

Morphological and electronic properties of the thin film phase of pentacene investigated by AFM and STM/STS

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Received 18 July 2005; received in revised form 31 August 2005; accepted 31 August 2005

Available online 6 October 2005

Abstract

We investigated the morphological, structural and electronic properties of Pentacene thin films grown by vacuum thermal evaporation on different inert substrates at room temperature. The results of our AFM and STM analysis give an interplanar spacing of 1.54 nm corresponding to the (0 0 1) distance of the so-called “thin film phase”. The STS measurements show an HOMO-LUMO gap of 2.2 eV.

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PACS: 61.66.Hq; 72.80.Le; 68.55.Jk; 68.37.Ef; 68.37.Ps

Keywords: Pentacene; Organic semiconductors; AFM; STM; STS

1. Introduction

In recent years organic molecules have been extensively studied for the potential applications in the microelectronic industry. The research looks for a reduction of the cost and dimensions of dispositives and organic electronics goes straightforward in this interesting direction [1,2]. Among other molecules Pentacene ($C_{22}H_{14}$) have been used for the realization

of OTFTs, solar cells, Schottky diodes, etc. since it has a field-effect mobility comparable or better than that of amorphous silicon and it is easy to grow in crystalline thin films on different substrates [3–11].

Pentacene (Pn) is a stable aromatic hydrocarbon constituted of five planar benzene rings. The Pn crystal has triclinic herringbone structure with two molecules in the unit cell. Depending on growth parameters (temperature, substrate, evaporation rate, thickness of the film) the Pn crystal appears in different polymorphs [12,13]. These polymorphs differ for lattice parameters and tilt of molecules respect to the substrate. Changes in the crystal packing can modify the overlap of orbitals of

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adjacent molecules and this is crucial for the electronic and transport properties. Among the studied phases, the so-called “thin film phase” seems to be the most useful for application in micro and nano electronics. This phase have been observed on inert substrates (SiO_2 , SiN , LiF) for thickness less than 50 nm in polycrystalline films with grains having micrometric dimensions [3,14–17]. Recent works suggest that the thin film phase has the highest mobility [4,17]. Understanding the morphological, electronic and structural properties of Pn on various interfaces is, therefore, of great scientific and technologic interest. The scanning probe microscopies have a privileged role in the investigation of local properties of such systems. In our work we studied by atomic force microscopy (AFM), scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) the morphological and electronic properties of the thin film phase of Pn grown on SiO_2 , Si_3N_4 , passivated $\text{Si}(1\ 0\ 0)$ and highly oriented pyrolytic graphite (HOPG) substrates. Here we report the results of our analysis.

2. Experimental details

The experiments are carried out at the Surface, Thin films and Nanostructures (STN) Laboratory of the Physics department of the University of L'Aquila. The films are prepared in an Ultra High Vacuum (UHV) chamber by vacuum thermal evaporation of Pn (Aldrich Chemicals) from a resistively heated quartz crucible. The pressure in the UHV chamber ranged from 1×10^{-6} to 1×10^{-8} Torr for different samples. The substrates were sonicated with acetone and ethanol before deposition and were kept at room temperature (RT) during deposition.

The STM and STS measurements are performed in situ at RT with an Omicron variable temperature STM using home-made W tips. For the STS measurement we interrupt the feedback control of piezo and we ramp the voltage from -3 to $+3$ V at steps of 30 mV in a grid of 625 points for image. The Tapping Mode AFM measurements are performed ex-situ in air on a Digital Dimension D5000 with commercial silicon nitride cantilevers (resonance frequency range = 200–300 kHz). The samples have been investigated by X-ray diffraction (XRD) using a Siemens 5000 diffractometer in the Bragg–Brentano geometry.

3. Results

Fig. 1 reports an overview of AFM micrographs of Pn films (nominal thickness = 20–30 nm) on different substrates: SiO_2 , Si_3N_4 , passivated $\text{Si}(1\ 0\ 0)$ and HOPG. The images are very similar one to another and mainly differ for the grain size. The film grows in a dendritic way with single crystallites whose shape and dimension strongly depend on the evaporation rate while pressure has little influence on the morphology and grain size. In Fig. 2 we report an AFM micrograph (a) of a 20 nm Pn thin film on a passivated $\text{Si}(1\ 0\ 0)$ surface and corresponding line profile (b) and height hystogram (c). We can observe from the image the terrace structure of crystallites and from the line profile and height hystogram we find an interplanar spacing of 15.4 Å comparable with the $d(0\ 0\ 1)$ of the thin film phase. Our observation is confirmed by the Bragg–Brentano XRD analysis: in Fig. 3 we report an XRD pattern that shows the presence of sharp peaks attributed to reflection (0 0 l) of the Pn thin film phase. Also the STM measurement of a 5 nm nominal thickness Pn film on HOPG (Fig. 4) show a similar morphology. The images of Pn film are acquired at gap

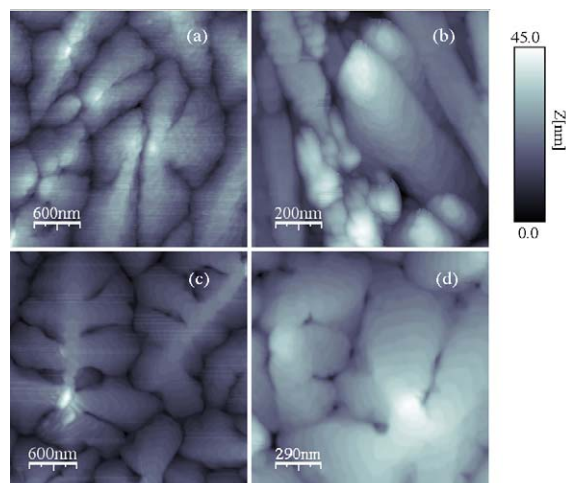


Fig. 1. AFM micrographs of Pn thin films on different substrates. (a) $3\ \mu\text{m} \times 3\ \mu\text{m}$ image of a 20 nm nominal thickness film on Si_3N_4 ; (b) $1\ \mu\text{m} \times 1\ \mu\text{m}$ image of a 30 nm nominal thickness film on HOPG; (c) $3\ \mu\text{m} \times 3\ \mu\text{m}$ image of a 20 nm nominal thickness film on a passivated $\text{Si}(1\ 0\ 0)$ surface; (d) $1.45\ \mu\text{m} \times 1.45\ \mu\text{m}$ image of a 20 nm nominal thickness film on SiO_2 . Deposition parameters: pressure = 1×10^{-6} Torr (a, c and d), 3×10^{-8} Torr (b); evaporation rate = 2 Å/min (a, c and d), 5 Å/min (b); substrate at RT.

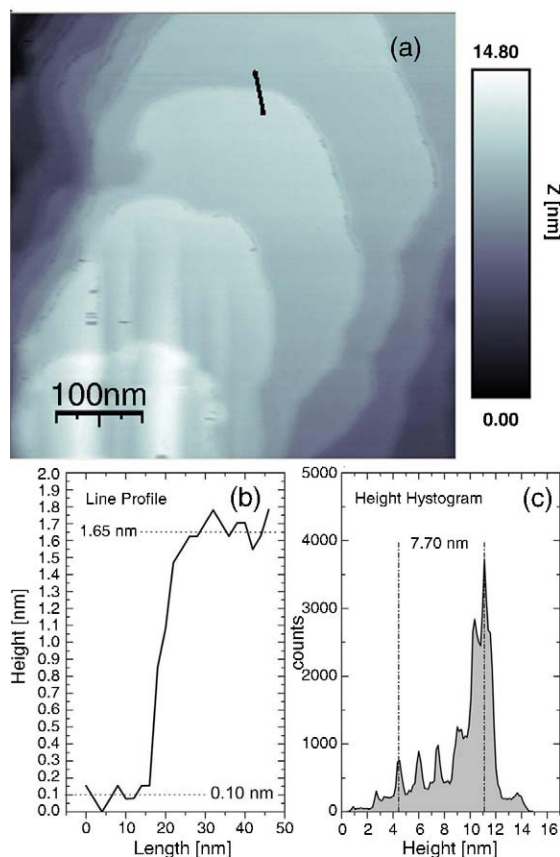


Fig. 2. 500 nm $\times$ 500 nm AFM micrograph (a) and corresponding line profile (b) and height histogram (c) of a Pn thin film on a passivated Si(1 0 0) surface (nominal thickness = 20 nm). Deposition parameters: pressure = 1×10^{-6} Torr, evaporation rate = 2 Å/min, substrate at RT.

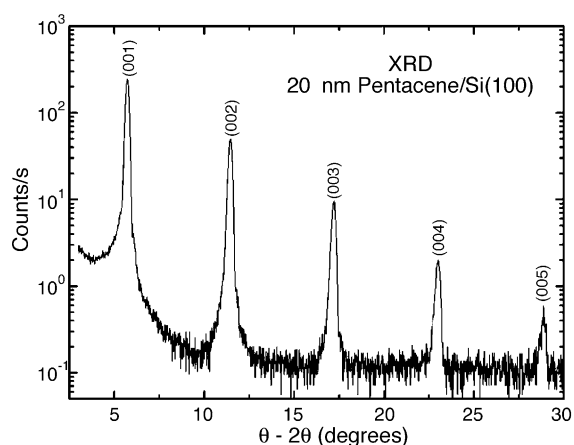


Fig. 3. Bragg–Brentano X-ray diffraction pattern of the thin film phase of Pn.

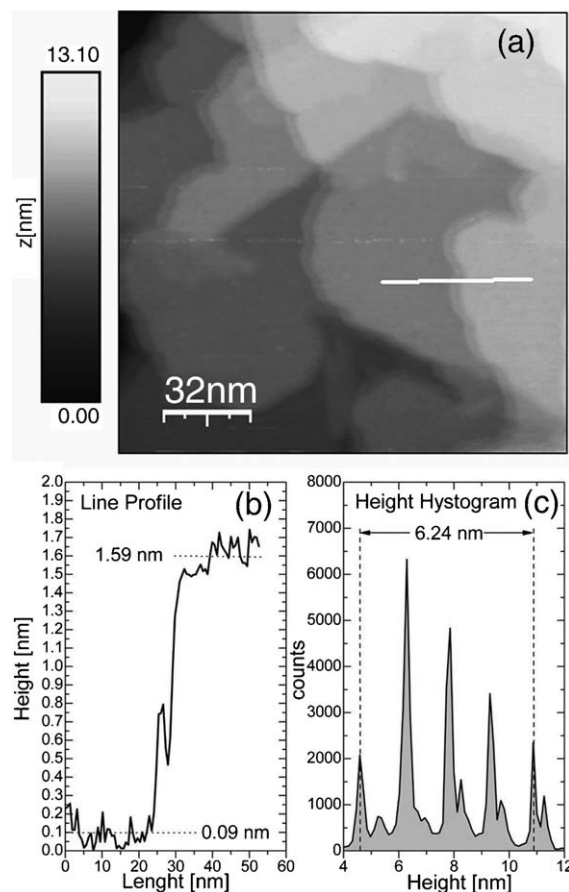


Fig. 4. 160 nm $\times$ 160 nm STM image (a) and corresponding line profile (b) and height histogram (c) of a Pn thin film on HOPG (nominal thickness = 5 nm). Measurement parameters: pressure = 3×10^{-8} Torr, gap voltage = -2.5 V, $I_T = 0.03$ nA. Shadowing around each terrace is a double tip effect.

voltage of $\pm 1.5/2.5$ V and tunneling current of 0.03 nA. Switching the gap voltage to +0.1 V and with a tunneling current of 0.5 nA we observe the HOPG substrate with atomic resolution. This observation is in good agreement with other works on organic molecules reported by Alvarado et al. [18]. The STM image (a) reveals a series of terraces and the line profile (b) and height histogram (c) give an interplanar spacing of 15.3 ± 0.3 Å suggesting that the Pn molecules on HOPG adopt a thin film phase structure. This is in contrast with other works that indicate an epitaxial growth on HOPG of layers of Pn with the long axis of molecules parallel or lightly tilted respect to the surface of the substrate [19,20]. Nevertheless,

we cannot know from our measurement if the first MLs of molecules stand up or parallel respect to the substrate. Our observation is that for next planes the film of pentacene adopts a thin film phase structure. The observation of Pn thin film phase studied by STM is not reported elsewhere in literature. Only Sadowski et al. report a direct STM observation of a thin film of Pn but in the so-called bulk phase [21].

During acquisition of STM images we perform also $I(V)$ measurements. In Fig. 5 we report the $I(V)$ curve (a) and the normalized conductance $(dI/dV)/(I/V)$ (b) obtained averaging the curves resulting from a series of images acquired at gap voltages of $\pm 1.5/2.5$ V and tunneling current of 0.03 nA. The $(dI/dV)/(I/V)$ curve shows two pronounced peaks around -0.8 and $+1.4$ V and no states in between (the peak around $+1.0$ V is due to division by zero). This suggest that the -0.8 ($+1.4$) V peak is attributed to the HOMO (LUMO) level of Pn and the gap resulting is 2.2 eV. The direct observation of HOMO–LUMO gap for the thin film phase of Pn is not reported elsewhere in literature. However, our value is comparable with other STS observation of Pn on $\text{Ag}/\text{Si}(1\ 1\ 1) - (\sqrt{3} \times \sqrt{3})R30$ [22], theoretical calculation [23] and photoelectric and optical absorption measurement for thin films of Pn [24]. As the STM measurement is heavily affected by the measurement conditions (gap voltage and tunneling current), the STS measurements at gap voltage of 0.1 V

and tunneling current of 0.5 nA show a metallic behaviour comparable with the electronic structure of HOPG. This is not surprising because at gap voltage near 0 V the tip penetrate the molecular film and is in tunnel contact only with the HOPG surface. We observe, therefore, the electronic structure and morphology of the substrate. This observation is a confirm of goodness of our results.

4. Conclusions

We studied the morphological, structural and electronic properties of the thin film phase of Pn on different inert substrates. The AFM and STM measurements show a dendritic growth in single crystallites. These crystallites, which dimension and shape depending mainly on the evaporation rate, have a terrace structure with an interplanar distance of 15.4 Å. The STS measurements give us the position of HOMO and LUMO levels respectively at -0.8 eV and $+1.4$ eV respect to Fermi Level and an HOMO–LUMO gap of 2.2 eV.

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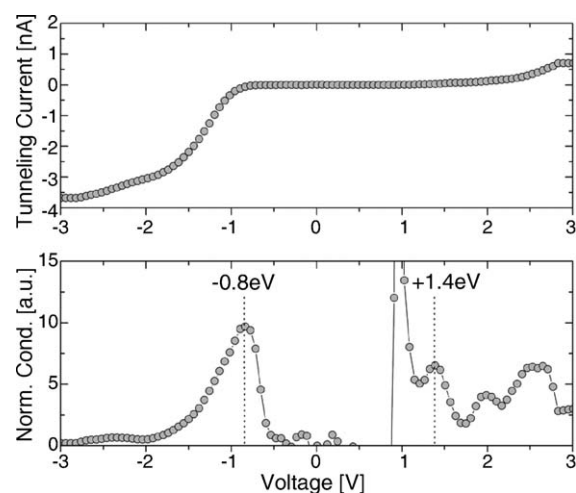


Fig. 5. Averaged $I(V)$ curve (upper panel) and normalized conductance spectra $(dI/dV)/(I/V)$ (lower panel) measured during STM images acquisition at gap voltage = $\pm 1.5/2.5$ V and $I_T = 0.03$ nA.