



Emerging interface dipole *versus* screening effect in copolymer/metal nano-layered systems



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ABSTRACT

Despite to the importance on the charge carrier injection and transport at organic/metal interface, there is yet an incomplete estimation of the various contribution to the overall dipole. This work shows how the mapping of the surface potential performed by Kelvin Probe Force Microscopy (KPFM) allows the direct observation of the interface dipole within an organic/metal multilayered structure. Moreover, we show how the sub-surface sensitivity of the KPFM depends on the thickness and surface coverage of the metallic layer. This paper proposes a way to control the surface potential of the exposed layer of an hybrid layered system by controlling the interface dipole at the organic/metal interface as a function of the nanometer scale thickness and the surface coverage of the metallic layer.

We obtained a layered system constituted by repeated sequence of a copolymer film, poly(*n*-butylacrylate)-*b*-polyacrylic acid, and Au layer. We compared the results obtained by means of scanning probe microscopy technique with the results of the KPFM technique, that allows us to obtain high-contrast images of the underlying layer of copolymer behind a typical threshold, on the nanoscale, of the thickness of the metal layer. We considered the effect of the morphology of the gold layer on the covered area at different thicknesses by using the scanning electron microscopy technique.

This finding represents a step forward towards the using of dynamic atomic force microscopy based characterization to explore the electrical properties of the sub-surface states of layered nanohybrid, that is a critical point for nanohybrid applications in sensors and energy storage devices.

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1. Introduction

A comprehensive understanding of electronic structures at organic/metal contacts is highly desirable for both performance control and optimization of organic devices [1–5]. The factors that determine the barrier heights at the organic/metal interfaces have been a subject of much interest and debate in recent years. Several models have been proposed to provide physical pictures on how and why the experimentally observed barrier heights depend on the metal contact [6–15].

The charge carrier injection and transport at organic/metal interface are governed by the injection barrier heights that are influenced by the balance of the work function (WF) at organic/metal interfaces that depend on the interface dipole (a.k.a.

Contact Potential Difference, CPD). In this context the organic/metal nanohybrid layered systems become a through for the understanding of charge injection and transport phenomena and for the estimation of each parameter (like work function) on each other at the nanoscale, and this is the reason why during the last years a huge amount of literature dedicated its attention to such systems [16–18].

The overlooking of physico-chemical processes that happen at the interface could determine many errors in the evaluation of the work function. For the atomically clean metallic surfaces strong variations of work function $\Delta\phi$ were experimentally found after the deposition of the organic molecules [19]. The cause of this variation of the work function $\Delta\phi$, also called interface dipole, is the rearrangement of electrons density distribution both on the metallic surface and in the molecules caused by the reciprocal interaction at the interface. Here we show that we cannot neglect the effect of the organic layers above and below the metallic surfaces when the metallic layers are few nanometers thick.

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Ultra-thin gold films could have a significant technological importance. In principles ultra-thin metal films ($<100 \text{ \AA}$) are attractive alternatives to indium-tin oxide in organic light-emitting diodes that are at the basis for flat panel displays and touch screens. Many recent papers report [20–22] progress in the development of robust, nano-scale thickness gold films, which exhibit remarkably low sheet resistance coupled with high optical transparency. Usually the modification of the work function due to the organic layer above the metallic film is considered but when ultrathin metallic electrodes are used it is necessary to take into account also the effect on the work function due to the organic layer below the metallic films. In this context the organic/metal nanolayered systems become a through for the estimation of critical parameters, like work function. This work proposes a way to control the work function of a nanolayered system as a function of the nanometer scale thickness and the surface coverage of the metallic layer. For example, many types of metallic nanostructures and metallic nanomorphologies, ranging from nanoparticles to nanocups [23] and nanorings [24] determines different surface coverage and the optical and electrical properties of such film could be strongly affected by the surface coverage parameter.

In this work, we show the possibility to access to the sub-surface electronic properties exploiting the Kelvin Probe Force Microscopy (KPFM) [25,26] to map the electrical potential of underlying block-copolymer layer inside nanohybrid polymer/metal multilayers based on insulating polymers. Moreover, hybrid multilayers (HyMLs) are tunable systems offering the possibility to tune the thickness of inserted components.

The CPD imaging of sub-surface assemblies of nanoscale hybrid layered system is a crucial point in the design and the fabrication of (opto)electronic devices. In particular, for photovoltaic applications the knowledge and the comparison of the WFs of different materials involved in the device are some of the means to reach good photovoltaic efficiency.

2. Materials and methods

A p-doped silicon wafer $<100>$ (doping 10^{15} cm^{-3}) was cut into $1 \times 1 \text{ cm}^2$ pieces. The silicon substrates were cleaned as follows: soaking in the cleaning bath at 75°C for 10 min. The cleaning solution was composed of 100 ml of 96% NH_4OH , 35 ml of 35% H_2O_2 and 65 ml deionized water. The cleaned substrates were further rinsed in deionized water for 10 min and finally deposited by horizontal precipitation Langmuir-Blodgett (HP-LB) method [27]. A CHCl_3 5 mg/ml solution of poly-n-butylacrylate-block-polyacrylic acid (PnBuA-*b*-PAA) (M_w 13,000 Da) was used for film deposition by means of HP-LB method. This solution was used for preparation of Langmuir polymer layers at the water/air interface in a computer controlled trough (LT-102, Microtest Machines, Belarus). The floating film was compressed at a rate of 0.5 mm/s (or $0.75 \text{ cm}^2/\text{s}$). In order to obtain a well-packed PnBuA-*b*-PAA film, the deposition was performed at a surface pressure of 25 mN/m [17].

The depositions of Au were carried out using an RF (60 Hz) Emitech K550X Sputter coater apparatus onto the substrates and clamped against the cathode located straight opposite of the Au source (99.999% purity target). The electrodes were laid at a distance of 40 mm under Ar flow keeping a pressure of 0.02 mbar in the chamber. The deposited Au effective thicknesses were: 3 nm (deposition time 30 s with working current of 10 mA), 8 nm (deposition time 180 s with working current of 10 mA), 12 nm (deposition time 60 s with working current of 50 mA), 25 nm (deposition time 120 s with working current of 50 mA).

The effective thickness h of the deposited Au film was measured by ex-situ Rutherford Backscattering Spectrometry (RBS) analyses. In particular, the physical unit of the thickness Q measured by

RBS is atoms/ cm^2 . So, Q was converted in the effective thickness h (measured in nm) using the Au bulk atomic density $\rho = 5.9 \times 10^{22} \text{ atoms/cm}^3$, i.e. $h = Q/\rho$. The so-obtained h is the effective Au thickness in the sense that the Au film would have such a thickness if it would be a continuous film (so that the bulk atomic density ρ corresponds to the real film atomic density). The RBS error in the Q measurement is 5%, so that the same error can be associated to the measure of h . In the sputtering deposition systems used for the present Au deposition, the emission current I and the time deposition t can be controlled (I by 5 mA step and t by 1 s step). So, by the RBS measurements, to each (I, t) values a h value is associated. The control of I and t allows to control h within 5% error.

Atomic Force Microscopy (AFM) images were obtained in tapping mode by employing a commercial microscope (MultiMode Nanoscope IIIa, Bruker). The device is equipped with a J scanner, which was calibrated using the manufacturer's grating. Ultrasharp tips (Noncontact "Golden" Silicon cantilevers, NSG10S, typical force constant 11.5 N/m, resonant frequency 255 kHz) were used. Height images are flattened to remove background "bow" and slopes. No other filtering procedures are performed on these images.

KPFM measurements were obtained by using a further module (Extender Electronics module, Bruker). In order to obtain a sufficiently large and detectable mechanical deflection, we used soft Pt/Ir coated ultra-lever silicon tips (SCM, Bruker, $k = 2.8 \text{ N/m}$) with oscillating frequencies in the range between 60–90 KHz. In the KPFM mode, topographic and surface potential images are acquired in the same measurement; a topographic line scan is first obtained by AFM operating in Tapping Mode and then that same line is rescanned in Lift Mode with the tip raised to a lift height of 20 nm. KPFM provides a voltage resolution of about 5 mV, while the lateral resolution amounts to a few tens of nanometers. Higher lateral resolution is achieved in AFM amounting to few nanometers.

AFM and KPFM images were analyzed using Nanoscope@ and Spip@ softwares. Detailed information about flattening procedures of the AFM image and the quantitative analysis using the frequency spectra can be found in [28].

Scanning electron microscopy (SEM) analyses were performed using a Zeiss FEG-SEM Supra 25 Microscope operating at 5 kV. The SEM images were analyzed by the Gatan Digital Micrograph software. From the SEM images, the fraction of the surface area covered by Au was evaluated. This was obtained by setting a threshold on the brightness of the SEM images, so that the bright regions in the images, with intensity value 1, represent metal and the dark regions, with intensity value 0, represent the copolymer exposed substrate.

3. Results and discussion

Fig. 1a reports the layer- by- layer schematic representation of the studied systems. Fig. 1a) represents the insulating block copolymer layer, indicated as 0.5 bilayer (0.5 BL) because it is half of the bilayer shown on the right-hand side of Fig. 1a), henceforth indicated as (1 BL), composed by a block copolymer film coated by an Au layer.

Fig. 1b and c displays the Morphology images and Contact Potential Difference (CPD) mappings, acquired using AFM and KPFM techniques, respectively, for the multilayered structures of PnBA-*b*-PAA/gold film deposited on silicon substrate. The structure of the film is the result of self-assembling processes of the different polymer blocks, basically yielding circular domains based on PAA chains and a matrix based on PnBuA chains [17]. Starting to characterize the simplest case corresponding to the deposition of pure PnBA-*b*-PAA on silicon substrate (Fig. 1b and c, left-hand side), the AFM analysis clearly shows a phase separation, we observe circular domains, $4.4 \pm 0.5 \text{ nm}$ higher than the matrix of the PnBA

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