GIXD Studies of Pentacene and Tetracene Thin Films

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Introduction

Aromatic molecular thin films (e.g. pentacene and tetracene) are attracting much interest for their potentials in applications as the active semiconducting material in organic thin film transistors [1]. It is well recognized that in device applications the transport properties of the film is closely related to the molecular packing and grazing-incidence X-ray diffraction (GIXD) is a well suited tool to probe such molecular ordering in the ultrathin films, particularly, at the interface between the semiconductor and the dielectric substrates [2-4]. On the other hand, out of plane X-ray diffraction (XRD) is effective to probe the vertically layered ordering of the film which usually possesses different crystalline polymorphs of the bulk crystal structure.

As part of continuing commissioning of the endstations at the CLS HXMA beamline [5], in Dec. 2007 and early Jan. 2008 we have carried out GIXD and out of plane XRD measurements on various pentracene and tetracene ultrathin films to test the feasibility of such experimentation using the HXMA Huber psi-8 diffractometer. The preliminary results of these activities are discussed in the following. In this report we focus on the surface/thin film type of diffraction development at the HXMA beamline, other diffraction commissioning activities (powder and under high pressure conditions) will be described in separate activity reports [6,7].

Experimental

The pentacene and tetracene thin film samples were prepared at Guelph several days before the beamtime run. Different substrates were used: i) hydrogen-passivated Si(001) substrates prepared ex situ [8]; ii) Si(001) surfaces cleaned by thermal annealing in UHV environment [9]; iii) SiO_2 thermally-grown on chemically prepared clean Si(001) surface. Pentacene and tetracene (97% and 98%, respectively, all from Sigma-Aldrich) were evaporated onto those substrates in an UHV chamber (base pressure $<3\times10^{-9}$ torr) [8,9]. Film thickness ranges from 1.2 monolayer (ML) to 15 ML was investigated.

The X-ray diffraction measurements were conducted ex situ, either in air or in a flowing helium gas environment. Data acquisition in two different beamline operation modes was tested: i) the focused monochromatic beam (15 keV with Si 220 mono crystal) mode with the beamline mirrors (collimating and toroidal focusing [5]) inserted; and ii) unfocused monochromatic beam (10 keV, Si 111 mono crystals) with mirrors withdrawn. In the latter case, a Pt-coated float-glass harmonic rejection mirror was used with an energy cut-off at 20 keV and the monochromator was fully tuned. The diffracted beam was detected by using a solid state detector (Cyberstar) mounted on the analyzer 2-circle stage on the psi-8 detector arm (δ-circle). The incoming beam intensity was monitored using a gas ion chamber filled with N_2. The Huber psi-8 was controlled through SPEC software.

Results

Representative out-of-plane XRD data for the sample series of tetracene/H/Si with physically prepared Si(001) substrates are shown in Figure 1. It is apparent that for these room temperature prepared samples [9] the thin-film phase dominates the film structure when the film thickness is less than 10 ML. This is consistent with our preliminary results obtained from similar measurements at beamline 20ID at the Advanced Photon Source [10], but the thickness range where the bulk-like phase becomes observable in out-of-plane XRD has been narrowed to around 10 ML. Similar results were also obtained for the growth process on chemically prepared H/Si(001) substrates (not shown). The data shown in Figure 1 are single scans with 1sec/point integration time and the mirror focused monochromatic beam at 15 keV (wiggler field was at 1.5 T).

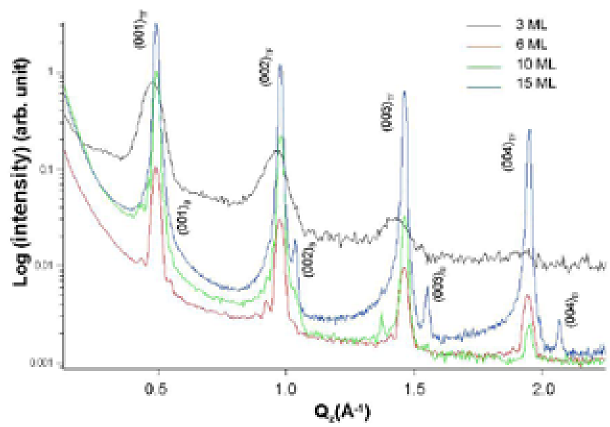

Figure 1. Out of plane XRD of tetracene film grown on UHV prepared H/Si(001) substrates. "B" and "TF" indicate the bulk-like and thin-film phase diffraction peaks, respectively. The film thicknesses were estimated from AFM measurements on similar samples.

The results shown in Figure 1 were with 'flat' Si(001) substrates, with a miss-cut angle less than a quarter of a degree. When the same growth was performed on vicinal Si(001) substrates, an earlier onset of the appearance of the bulk-like phase was observed and with a stronger bulk-like phase signal which is approximately equal to that of the thin-film phase at 15 ML. An abrupt change in the diffraction peak width from 3 ML to higher film coverage is noticeable. This can be correlated to the drastic growth morphology change around 3 ML observed in real space and the change in average molecular tilting angle from NEXAFS [9, 11].

Figure 2 shows representative in-plane GIXD data obtained in the commissioning tests from pentacene films grown on SiO_2. The in-plane diffraction peaks in the 15 ML data correspond well with the pentacene data in the literature [2] as do our monolayer data. High Q_{xy} detail needs better statistics to be revealed.

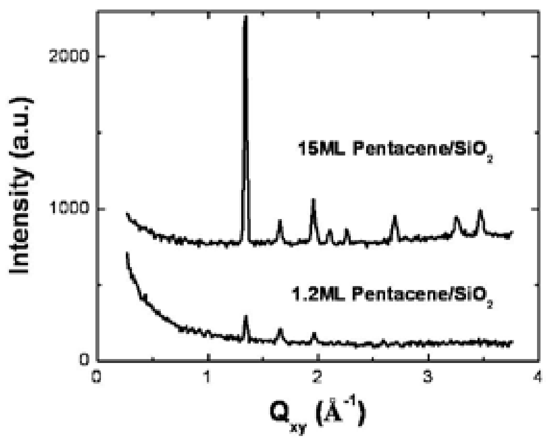

Figure 2. In-plane GIXD of pentacene films on silicon dioxide substrate, data acquired in the unfocussed monochromatic beam mode (about two orders of magnitude weaker in the usable flux at the sample in gazing-incidence geometry than that with HXMA beamline mirror focussed beam).

Discussion

The preliminary commissioning results demonstrate the GIXD capability on HXMA beamline, with the sensitivity of monolayer organic crystalline film under ambient conditions and even in the unfocused beam mode. The thickness range where the bulk-like phase becomes observable in out-of-plane XRD in the growth of tetracene on a hydrogenated silicon surface has been refined. Clear correlations between the growth mode and the substrate step characters were observed in the out-of-plane XRD data for tetracenene. The experiment would certainly benefit from more sophisticated detector capabilities such as an area detector combined with the Huber psi-8 diffractometer, which would efficiently enhance other aspects of the GIXD technique, such as crystal truncation rod analysis of the monolayer organic systems [12]. Data analysis of these commissioning results is still in progress and more systematic GIXD experiments are being planned.

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