Chemical and Materials Science

NEXAFS Studies of Pentacene and Tetracene Thin Films

D.T. Jiang (1), J. Shi (1), A. Tersigni (1), T. Regier (2,3), and X.R. Qin (1)

(1) Department of Physics, University of Guelph

(2) Canadian Light Source, Inc.

(3) Department of Physics and Engineering Physics, University of Saskatchewan

9

PRINCIPAL CONTACT:

D.T. Jiang
University of Guelph
detong@physics.uoguelph.ca

Introduction

Organic semiconductors [1-4] are envisaged as a viable alternative to conventional inorganic material-based electronics applications, in providing low cost manufacturing, compatibility with flexible substrates, and multifunctionalities using simple device structures. Among oligomer candidates for such device applications, pentacene and tetracene have attracted significant current interest for their potentials in field-effect transistors (FETs) and organic light-emitting field-effect transistors (OLETs), respectively. In these structures, a thin film of the polyacene molecules serves as the active semiconducting material, the field-induced charge carriers are located mostly within a few monolayers from the semiconductor-dielectric interface. Therefore the structure of the film-substrate interface strongly influences the carrier transport and luminescent properties of the organic semiconductors. In organic molecular film growth the direction of the molecule plays a crucial role in determining the film structure. Polarization dependent C *1s* NEXAFS [5] is a very powerful technique to probe such orientational ordering and we have used it in combination with other techniques such as scanning probes (STM and AFM) and grazing-incidence X-ray diffractions to investigate the early formation stage of the polyacene films [6-8]. This report summarizes our recent results on pentacene and tetracene films on various substrates characterized using polarizatin dependent NEXAFS.

Experimental

The pentacene and tetracene thin film samples were prepared shortly before the beamtime. Two types of substrates (H/Si(001) and SiO_2) were used and the growth condition resulting in layered film morphologies was used [6-8]. Several aspects about the substrates that may influence the growth were investigated. These include hydrogenated silicon substrates prepared via two different hydrogenation methods were used, namely by wet chemistry method and by via UHV atomic hydrogen dosing, respectively, and substrates prepared on silicon wafers with different surface step densities (0.25° and 4° wafer miscue angle, respectively). 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). Three different thicknesses were prepared on the above mentioned substrates: 1.2 monolayer (ML), 3 ML, and 15 ML, respectively, for pentacene and tetracene.

NEXAFS measurements on the CLS SGM beamline were carried out in two sample geometries: i) sample rotation axis was perpendicular to the storage ring plane (default setup of the SGM solid state chamber) and ii) sample rotation axis was collinear with the X-ray beam path. The second geometry has the advantage of maintaining the beam penetration depth the same when changing the beam polarization with respect to the film surface. For the sample thicknesses in this report the two methods were found to be equivalent. Total electron yield detection was the primary method used in this study. The exposure of the sample to the X-ray illumination on the films was limited to avoid beam damage effect and measurements at multiple sampling areas were averaged to obtain the data.

Results and Discussion

Figure 1 shows typical examples of the polarization dependent NEXAFS spectra of the pentacene films of different thicknesses on the hydrogenated silicon and silicon dioxide substrates, respectively. The raw data background correction and normalization were carried out using the same multiple step procedure as that reported by Rei et al. [9]. The tetracene NEXAFS data (not shown) exhibit similar polarization dependence [7].

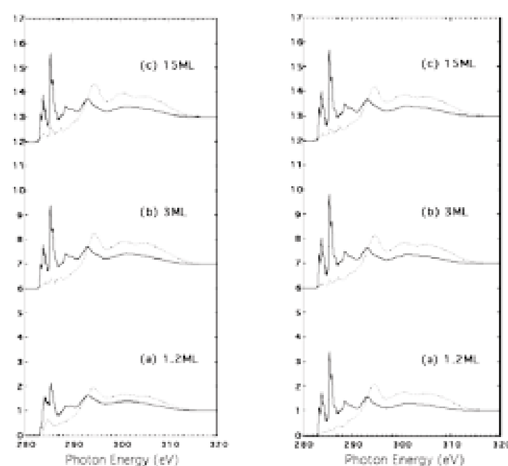

Figure Figure 1. NEXAFS spectra for pentacene films on H-Si(001) (left) and SiO_2 (right) surfaces at different coverages (1.2ML, 3ML and 15ML) as marked in the figure. The spectra for X-ray beam at normal (θ=90°) and grazing (θ=10°) incidences are plotted by the solid lines and dotted lines respectively.

As shown in Figure 1 there is a clear enhancement of the π^* resonance features below the ionization potential (IP) at ~291 eV when the X-ray polarization is near parallel with the film surface (i.e. X-ray beam normal incidence). The polarization dependence indicates that the molecules in these films are

orientationally ordered in an upright standing state [7]. Compared to the spectra of gas-phase pentacene [10], the nearly identical spectral features shown in Figure 1 suggest that the molecules are indeed intact chemically in the film and therefore similar spectral assignments as that in the gas-phase case can be applied. Two different methods of enumerating π^* resonance intensity were used in the analysis: i) consider all spectral intensity below the IP as from π^* resonance [7]; ii) curve fit the entire spectrum and identify the π^* resonance components. The first method has the advantage of simplicity and model independency, but it may be subject to systematic errors due to the inclusion of spectral intensity near IP which are not originated from π^* resonances. The curve fitting method could reveal more insights about the spectral features but it is subject to uncertainties due to the fitting parameter correlations. With some systematic constraints applied in the curve fitting method, consistent analysis results on the average molecule tilting angles with respect to the substrate surface were obtained from the two methods. There is a systematic upwards shift of the tilting angle about 3° from method 1 to method 2, which is just above the size of the experimental uncertainties when relevant experimental factors such as the angle alignment errors and the uncertainties in the X-ray beam polarity are taken into account [7].

The trends of average molecule tilting angle as a function of the film thickness are shown in Figure 2 for representative systems. Several general trends can be observed from the data in Figure 2. First of all the molecules in all of the films in this study possess an upright standing geometry, and at thicker coverage the average tilting angle all tend to converge to their bulk crystalline values. More importantly, for both tetracene and pentacene on H/Si(001), there is a significant change in the tilting angle in the first few monolayers of growth. In both of the experimental geometries used in this study (i.e. the sample rotation axes perpendicular or collinear to the X-ray beam path) the X-ray penetration depth ensured that the molecules in the entire film were monitored. Therefore tilting angle increase at 3 ML appears to describe a structural change occurred in the entire film, i.e. the result of a self-organized film structure evolution induced by the film thickness. The tilting angle increase at 3 ML for tetracene on H/Si(001) corresponds to a growth mode change observed by scanning probe microscopes [7], which also indicates a different substrate structure has formed after 3 ML. However, this change is not related to the appearance of the bulk-like phase of either the pentacene or tetracene crystals, as our X-ray diffraction results indicate that at the 3 ML coverage the structure is predominantly in the thin film phase of the polyacenes [11]. The tilting angle change at 3 ML was observed to be independent to how the H/Si(001) surface was formed, either by the wet chemistry method or the UHV atomic hydrogen dosing, and independent to the step density on the surface (additional azimuth dependence occurs in this case). Therefore the observed molecular tilting angle change as the function of film thickness appears to be an intrinsic property of the polyacene growth on such inert substrate surfaces. The lack of such change in NEXAFS data for the pentacene growth on SiO_2 (Figure 2) is either due to the limitation of our ex situ experimental procedure, or indicating the difference of the chemical nature of the substrate.

Conclusion

Polarization dependent C 1*s* NEXAFS was used to characterize the film structure as a function of film thickness. Tetracene and pentacene films grown on hydrogenated silicon surfaces are shown to experience a thickness dependent film structure self-organization at 3 ML coverage. However, for pentacene on SiO_2 surface, such reorganization was not observed.

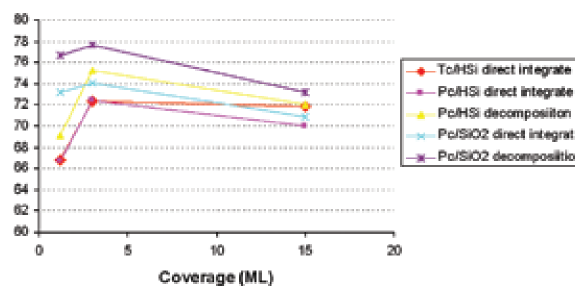

Figure 2. Molecule tilting angle as a function of nominal film thickness. Tc and Pc indicate tetracene and pentacene respectively.

Acknowledgements

The research was supported by NSERC. We would like to acknowledge the supports from CLS staff.

References

1. Forrest, S.R. 1977 Chem. Rev. 97, 1793.
2. Schreiber, F. 2004 Phys. Stautus Solidi A 201, 1037.
3. Witte, G. Wöll, C. 2004 J. Mater. Res. 19, 1889.
4. Muccini, M. Nature Mater. 5, 605 (2006).
5. Stöhr, J., NEXAFS Spectroscopy, Surface Science Series (Springer 2003), Second Printing.
6. Shi, J., Qin, X.R. 2006 Phys. Rev. B., 73, 121303(R).
7. Tersigni, A., Shi, J., Jiang, D.T., Qin, X.R. 2006 Phys. Rev. B. 74, 205326.
8. Shi, J., Qin, X.R., Phys. Rev. B., Submitted.
9. Rei, S., Krumm, H., Nikiewski, A., Staemmler, V., and Wöll, C. 2002 J. Chem. Phys. 116, 7704).
10. Alagia, M., Baldacchini, C., Betti, M. G., Bussolotti, F., Carravetta, V., Ekstrom, U., Mariani, C., Stranges, S. 2005 J. Chem. Phys. 122, 124305.
11. Jiang, D.T., Kim, C.Y., Tersigni, A., Shi, J., Regier, T., Chen, N., Qin, X.R. 2008. This report.