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Photoemission, NEXAFS and STM studies of pentacene thin films on Au(1 0 0)

O. McDonald [a,b,*], A.A. Cafolla [a,b], D. Carty [a], G. Sheerin [a], G. Hughes [a,c]

[a] School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland
[b] Institute for Advanced Material Science (IAMS), Trinity College Dublin, Dublin 2, Ireland
[c] National Centre for Sensor Research (NCSR), Dublin City University, Glasnevin, Dublin 9, Ireland

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Abstract

We have investigated the initial stages of the growth of pentacene thin films on the Au(1 0 0) substrate using synchrotron radiation photoelectron spectroscopy (PES), near edge X-ray absorption fine structure (NEXAFS) and scanning tunnelling microscopy (STM). Results indicate a well-ordered structure with the pentacene molecules adopting a predominantly flat orientation with respect to the substrate for coverages of less than three monolayers. NEXAFS and photoemission data indicates the presence of a second molecular orientation for thicker films, with the introduction of a slight tilting away from planar bonding geometry at higher pentacene coverages. STM images of coverages less than three monolayers indicate a well-ordered pentacene structure allowing for the calculation of pentacene unit cell parameters. The pentacene molecular rows adopt a side-by-side bonding arrangement on the surface. For pentacene deposited at room temperature, step edges were observed to act as nucleation centres for film growth. Annealing of the substrate to 373 K was found to remove excess molecules and improve film quality, but did not otherwise change the bonding geometry of the pentacene with respect to the surface.

Keywords: Soft X-ray photoelectron spectroscopy; Near edge extended X-ray absorption fine structure (NEXAFS); Scanning tunneling microscopy; Pentacene; Workfunction; Interface dipole; Metal–organic interface

1. Introduction

The study of the bonding interaction between organic layers and metal surfaces is a subject that has attracted great interest in recent years due to the promising potential that these layers have in the fabrication of various electronic devices, such as organic field effect transistors (OFETs) [1] and optoelectronic devices.

One group of molecules that has attracted a large amount of interest are the polyacenes, the molecular group to which pentacene belongs. These are planar molecules, made up of differing numbers of aromatic rings bonded in a linear fashion, resembling a number of benzene molecules bonded in a row. Molecules in the acene group share the common characteristics of σ-bonds in the plane of the molecule and π-bonds perpendicular to the plane of the molecule. This group of molecules, and in particular pentacene, have been primarily studied due to their high charge carrier mobility [2]. However, in addition to this, their planar geometry presents an ideal opportunity to study the interaction between organic molecules and ideal metal surfaces without the geometrical difficulties encountered using more complex molecules.

Recent studies have shown that defects and impurities play a major role in determining the electronic properties of molecular thin films [3,4], and so a well-ordered molecular overlayer is likely to have more favourable electronic properties for device applications. In addition to this, the

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[*] Corresponding author. Address: School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland. Tel.: +353 1 7008837.
E-mail address: omd@physics.dcu.ie (O. McDonald).

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orientation of the molecules in the film is thought to play a major role in charge transport within the film, with charge transport being more favourable along certain directions in the molecular thin film.

The growth and orientation of molecular thin films depends primarily on the subtle competition between the intermolecular and molecular-substrate interactions, primarily those occurring in the first few monolayers (MLs). It has been shown that in many cases, that the intermolecular forces, which determine the relative orientation of the molecules in the bulk crystal, are very different to those experienced by molecules bonded to metal surfaces. The interaction between planar molecules and metal surfaces often leads to a planar or near planar bonding geometry in the initial monolayer [5–12] in cases where the molecular bonding geometry in the bulk is non planar [13–15]. For pentacene thin films grown on Cu(110) [5], studies have shown the changeover in molecular orientation within the film from a flat bonded molecular orientation for the initial monolayer to the upright herringbone molecular orientation evident in the molecular crystal [13–15].

There have been numerous studies of pentacene thin films grown on the Au(110) [8,16–18] and Au(111) [11,12,19,20] substrates using a variety of different techniques, but to date no studies have been carried out of pentacene thin films grown on the Au(100) substrate. In this study we have investigated the growth of pentacene thin films on the Au(100) substrate using synchrotron based PES, NEXAFS and STM. With the PES study, we were able to investigate the electronic interaction between the pentacene and the substrate and measure the magnitude of the interface dipole (ID) formed in addition to investigating the hole injection barrier via the position of the highest occupied molecular orbital (HOMO). NEXAFS has been used to investigate the orientation of the pentacene molecules in the thin film, and the STM studies allowed the molecular ordering within the film to be investigated.

2. Experiment

The photoemission experiments were carried out on the SGM1 beamline of the Astrid synchrotron radiation source at the University of Aarhus in an ultrahigh vacuum (UHV) system consisting of a preparation chamber (6.5×10^{-10} mbar) and an analysis chamber (2.5×10^{-10} mbar). The analysis chamber is equipped with a 200 mm mean radius spherical electron analyser (Scienta), with a video based multichannel detector system. The evaporation of pentacene was carried out in situ, at pressures of 3.0×10^{-9} mbar. Pentacene (purchased from Aldrich Chem. Co.) was evaporated from a resistively heated crucible, maintained at 423 K during evaporation. The pentacene had been previously degassed using a stepped degas program, that ramped the pentacene temperature up to 418 K over a 12 h period. A quartz microbalance was used to confirm a constant flux of pentacene when the evaporator was maintained at a temperature of 423 K. The pentacene was evaporated at normal incidence to the gold surface in a stepwise manner in the preparation chamber, after which the sample was transferred under UHV to the analysis chamber. The sample was cleaned using repeated cycles of Ar bombardment and sample annealing to 673 K, until the expected sharp (5×20) LEED pattern for Au(100) was observed, and no carbon was visible in the photoemission scans. The sample was heated to 673 K by resistive heating of the crystal. The sample temperature was measured using a thermocouple in contact with the crystal.

At the normal emission position, the crystal orientation was such that the synchrotron light vector made an angle of approximately 35° with the surface of the crystal. All photoemission scans unless stated were taken at the normal emission sample position. At the s-polarised sample position additionally used for the valence band scans, the synchrotron light vector was parallel to the crystal surface yielding a takeoff angle of 35° off normal to the analyser. The synchrotron radiation, the sample normal and the analyser were all in the same plane. The resolution of the spectrometer was measured to be 0.25 eV for the Carbon 1 s (C1s) peak taken with an incident photon energy of 340 eV, 0.1 eV for the Gold 4f 7/2 (Au4f 7/2) peak taken with an incident photon energy of 130 eV, and 0.12 eV for the valence band and workfunction scans taken with an incident photon energy of 31 eV. Spectrometer resolution was calculated using the width of the Fermi edge from 80% to 20% of the overall intensity drop at a given incident photon energy. The secondary electron cutoff was recorded with the sample biased negatively with respect to the electron spectrometer. The energy position of the cutoff and the onset of the HOMO were determined by linear extrapolation to the background. The workfunction was calculated by subtracting the sample bias from the extrapolation of the position of the secondary electron cutoff. The vacuum level of the surface was found by the addition of the photon energy to the cutoff energy.

The NEXAFS experiments were carried out on the SX-700 beamline of the Astrid synchrotron radiation source at the University of Aarhus, in a UHV system with a base pressure of 3.0×10^{-10} mbar, which was equipped with a fixed 100 mm mean radius hemispherical analyser (VG-CLAM2). All NEXAFS measurements were carried out for an energy width of the incident synchrotron radiation of 200 meV at the carbon K-edge by using the corresponding exit slit on the monochromator. The NEXAFS data was gathered using a slight variation on the Auger electron yield detection method, by integration of the carbon Auger signal obtained in the 252 eV−272 eV energy range for a given incident photon energy, after which the photon energy was incremented and the process was repeated. The NEXAFS raw data has been normalized using a two-step process. The data was initially divided by the NEXAFS scans taken of the clean Au(100) surface for the corresponding incident angle. A constant was then subtracted