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Journal of Colloid and Interface Science 287 (2005) 388–393

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Adsorption of *n*-butyl-substituted tetrathiafulvalene dodecanethiol on gold

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Received 15 October 2004; accepted 3 February 2005

Abstract

Tetrathiafulvalene (TTF) derivative substituted with two butyl- and two dodecylthiol chains is adsorbed on polycrystalline gold. The TTF-derived thiol adsorbates were characterized by ellipsometry, contact angle goniometry, infrared and X-ray photoelectron spectroscopy and cyclic voltammetry. The molecule is strongly anchored on the gold surface through the sulfur terminating the alkylthiol chains. On the average, the TTF moiety is oriented extended away from the gold surface. The topmost layer of the film containing the dibutyl chains is disordered with gauche defects. The molecule was organized with majority of the alkylthiol chains bound to the gold surface. There are indications of pinholes in the monolayer due to steric hindrance of the bulky TTF rings. The molecular systems consisting of an electroactive π-system such as TTF, are promising for thin-film field effect transistor application.

Keywords: Tetrathiafulvalenes; Thiols; XPS; IRAS; Cyclic voltammetry

1. Introduction

Tetrathiafulvalenes (TTFs) are molecular systems that successfully create highly conducting organic molecular crystals [1]. TTF derivatives readily form dimers, highly ordered stacks, or two-dimensional sheets, which are stabilized by the π–π interactions and non-bonded sulfur–sulfur interactions [2]. Because of the π-rich redox-active building block of TTF, substituted TTFs are of importance in the following fields (as reviewed by Bryce [3]): cation sensors, liquid crystals, intramolecular charge transfer and non-linear optical materials, supramolecular switches and devices, and redox polymers. Although very versatile building blocks in many areas of material chemistry, applications in molecularly based electronics have not been fully reached. One modification of TTF to enhance processability is to make self-assembled monolayers (SAMs) by substituting the central aromatic core with alkylthiols. The self-assembly technique is one way to prepare ordered thin films of organic materials [4,5]. Several studies have been made on SAMs systems with tetrathiafulvalenes [6–12]. SAMs with TTFs have been suggested for different possible applications as organic electronic thin-film devices [13,14].

The previous works of Dahlstedt et al. [15,16] are focused on the synthesis of several TTF-alkylthiol systems. Electrochemical behavior of TTFs has also been investigated in these previous works. In this article, we present a study of one of these systems, i.e., a TTF derivative substituted with two butyl- and two dodecylthiol chains adsorbed on polycrystalline gold. Chemical composition, molecular orientation and binding strength to the surface are investigated by X-ray photoelectron spectroscopy (XPS) and infrared-reflection absorption spectroscopy (IRAS). Cyclic voltammetry (CV) and impedance measurement are used to investigate the electronic blocking capacity of the adsorbates, the assemblies' defect structure and the interfacial capacitance of the films. The aim of this work is to electronically insulate the substrate and use the redox group to produce a laterally electroactive region parallel to the surface for possi-

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doi:10.1016/j.jcis.2005.02.046

ble use in organic thin film-field effect transistor (OTF-FET) applications. The system that is characterized in this paper is envisioned to work as an OTF-FET with a stable SAM consisting of a relatively densely packed electroactive π-system (e.g., TTF).

2. Materials and methods

2.1. Sample preparation

The molecular system used in this study is 12-[5,4′-dibutyl-5′-(12-mercaptododecylsulfanyl)-[2,2′]bi[1,3]dithiolylidene]-4-ylsulfanyl]-dodecane-1-thiol. A synthetic pathway for preparing the TTF-derived molecule was described elsewhere [16]. For adsorption of the TTF-SAMs, fresh toluene-based solutions of 200 µM with the presence of 0.5 µmol of (10 mol%) $MeSO_3H$ were prepared. After cleaning, the single crystal Si(100) wafers were mounted in a Balzers UMS 500P electron beam evaporation system. They were first coated with an adhesion layer of 20–25 Å thick Ti at an evaporation rate of 2 Å/s followed by the evaporation of 2000 Å thick Au layer at a rate of 10 Å/s. The base pressure was always $<5 \times 10^{-9}$ Torr and the evaporation pressure, $<2 \times 10^{-8}$ Torr. The gold surfaces were cleaned in a 5:1:1 mixture of Milli-Q water, 25% hydrogen peroxide, and 30% ammonia for 5 min at 80 °C and then thoroughly rinsed in Milli-Q water. The gold surfaces were incubated in the n-butyl-substituted TTF dodecanethiol solution at 70 °C for the duration of 24 h, rinsed in toluene and then ultrasonicated in toluene for about 10 min. It is followed by blow-drying of the surfaces with nitrogen gas and then immediately analyzed.

2.2. Ellipsometry and contact angle goniometry

Single-wavelength ellipsometry was performed using an automatic Rudolph Research AutoEL ellipsometer with He–Ne laser light source, $\lambda = 632.8$ nm, at an angle of incidence of 70°. The freshly cleaned gold sample substrates were measured prior to their incubation, and the collected average values of the refractive index were later used in a model “ambient/organic film/gold,” assuming an isotropic, transparent organic layer with the refractive index of $n = 1.5$. The film thickness is calculated as an average of measurements at five different spots on each sample.

Contact angles were measured with Ramé-Hart NRL 100 goniometer, in air, i.e., without control of the humidity in the ambience, using fresh Milli-Q water. More than five measurements of advancing and receding contact angle were taken per sample.

2.3. X-ray photoelectron spectroscopy

XPS analysis was performed in a VG instrument with a CLAM2 analyzer and a twin Mg/Al anode. The pressure in the analysis chamber was approximately 5×10^{-10} mbar. The measurements were carried out with unmonochromated Mg$K\alpha$ photons (1253.6 eV). The resolution was determined from the full width at half maximum (FWHM) of the Au($4f_{7/2}$) line, which was 1.3 eV with pass energy of 50 eV. The power of the X-ray source was kept constant at 300 W. The binding energy scale of the spectra was aligned through the Au($4f_{7/2}$) peak at 84.0 eV. Angle dependent measurements were made using photoelectron take-off angles of 30° and 80° with respect to the surface normal to the sample. The VGX900 data analysis software was used to calculate the elemental composition from the peak areas and to analyze the peak positions. Curve fitting is done using the XPSPEAK95 version 2.0 program.

2.4. Infrared spectroscopy

Transmission infrared measurements were made on a Bruker IFS48 Fourier transform infrared spectrometer, continuously purged with N_2 gas. Samples were prepared by smearing an ample amount of the molecules on a KBr window. Each spectrum is obtained by averaging 100 interferograms at 2 cm^{-1} resolution using a deuterated triglycine sulfate (DTGS) detector.

Infrared reflection absorption spectroscopy (IRAS) measurement were performed on a Bruker IFS66 Fourier transform spectrometer equipped with a grazing angle of incidence reflection accessory aligned at 85°. The infrared radiation was polarized parallel to the plane of incidence. Interferograms were apodized with a three-term Black–Harris function before Fourier transformation. Flushing the instrument with nitrogen gas for 30 min after mounting of a sample and during the measurement reduced the water signal in the spectra. The spectra were recorded by averaging 2000 interferograms at 4 cm^{-1} resolution using liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The measurement chamber was continuously purged with nitrogen gas during the measurement.

2.5. Cyclic voltammetry and impedance spectroscopy

The cyclic voltammograms and impedance data were recorded using an Autolab PGSTAT 20 (EcoChemie, Utrecht, The Netherlands), equipped with a FRA2 frequency response analyzer module. All experiments were performed in the three-electrode mode using an Ag/AgCl reference electrode. The electrochemical cell was made of Kel-F. The SAM-coated gold surfaces (working electrodes) were brought into contact with the solution via press-fitting to an O-ring, in the side of the cell [17]. The exposed area of the electrode was 0.2 cm^2. The CV experiments were recorded by scanning the potential from -0.30 to $+0.60$ V (vs Ag/AgCl) and back, employing a scan rate of 10 mV/s. Prior to the scan, the electrode was kept at -0.30 V for 10 s. To provide redox species, a 1.0 mM $K_3Fe(III)(CN)_6$ (Merck) solution, also containing 100 mM KNO_3 (Merck) as