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Examination of polymer/metal interface modified by self-assembled monolayer by Kelvin probe force microscopy and secondary ion mass spectrometry

M.M. Marzec[a,*], A. Bernasik[a], J. Rysz[b], W. Łużny[a], A. Budkowski[b]

[a] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. A. Mickiewicza 30, 30-059 Kraków, Poland
[b] Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, 30-059 Kraków, Poland

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ABSTRACT

Buried interfaces between a polystyrene (PS) or polar poly(methyl methacrylate) (PMMA) thin film and the gold surface patterned with CH_3- and COOH-terminated alkanethiols self-assembled monolayers (SAM) were examined via Kelvin probe force microscopy. Chemical composition of the interface was probed by secondary ion mass spectrometry. The contact potential difference maps measured on the PS and the PMMA films show inverted contrast. This observation is discussed in terms of reorientations of the COOH-SAM net dipole moments induced by interactions with PMMA.

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1. Introduction

Polymer/metal interfaces have significant impact on the properties of organic semiconductor devices, such as light emitting diodes, solar cells, field-effect transistors or light emitting transistors [1,2]. A detailed study and modeling of carrier transport at these interfaces is fundamental for an effective tailoring and optimization of such devices. The relative importance of the molecule/metal junction increases when device dimensions decrease.

Among possible model systems, affecting interfacial energy level alignment, self-assembled monolayers (SAMs) on metals are of particular interest due to the central role they play in the design of organic devices [3]. Recent studies have shown, for instance, that chemisorptions of polar SAMs on the surface of the metal electrode can lower the energy barrier for charge injection on the interface and thus increase performance of organic electronic devices [4–6]. Furthermore, their presence on the substrate surface influences the morphology of thin polymer films.

The dipole layer present at organic/metal interfaces formed by organic monolayer and interfaces formed by polymer thin solid film and metal were mostly studied by methods which collect information from relatively large areas (about 1 mm^2) [7–12]. These methods do not allow to determine local inhomogeneities on the submicrometer scale.

In this work we applied Kelvin probe force microscopy (KPFM) to examine buried polymer/metal interfaces, with sub-micrometer lateral resolution, in polymer films with thickness up to 120 nm. In order to determine chemical compositions of the interfaces we performed dynamic secondary ion mass spectrometry (SIMS) measurements. Two different systems were studied: a nonpolar polystyrene (PS) film and a polar poly(methyl methacrylate) (PMMA) film, both deposited on gold substrate patterned with CH_3- and COOH-terminated alkanethiol self-assembled monolayers. The results obtained in the course of the present work as well as further discussion allow us to emphasize the importance of substrate interactions between a polymer and a SAM modified metal and specifically the effects of hydrogen bonds between the polar polymer film and the polar SAMs on the net interfacial dipole moment.

The studied multilayer organic systems placed on the metallic electrodes can be recognized as a model structures for gas sensing devices, sensitive to the work function changes which induce conductance, capacitance and electrochemical potential changes of the modified electrode [13,14].

2. Experimental

2.1. Sample preparation

The substrates were prepared by thermal evaporation of Au (ca. 300 nm) onto silicon wafers. The gold surfaces were

* Corresponding author. Tel.: +48 12 617 27 16.
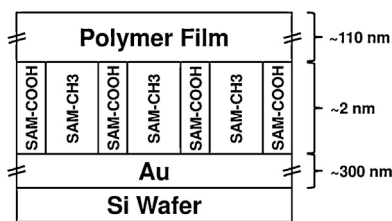 E-mail address: marzecm@agh.edu.pl (M.M. Marzec).

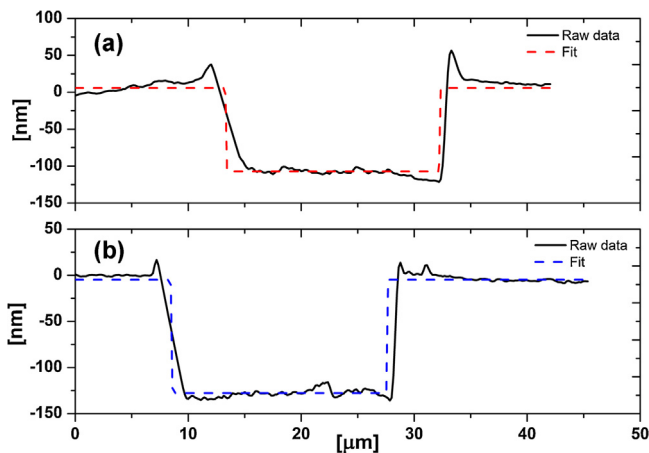**Fig. 1.** Schematic view of the sample structure.

Fig. 2. Cross sectional analysis of the furrow region scratched in (a) PMMA and (b) PS films. Raw data (solid line) fitted with a negative step function (dashed line) indicates film thickness equal to 113 ± 6 nm and 123 ± 3 nm for PMMA and PS, respectively.

further on patterned with self-assembled monolayers (SAMs) of thiols containing a CH_3 tail group (16-hexadecanethiol, $HS(CH_2)_{15}CH_3$) and a COOH tail group (16-mercaptohexadecanoic acid, $HS(CH_2)_{15}COOH$). The COOH-SAM patterns were formed on gold surfaces using a one-step micro-contact printing (μCP) method [15]. Polydimethylsiloxane (PDMS) stamp, with relief structures (with 25 μm period), was inked with COOH-SAM dissolved in ethanol (10 mM) (for details see previous works [16,17]) and then gently pressed on the gold surface. Functionalization of gold areas not initially printed was performed by immersing the support in the CH3-SAM ethanol solution (10 mM) for 10 min [18]. After this step samples were rinsed with ethanol and dried under a flow of Ar for 5 s. In the next step polystyrene (Polymer Standard Service, $M_w = 65$ kDa) dissolved in chloroform (20 mg/ml) or poly(methyl methacrylate) (PMMA) (Polymer Standard Service $M_w = 58.3$ kDa), dissolved in chloroform (20 mg/ml) were spin-cast on the substrates with a KW-4A spin-coater (Chemat Technology). As a result PS and PMMA films were formed with thickness ranging from 105 to 130 nm (controlled by varied coating speed, 1000–2000 rpm) [19]. Schematic view of the sample is given in Fig. 1. All the above steps were performed in inert argon atmosphere (glove box) with amounts of oxygen and water maintained under 0.1 ppm. Thicknesses of PS (123 ± 3 nm) and PMMA (113 ± 6 nm) films were determined with topographic AFM measurements performed on previously scratched regions of the films. Diagrams of a cross sections through a scratches with negative step function fitted are shown in Fig. 2. Furrow was formed on the films by scratching the surface with gently pressed stainless steel needle.

2.2. Kelvin probe force microscopy

Measurements with Kelvin probe force microscopy, working in amplitude modulation (AM) and tapping mode, were performed with an Agilent 5500 apparatus in a single-pass technique, where
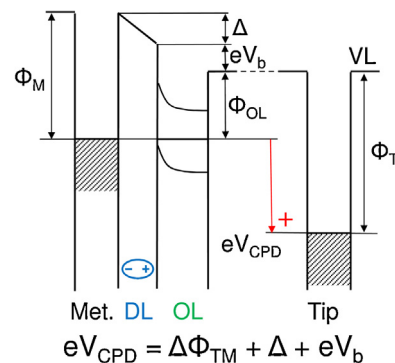

Fig. 3. Electron energy diagram of a metal (Met.), with an organic directed dipole layer (DL) and organic overlayer (OL) being in electronic equilibrium, examined with a tip (E_F – Fermi level, $\Phi_{M,T}$ – work function, $\Delta\Phi_{TM}$ – tip-metal work function difference, eV_b – band bending energy shift, Δ – dipole energy step, eV_{CPD} – energy induced by contact potential difference (CPD) when vacuum levels (VL) of the tip and the surface are aligned; M, OL and T subscripts denotes metal, organic layer and tip, respectively).

topography and contact potential difference (CPD) signals were acquired simultaneously, each recorded at a different cantilever oscillation frequency. The Agilent 5500 is a tip-scanning system, in which the cantilever sits on a scanner and is moved in raster fashion across the stationary sample. The Agilent large multi-purpose A-type scanner was used which includes four piezo elements for X and Y motion and two piezo tubes for Z motion.

DC voltage was applied to a conducting KPFM tip with the sample being on ground potential. All measurements were performed in air at room temperature. Some of them were repeated in dry (argon) atmosphere. The samples were measured using Au covered monolithic silicon cantilevers (BudgetSensors) with a spring constant of 3 N/m, quality factor of about 100 and resonance frequency of 64.35 kHz. Scan sizes used were 100×100 μm^2. AC voltage frequency was equal to 10 kHz and applied to the cantilever in all measurements. The CPD signal measured in the KPFM method consists of the following components: (i) the work function difference between the tip and the metal substrate ($\Delta\Phi_{TM}$), (ii) the vacuum level shift caused by the dipole layer (Δ) and (iii) a further shift of the vacuum level due to band bending (eV_b) in the organic layer (Fig. 3) [20].

2.3. Secondary ion mass spectrometry

The samples were analyzed with a time-of-flight secondary ion mass spectrometer. Dual-beam depth profiling in negative polarity (negatively charged ions measured) was performed using ION-TOF ToF.SIMS 5 instrument. Depth profiling was performed with a 1 keV Cs^+ ion beam operating at 37 nA, which was sputtering the area of 450×450 μm^2. After each sputtering cycle sample composition at a given depth was determined using 30 keV Bi_3^+ clusters, in which case the beam current was 0.1 pA and the area of analysis was 100×100 μm^2. The Bi_3^+ beam operated in the mapping mode, that is at each depth a 256×256 map of chosen secondary ion intensities was collected [21], showing the lateral distribution of sample components. The sputter rates were estimated at 0.7 nm/s for PMMA and 0.05 nm/s for PS. The maps shown are the sums of the maps collected starting from the 110 nm and 100 nm depth for PS and PMMA respectively, finished when homogenous Au^- ions map was revealed.

3. Results and discussion

Terminal groups of the SAM molecules induce different dipole moments. Both CH3-SAM and COOH-SAM molecules used in our