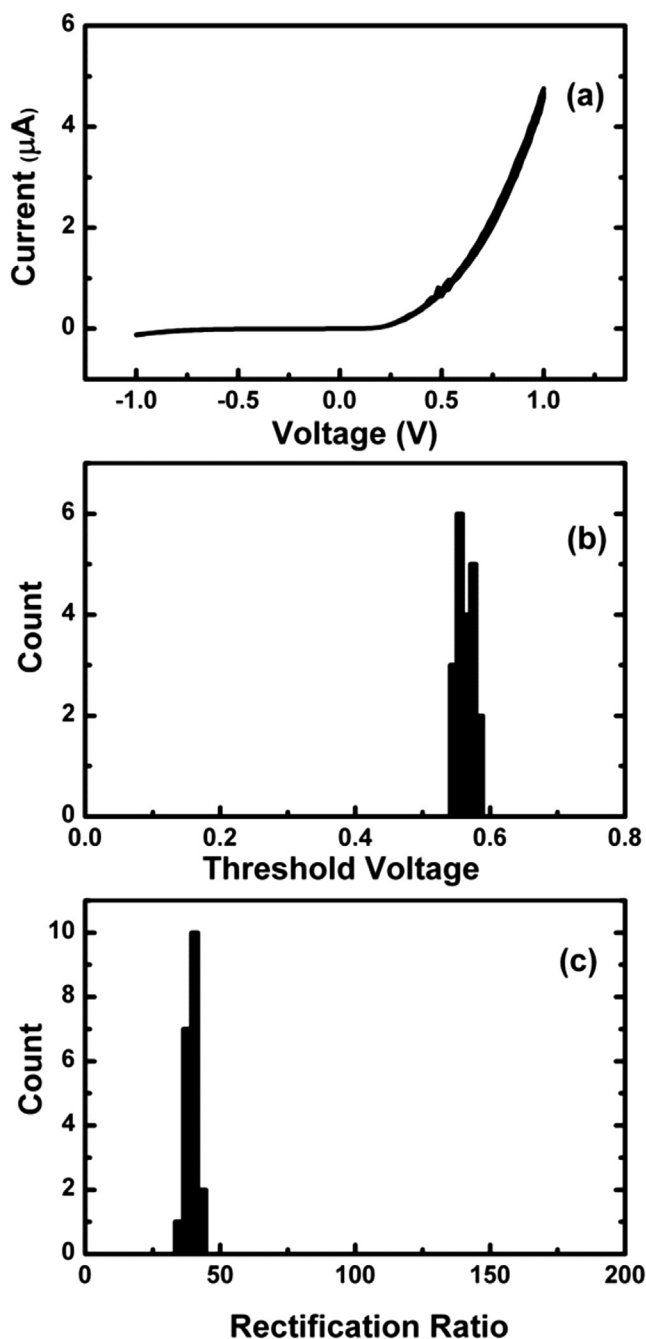


Fig. 1. (a) Ten cyclic IV measurements, (b) a histogram of the threshold voltage, and (c) a histogram of the rectification ratio from drop-dry sample.

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