Temperature Driven Changes in the Electronic Properties of Pentacene Films: A High-Resolution ARPES Study

Richard C. Hatch\textsuperscript{2}, Kathleen DeWahl\textsuperscript{1}, and Hartmut Höchst\textsuperscript{2}

\textsuperscript{1}Gustavus Adolphus College, St. Peter, MN 56082

\textsuperscript{2}Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, WI 53589

The Pentacene (Pn) molecule, C\textsubscript{22}H\textsubscript{14}, is a linear chain of five Benzene rings with conjugated \(\pi\)-bonds. Crystals or thin films of Pn have unique semiconducting properties that lend themselves nicely to novel electronic applications such as flexible displays, spray on solar cells, and electric wallpaper.

We used high-resolution angle-resolved photoemission spectroscopy (ARPES) to study the evolution of the electronic structure of Pn thin films grown on Si(111) and highly ordered pyrolytic graphite (HOPG) as a function of film thickness and film-growth parameters such as source and substrate temperature. Furthermore, the temperature dependence of the highest occupied molecular orbital (HOMO) states has been explored.

We found that the peak positions of the photoemission spectra for what one would consider bulk films resemble the molecular orbital energies as calculated by a density functional theory [1] suggesting that, despite the large number of molecules in close proximity to one another, the interactions between the Van der Waals-bonded molecules are weak.

We compared the normal emission valence band spectra of Pentacene films grown at 85 K and room temperature (RT). The top of the valence band region of the RT-grown film shows a pronounced structure (S1) which is highly dependent on the photon energy while the film grown at low temperatures lacks this structure and shows no photon energy dependence indicative of a polycrystalline film.

Shown on the left is the HOMO region close to the Fermi-level. The spectrum was measured at 175 K with 18 eV photons and normal emission geometry. The spectral feature can be easily simulated by a free fit using four Gaussian peaks and a polynomial simulating the inelastic background. Structure, S1, is at -0.99 eV and has a width of 140 meV. Both peak energies and widths show temperature dependence some of which are atypical for a solid crystal. Structures S1-S4 are non-dispersive, in normal emission, for varying photon energies. Whether they reflect critical point energies of the Pentacene band structure or if S2-S4 are related to hole- or electron-vibrational couplings will require further investigation [2].

The lifetime broadening of the S1 structure is distinctly different from the simple Debye model which would predict that the lifetime broadening would be strictly increasing as a function of temperature. This result indicates that the lifetime broadening cannot be solely explained by electron-phonon interactions.

\textbf{Acknowledgement:} The Synchrotron Radiation Center (SRC) is funded by the National Science Foundation (NSF) under Grant No. DMR-0084402.

\textbf{References:}
