Ultramicroscopy 111 (2011) 267–272

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Ultrasonic force microscopy: Detection and imaging of ultra-thin molecular domains

Franco Dinelli [a],*, Cristiano Albonetti [b], Oleg V. Kolosov [c]

[a] CNR, Istituto Nazionale di Ottica (INO), via Moruzzi 1, 56124 Pisa, Italy
[b] CNR, Istituto Studio Materiali Nanostrutturati (ISMN), via Gobetti 101, 40129 Bologna, Italy
[c] Department of Physics, Lancaster University, Lancaster LA1 4YB, UK

ARTICLE INFO

Article history:
Received 3 September 2010
Accepted 17 December 2010
Available online 28 December 2010

Keywords:
Scanning probe microscopy
Ultrasonic force microscopy
Organic conjugated molecules
Sexithiophene
Ultra-thin films
Organic film growth

ABSTRACT

The analysis of the formation of ultra-thin organic films is a very important issue. In fact, it is known that the properties of organic light emitting diodes and field effect transistors are strongly affected by the early growth stages. For instance, in the case of sexithiophene, the presence of domains made of molecules with the backbone parallel to the substrate surface has been indirectly evidenced by photoluminescence spectroscopy and confocal microscopy. On the contrary, conventional scanning force microscopy both in contact and intermittent contact modes have failed to detect such domains. In this paper, we show that Ultrasonic Force Microscopy (UFM), sensitive to nanomechanical properties, allows one to directly identify the structure of sub-monolayer thick films. Sexithiophene flat domains have been imaged for the first time with nanometer scale spatial resolution. A comparison with lateral force and intermittent contact modes has been carried out in order to explain the origins of the UFM contrast and its advantages. In particular, it indicates that UFM is highly suitable for investigations where high sensitivity to material properties, low specimen damage and high spatial resolution are required.

1. Introduction

In organic electronics, conjugated oligomers represent an important class of molecules besides conjugated polymers [1,2]. While polymers are generally more amenable to processing, the oligomers, having lower molecular weight, can be deposited in a much more controlled fashion down to the molecular scale. As a consequence, the oligomer film morphology results are easier to characterize and to relate to properties such as molecular conformation and organization, crystallinity, grain size and orientation [3,4]. This provides an important path for the identification and the exploration of key issues, necessary for improving organic electronic properties such as charge conductivity and recombination. In particular, the film formation in the proximity of a dielectric substrate has turned out to be vital for the performances of organic ultra-thin film transistors and the morphological properties of the first Monolayer (ML) [5] have been correlated to the conduction properties of these devices [6–9]. This is principally significant for the fabrication of electroluminescent devices where it is necessary to combine two organic films providing, respectively, paths for electron and hole conduction [10-12].

Therefore, in the past few years, the initial growth stages (i.e. at a sub-monolayer coverage) have been intensively studied by both X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM). Whereas it has provided accurate details on the crystallinity (i.e. unit cell size and molecular orientation) and grain size distribution [9,13], XRD is applicable to relatively thick samples when at least the first ML is complete [13]. On the other hand, AFM represents the key approach linking XRD data and film morphology in the real space [12], as well as providing access to local information with nanometer scale spatial resolution rather than averaged over a large sample area [14,15]. In some cases, AFM, however, cannot detect and image small molecular agglomerates. For instance, in the case of sexithiophene (T6) deposited on silicon oxide (SiO_2) surfaces, it has required other techniques, such as Photoluminescence (PL) spectroscopy, to reveal crucial information on the molecular organization [16]. AFM operating in contact (CM) or Intermittent Contact (ICM) modes, while possessing better spatial resolution, has not been capable of detecting such domains, mainly due to the roughness of the SiO_2 surface being larger or comparable with the molecular dimensions (<0.2 nm when lying flat). On the contrary, PL has revealed that, besides the upright configuration with molecular axis normal to the sample surface usually detected by AFM and XRD [13], T6 molecules can also arrange themselves in a flat configuration. Laser Scanning Confocal Microscopy (LSCM) has allowed to identify a significant population of domains made of T6 molecules lying flat in direct contact with the substrate, depending on the SiO_2 surface properties

---

* Corresponding author.
E-mail address: franco.dinelli@ino.it (F. Dinelli).

0304-3991/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultramic.2010.12.019

[15]. However, whereas LSCM has allowed for the first time to provide insight into the initial growth stages of organic films, it has not been capable of investigating the domain morphology as they are smaller than its spatial resolution [16].

In this paper, we present an investigation carried out by means of Ultrasonic Force Microscopy (UFM) [17] that provides both the nanometer scale spatial resolution as well as the material sensitivity necessary to identify both upright and flat domains in the initial stages of T6 film growth. UFM is based on a standard AFM operating in CM with the additional application of an ultrasonic vibration to the substrate, well above the AFM cantilever resonance. In this way, the friction force can be eliminated because the tip–sample contact is

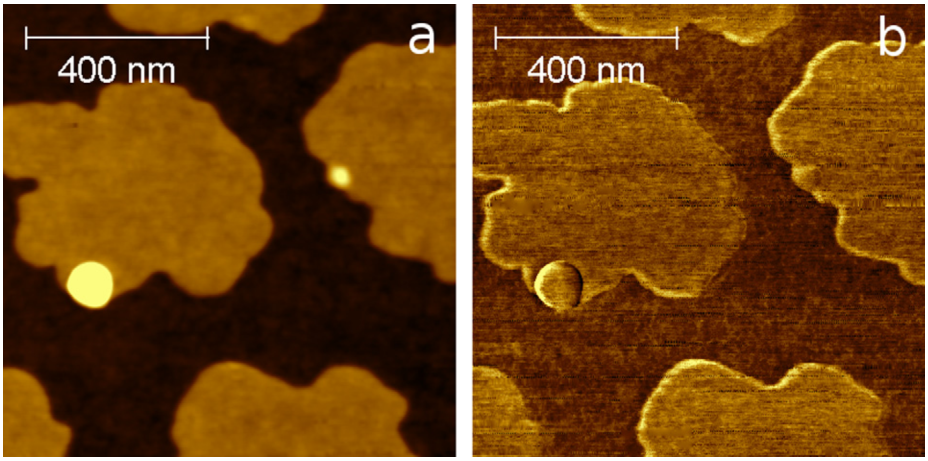

Fig. 1. Thin film with coverage around 0.4 ML imaged in contact (CM) and Lateral Force Modes (LFM): (a) topography and (b) lateral force. The terraces are 2.5 nm high, corresponding to the full length of T6 molecules. The lateral force contrast in the interstitial regions surrounding the terraces is homogeneous. The friction force is found to be higher on the terraces.

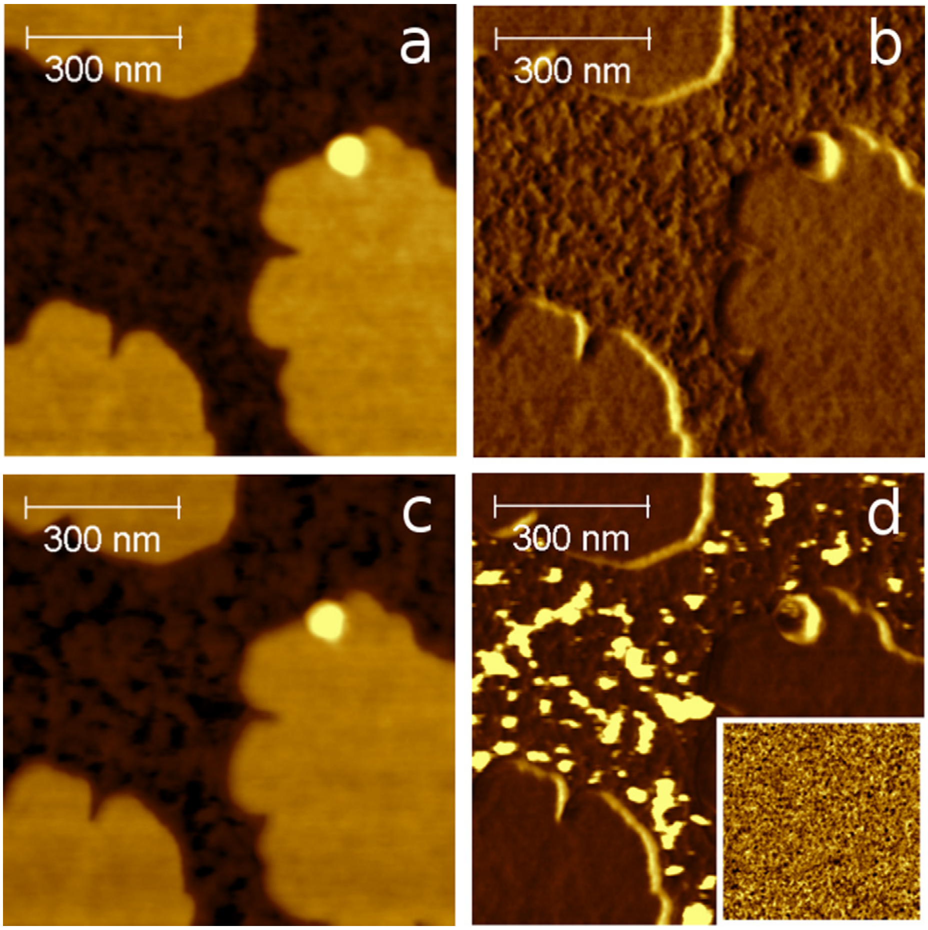

Fig. 2. Thin film with a coverage around 0.4 ML imaged in intermittent contact (ICM) mode: (a and c) topography and (b and d) phase signal. The terraces are 2.5 nm high, as reported in Fig. 1a. At high amplitude setpoint (a and b), no material contrast in the interstitial regions is visible in the phase signal. At a lower amplitude setpoint (c and d), a phase contrast appears in the interstitial regions. The dark areas in the interstitial regions between T6 terraces show the presence of molecular aggregates. For control, the inset reports the phase contrast obtained on bare SiO_2.