Contents lists available at ScienceDirect

Applied Surface Science

Full Length Article

Energy level alignment and molecular conformation at rubrene/Ag interfaces: Impact of contact contaminations on the interfaces

Sumona Sinha [a,*], C.-H. Wang [b], M. Mukherjee [a]

[a] Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India
[b] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

ABSTRACT

This paper addresses the impact of electrode contaminations on the interfacial energy level alignment, the molecular conformation, orientation and surface morphology deposited organic film at organic semiconductor/noble metal interfaces by varying of film thickness from sub-monolayer to multilayer, which currently draws significant attention with regard to its application in organic electronics. The UHV clean Ag and unclean Ag were employed as substrate whereas rubrene was used as an organic semiconducting material. The photoelectron spectroscopy (XPS and UPS) was engaged to investigate the evolution of interfacial energetics; polarization dependent near edge x-ray absorption fine structure spectroscopy (NEXAFS) was employed to understand the molecular conformation as well as orientation whereas atomic force microscopy (AFM) was used to investigate the surface morphologies of the films. The adventitious contamination layer was acted as a spacer layer between clean Ag substrate surface and rubrene molecular layer. As a consequence, hole injection barrier height, interface dipole as well as molecular-conformation, molecular-orientation and surface morphology of rubrene thin films were found to depend on the cleanliness of Ag substrate. The results have important inferences about the understanding of the impact of substrate contamination on the energy level alignment, the molecular conformation as well as orientation and surface morphology of deposited rubrene thin film at rubrene/Ag interfaces and are beneficial for the improvement of the device performance.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, organic electronic technologies are emerging as prospective future options due to their high application potential in electronic devices [1]. The performance of organic electronic devices, such as organic field effect transistors (OFET)s, organic light emitting diodes (OLED)s, organic photovoltaic cells (OPV)s strongly depends on the efficiency of charge carrier injection from an electrode into the organic semiconductor (OSc) [2,3]. Substantial experimental and theoretical researches have been done in the field of OSC/electrode interfaces [3–7]. The main attention has been dedicated on the electronic energy level alignment between OSCs and under ultra-high-vacuum (UHV) conditions prepared clean metal substrate surfaces [3–15]. It has been transpired some detailed organic/metal interface investigations [16–20] that contact contaminations play an important role at OSC/electrode interfaces and

for the corresponding interface energetics. Generally, the device fabrication involves the processing of the electrode surfaces in controlled atmospheres (e.g. in a glove box, N_2-atmosphere or under poor vacuum conditions) as well as under ambient conditions; not under UHV conditions. Under that condition the molecules of atmosphere (N_2, H_2O, O_2 and hydrocarbons) adsorb on the electrode surface. A contamination layer on top of the electrode surface, a partial oxidation, and/or the passivation of the electrode surface can be the consequence due to the adsorbed molecules. Hence, it is crucial to investigate the differences in the interface energetics that have been shown for interfaces involving contaminated electrode surfaces with respect to interfaces of OSCs in contact to clean substrate surfaces formed under UHV conditions. It is also expected that contamination of substrate surface with respect to clean one may affect the molecular conformation and orientation as well as surface morphology of deposited OSc thin films.

Rubrene ($C_{42}H_{28}$) with its extended system of delocalized π electrons is one of the most promising materials for its high field effect mobility, among the low weight organic semiconductors, used as active materials in OFETs. Rubrene single crystal based field effect transistor show the mobility $\sim$40 cm^2/V.s [21]. Even the

* Corresponding author. Present address: S.N. Bose National Central for Basic Sciences, Kolkata 700106, India.
E-mail address: sumona.net.09@gmail.com (S. Sinha).

mobility of rubrene thin film transistors (TFT), achieved as high as 2.5 cm^2/V.s is comparable to that of hydrogenated amorphous silicon TFT [22]. It is also used as a donor material of OLED and OPV devices [23,24]. On the other hand, gold is a primary choice for the electrode material for its noble property and high work-function. Unfortunately, the high cost of gold hinders its use in realistic applications. Consequently, finding low cost and environment-friendly electrode materials as substitutes of gold are of great technical significance [25–27]. Silver is also noble-metal of sufficient high work function and it is commercially available as form of paste and ink [28,29].

Under this circumstance, we have motivated to investigate the impact of contact contaminations on the energy level alignment, the molecular conformation, molecular orientation and deposited film surface morphology at rubrene/Ag interfaces by varying thickness of rubrene films from sub-monolayer to multilayer. In this present work, we used a UHV clean Ag substrate and an unclean Ag substrate. Ultra Violet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) were employed for studying interfacial electronic energy level alignment whereas angle dependent near edge x-ray absorption fine structure spectroscopy (NEXAFS) was used to probe conformation and orientation of rubrene molecules. Morphologies of the films were investigated using atomic force microscopy (AFM). Our present study has revealed that the adventitious contamination layer was acted as a spacer layer between Ag substrate surface and rubrene molecular layer. Consequently, we have found that hole injection barrier height, interface dipole as well as molecular-conformation, molecular-orientation and surface morphology of rubrene thin films depend on the cleanliness of Ag substrate. Our results have significant consequences about the understanding of the impact of substrate contamination on the energy level alignment, the molecular conformation as well as surface morphology of deposited rubrene thin film at rubrene/Ag interfaces and are beneficial for the development of the organic electronic device.

2. Experimental details

The UPS and XPS studies were carried out using Omicron Multiprobe (Omicron NanoTechnology, UK) ultrahigh vacuum (UHV) system (base pressure ∼5.0 × 10^{-10} mbar) equipped with He I gas discharge lamp with photon energy 21.2 eV and a monochromatic Al K$_\alpha$ X-ray source with photon energy 1486.6 eV. All UPS measurements were done by applying a sample bias of −5.0 V. The organic vapour deposition chamber (base pressure ∼9.0 × 10^{-9} mbar) was directly attached to the analysis chamber allowing the samples to be studied without breaking the vacuum. The Ag coated substrate was prepared by depositing Ag thin films on H terminated Si (100) using DC magnetron sputtering (PLS 500, Pfeiffer) at 25 W power and 4.0 × 10^{-3} mbar argon pressure for 25 min. The thickness of Ag films (∼75 nm) was measured by ellipsometry (Nanofilm ep3 BAM, Accurion). The Ag substrate, designated as "unclean" Ag, was first kept in ambient environment (temp ∼25 ± 1 °C, relative humidity ∼40 ± 5%, light: laboratory fluorescent lamp) for 30 min after preparation then introduced into a first load-lock chamber and next directly was used for deposition without using the UHV cleaning procedure. Another substrate, used as UHV cleaned Ag one, was immediately loaded into the UHV chamber after preparation. To obtain UHV "clean" Ag substrates, Ar$^+$ sputtering was used until the C 1s and O 2p XPS signals were vanished and consistent values of the work functions were obtained. Rubrene films were grown on both substrates in a stepwise manner by thermal evaporation of rubrene powder (Acros Organics, 99%) from a resistively heated quartz crucible of an organic material effusion cell (MBE-Komponenten GmbH, Germany). The nominal thickness of the rubrene films were calibrated by monitoring the evaporation rate with a quartz crystal microbalance (Sycon Instruments. Inc, USA). The evaporation rate for all the films was kept within 0.04-0.06 Å/s. After each deposition the samples were characterized by in-situ XPS and UPS. All spectra were taken in near normal emission geometry. XPS core level and UPS highest occupied molecular orbital (HOMO) peak positions, intensity and full width at half maximum (FWHM) were determined by using Peakfit data evaluation software. The background correction of the C 1s was done by straight line method whereas Shirley method was used for Ag 3d XPS spectra [30]. Assuming the instrumental broadening to be negligible, HOMO peaks were fitted by Gaussian functions.

By following the same manner of sample preparation, near edge x-ray absorption fine structure spectroscopy (NEXAFS) experiments were carried out at BL24A beam line of the storage ring of the National Synchrotron Radiation Research Center, Taiwan. To overcome the difficulty of performing a reliable C–K edge NEXAFS measurement for ultra-thin adsorbate films, the incident photon flux monitoring was done by measuring ion current of the ion chamber situated between the beam-line and the sample chamber, instead of traditional gold mesh method. The ion chamber is filled with Ar up to a working pressure of 10^{-3} torr and terminated with 0.1 μm thick Ti foils at both ends [31]. The NEXAFS spectra were measured in the partial electron yield (PEY) detection mode using a homemade electron detector based on a micro-channel plate and a retarding field of −150 V to optimize the signal to noise ratio. The polarization dependent NEXAFS spectra were obtained by varying the X-ray incident direction between normal incidence (90°) and glancing incidence (20°). The base pressure of deposition and analysis chambers were 1.0 × 10^{-8} torr and 1.0 × 10^{-10} torr respectively. The use of ion chamber for monitoring the incident photon flux also simplifies the NEXAFS data normalization schemes. The step of so-called mesh current normalization is not required here. Rest of the raw data background correction and normalization were carried out according to the established procedure [32]. In order to identify changes to the absorption features, all spectra are fitted using the same procedure with Gaussian peaks (corresponding to the π* excitations) and asymmetric Gaussian peaks (representing the σ* transitions) and a step function for the background [33].

Surface morphologies of the films were studied by using tapping mode AFM (Innova, Veeco) in air. The images were analyzed by using WSxM software [34]. Scans of different area over several regions of the films were taken to check the consistency of the surface morphology of the samples.

All the depositions and characterizations were performed at room temperature.

3. Results and discussions

Fig. 1(a) and (b) is the valence region of UPS spectra that were collected during stepwise deposition of rubrene on unclean and clean polycrystalline Ag substrates respectively. Here we assume that the thermodynamic equilibrium prevails and E$_F$ is taken as constant for the entire system.

The spectra of bare substrates are shown in the figures for comparison. One can clearly observe from the figure that the spectrum of unclean Ag substrate is completely different from that of clean Ag substrate. But the presence of E$_F$ can be evidenced on unclean Ag substrate also. In addition, the signals due to the substrates are found to suppress and that of deposited rubrene becomes pronounced with successive depositions. The peak at lower binding energy region of the UPS spectra close to the Fermi level (encircled region in figure), which is the HOMO peak of rubrene, shows gradual increase of intensity with successive depositions. The true signal for the adsorbate was extracted by dividing the spectrum