Experimental report

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Proposal: 5-21-1088 **Council:** 10/2014

Title: Structure of sub-monolayer deuterated pentacene islands on exfoliatedgraphite studied with neutron surface diffraction

Research area: Other...

This proposal is a new proposal

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Samples: C22D14/graphite

Instrument	Requested days	Allocated days	From	To
D20	4	3	03/07/2015	06/07/2015

Abstract:

Organic thin films such as pentacene (C22H14) films are promising systems for the development of novel electronic devices. However, the electrical properties of the resulting devices are limited by the quality of the films, which strongly depends on the growth process. It is of particular importance to understand the interplay between the dynamics of the organic molecules on the substrate and the structure of the resulting aggregates, above all in the early stages of the film deposition. In this perspective experiments which link structure and dynamics of pentacene on technologically relevant substrates, such as graphite, are essential to set the most favorable conditions for growing epitaxially ordered organic films. In the present experiment we propose to observe with neutron diffraction the structure of pentacene islands in the same range of coverages and temperatures at which dynamics experiments of neutron and helium atom spin-echo spectroscopy will be performed.

Structure of sub-monolayer deuterated pentacene islands on exfoliated graphite studied with neutron surface diffraction

Organic thin films are an emerging area for the development of novel electronic devices such as organic thin films transistors (OTFT) because of their charge transport properties and their low cost (compared to single crystalline materials). In particular, pentacene ($C_{22}H_{14}$), a chain like aromatic molecule, is widely used due to its high field-effect mobility and its tendency to form ordered films on a variety of substrates [1,2]. However, the electrical properties of the resulting devices are limited by the quality of the films, which strongly depends on the growth process. Therefore, understanding the mechanisms which underlie the formation of the first layer and the interplay between the dynamics of the adsorbates and the structure of the film, are crucial steps to set the most favorable conditions in the growth of well-ordered epitaxial organic thin films. Diffusion is an important mechanism in film growth and strongly affects the structure of the adsorbate islands on the surface during the early stages of the film deposition [2]. *In order to link dynamics to structure in the process of organic film growth, we have measured in D20 the neutron diffraction pattern of islands of deuterated pentacene molecules adsorbed on exfoliated graphite for two coverages 0.5 ML and 0.9 ML in a wide thermal range from 10 K up to 450 K. This structural experiment is complemented by our study of the dynamics of pentacene molecules on exfoliated graphite performed at IN11 and IN6.*

Measurements and experimental procedure:
The measurements of the diffraction pattern for each sample consisted into two steps:

- diffraction pattern of the sample containing only the clean exfoliated graphite substrate
- diffraction pattern of the sample filled with pentacene and exfoliated graphite.

This procedures allows us to subtract the background of graphite from the total diffraction pattern and obtain the diffraction pattern of the pentacene adsorbed layer.

Sample preparation:
In order to prepare the samples, first of all we clean the exfoliated graphite (Papyex) substrate by heating under vacuum conditions in a pyrolytic oven for 24 hours at 350 C. Secondly, we fill our aluminum sample holder with 26 grams of exfoliated graphite substrate. Finally we dose the corresponding amount of deuterated pentacene (powder) under a nitrogen controlled atmosphere in a glove bag and we closedhermetically the sample holder with a stainless steel cutting edge head. The amount of pentacene per sample is the following:

- 0.5 ML require 80 mg of $C_{22}D_{14}$ for 26 g of exfoliated graphite.
- 0.9 ML require 100 mg of $C_{22}D_{14}$ for 26 g of exfoliated graphite.

The deuterated pentacene was synthesized by Dr. M. Kohout (University of Chemistry and Technology, Prague, Czech Republic).

Sample environment:
The measurements have been performed with the cryofurnace set-up which allows us to cover a wide thermal range from 10 K up to 550 K. We first heat up the sample (pentacene/graphite) up to 550 K for few minutes to sublimate the pentacene powder and promote its uniform adsorption in the whole volume of the sample. Afterwards we cooled down and performed measurements of 2 hours at 10 K, 100 K, 250 K, 350 K and 450 K. The desorption of pentacene on graphite takes place between 400 K and 425 K [3].

Experimental set-up:
The measurements were carried on in the D20 neutron diffractometer with an incoming wavelength of 2.4 Å selected with the [002] reflection of the HOPG graphite monochromator oriented at 40 degrees with respect to the direction of the incoming neutron beam in the guide.

Experimental results:
We have explored the formation of ordered pentacene structures on the basal plane of graphite crystals at different coverage and temperature conditions. We observe the signature of pentacene ordering on the surface through the emergence of different Bragg peaks (see top panel of Fig. 1), which are non visible in the diffraction pattern of exfoliated graphite. These diffracted feature were already observed in Ref. [3]. The position of the pentacene Bragg peaks is sensitive to the temperature (see left panel of Fig. 2), which can be related to a thermal expansion of the cluster. However the structure remains the same for different coverages (see right panel of Fig. 2). Such a behavior indicates that the molecules do not spread evenly on the surface but they have tendency to form islands on the surface. A further analysis of the diffraction pattern will yield the geometry of the islands and its dimensionality.

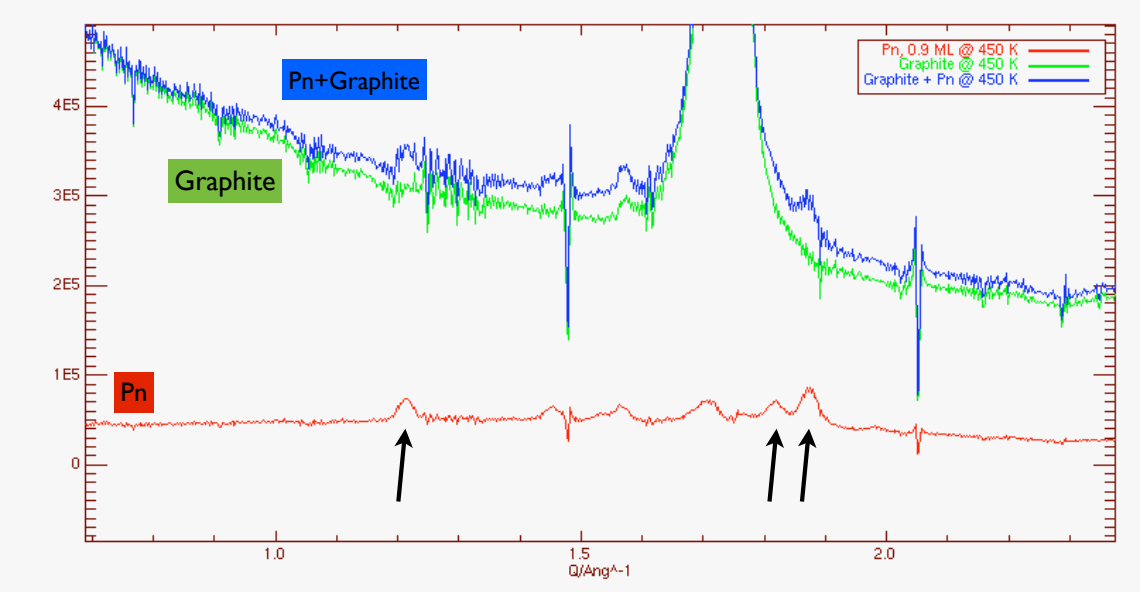

Figure 1: Diffraction pattern of clean exfoliated graphite (green), pentacene adsorbed on exfoliated graphite (blue) and the subtracted signal which should correspond to the pentacene adsorbed layer (red) at 450 K for 0.9 ML. The black arrows indicate the position of the Bragg peaks associated to the pentacene ordered layer.

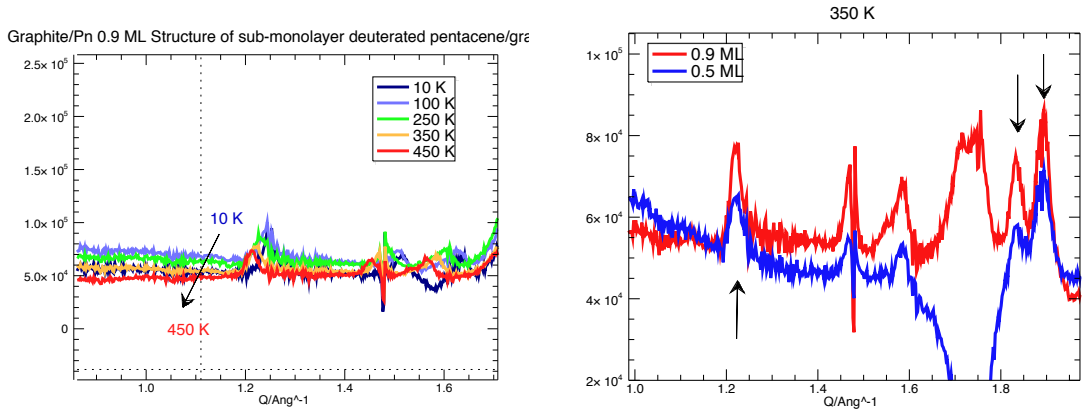

Figure 2: Left panel: evolution with temperature of the first pentacene layer Bragg peak position with temperature for the 0.9 ML sample. Right panel: comparison of the Bragg peaks positions and intensity for the 0.5 ML and the 0.9 ML at 350 K.

References

[1] R. Ruiz, et al. Chem. Mat. 16, 4497 (2004).

[2] B. Nickel, *et al.* Phys. Stat. Sol. 205 , 526 (2008); A. Winkler J. Phys. Chem. Lett. 4, 4080 (2013).

[3] J. Götzen, *et al.* Phys. Rev. B 81, 085440 (2010).