6-12-2007

Changing band offsets in copper phthalocyanine to copolymer poly(vinylidene fluoride with trifluoroethylene) heterojunctions

Jie Xiao
University of Nebraska - Lincoln

Andrei Sokolov
University of Nebraska-Lincoln, sokolov@unl.edu

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/physicsdowben
Part of the Physics Commons

Xiao, Jie; Sokolov, Andrei; and Dowben, Peter A., "Changing band offsets in copper phthalocyanine to copolymer poly(vinylidene fluoride with trifluoroethylene) heterojunctions" (2007). Peter Dowben Publications. 175.
http://digitalcommons.unl.edu/physicsdowben/175

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
For many large molecular adlayers, including a number of organic and metal-organic species, the energy level alignment (of the adsorbate) is dependent on the interfacial electronic structure and the interfacial dipole layer, as has been readily demonstrated for many large molecules, including the metal phthalocyanines. Although copper phthalocyanine (CuPc) is considered a planar molecule with no permanent electric dipole, the molecular orbital alignment of adsorbed copper phthalocyanine is affected by both interface dipoles and molecular orientation. While interactions or charge transfer influence the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap. Indeed, with adsorption on metallic substrates, copper phthalocyanine exhibits an electric dipole as the molecular center copper is not in the same plane as the surrounding ligand and adopts a position that is typically closer to the interface. The changes in the CuPc orientation and dipole make this metal-organic semiconductor a useful adsorbate in studying the effects of dipole interactions at a heterojunction interface.

The obvious way to control interface dipoles is to use a semiconducting ferroelectric: ideally an organic ferroelectric as this minimizes band bending and ensures compositional control of the interface. Organic ferroelectrics have been exploited as components in heterojunction devices, in particular, using the better known copolymers of the ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene) (P(VDF-TrFE)). Organic heterojunction diodes and transistors have been fabricated with the crystalline ferroelectric P(VDF-TrFE). The copolymer poly(vinylidene fluoride with trifluoroethylene) has been used as a component in ferroelectric transistors, both fully organic heterojunctions and hybrid heterojunctions with an inorganic SiO₂ buffer layer integrated state gate over silicon. Both types of transistors exhibit gate voltage dependent hysteresis, indicating the potential of P(VDF-TrFE) copolymers for nonvolatile random access memory devices. Evidence for interface dipole coupling, however, is better demonstrated in the diode geometry, as described here. CuPc is an organic semiconductor and has been used in field effect transistors. Because of the small, adsorption induced, instantaneous dipole, CuPc was chosen for the organic heterostructure with P(VDF-TrFE) in preferential to polyaniline, poly(methoxy(ethyl-hexloxy)-p-phenylene-vinylene), or poly(ethyenedioxythiophene)-polythiene-sulphonic acid. Combined photoemission and inverse photoemission spectra were taken of 2 nm CuPc films (nominally 5 ML) and nominally 5 ML of the P(VDF-TrFE) copolymer films on graphite (roughly 2–3 nm thick films) and Au(111). The choice of substrates was suggested by prior electronic structure studies undertaken on these substrates. The thin films thickness was dictated by a need to ensure layers free of pin holes while still as thin as possible to diminish contributions of final state photoemission effects. The P(VDF-TrFE) thin films were made on Au and graphite substrate surface by using the Langmuir-Blodgett technique, as described elsewhere, and are seen to be highly crystalline on graphite substrates. The CuPc thin films, of 2 nm thickness and greater, were evaporated onto Au and P(VDF-TrFE) substrates in a preparation chamber, vacuum continuous with the spectroscopy ultrahigh vacuum (UHV) chamber, at a rate of about 0.2 nm/min. The photoemission spectra were taken with He I radiation of 21.2 eV, and the photoelectrons are collected along the surface normal. The inverse photoemission spectra were taken using a He I Geiger Müller detector with a CaF₂ window and the electron were incident along the surface normal, in the same UHV chamber.

The combined occupied and unoccupied electronic structures of P(VDF-TrFE) on Au (Fig. 1) and graphite from photoemission and inverse photoemission provides the expected agreement with prior experimental studies and the PM3 semiempirical theoretical calculations. Similarly, for CuPc deposited on Au (Ref. 6) [Fig. 2(a)], there is qualitative agreement with prior photoemission and inverse photoemission experimental data. The positions of the band edges, as determined by photoemission and inverse photoemission at room temperature, suggest that P(VDF-TrFE) is n type, as previously noted, while CuPc is more p type relative to P(VDF-TrFE). These different positions of the valence and conductance band edges make it possible to construct a heterojunction...
The shifts in the band edges for CuPc on P(VDF-TrFE) are more dramatic for the combined photoemission and inverse photoemission spectra of CuPc on P(VDF-TrFE) at temperatures well below room temperature (in the region of 170 K), as seen in Fig. 2. At 160 K there is a strong dipole ordering transition for crystalline copolymer thin films of P(VDF-TrFE),

22,23 while there is a surface phase dipole transition at about 300 K (20 °C).

8,22,23 Although the P(VDF-TrFE) remains ferroelectric, as the temperature range is well below the bulk ferroelectric transition temperature of 80 °C,8 either dipole ordering transition may lead to a change in band offset due to changes in the interface dipoles, as is indicated by the change in the combined photoemission and inverse photoemission spectra shown for CuPc on P(VDF-TrFE) with decreasing temperature [Figs. 2(b) and 2(c)]. This is indirect evidence suggestive of the initial state influence of the interface dipole on the molecular orbital alignment of CuPc, but the influence may not be direct as a change in the CuPc molecular orientation on P(VDF-TrFE) could also occur with temperature, as has been seen for some highly oriented adsorbate organic molecules with intermolecular π-π interactions.24 Effects, such as a shift in the band edges, are seen with increasing molecular cant angles for

As noted, strong interactions or charge transfer to CuPc is believed to decrease the size of the HOMO-LUMO gap for CuPc inferred from combined photoemission and inverse photoemission spectra.6 There is an increase in the HOMO-LUMO gap, as observed for CuPc on P(VDF-TrFE) compared to CuPc on Au. In fact, the similarity of the HOMO-LUMO gap for CuPc on P(VDF-TrFE) and the density of states obtained from theory (Fig. 1) suggests that the electronic structure more closely resembles that of an isolated molecule, not the gap representative of the fully screened adsorbed CuPc molecule on a metal substrate or the gap suggested by DFT (which is typically too small by a factor 2). This tends to suggest weaker interactions and no significant charge transfer as would occur with a conducting substrate such as Au, Ag, or Cu, particularly in the photoemission or inverse photoemission final state.
adsorbed CuPc. Final state effects can be generally excluded as shift in the band edge binding energies is far greater than the change in the HOMO-LUMO gap. Large changes in the charge transfer across the molecular interface are also unlikely as the P(VDF-TrFE) and CuPc are both very stable molecule systems, and such charge transfer would be extramolecular.

Although we cannot ascertain the majority carrier for CuPc thin films alone (i.e., is it n type or p type), the band alignment suggests that a heterojunction diode can be fabricated with P(VDF-TrFE), as has been done for polyanieline and P(VDF-TrFE). Using pretemplated Au bottom electrodes and evaporated Al top electrodes (to ensure Ohmic contacts), such diodes were fabricated using 3–4 nm P(VDF-TrFE) deposited by the Langmuir-Blodgett technique and 4 nm CuPc deposited by vapor deposition (as described above), as seen in Fig. 3. The onset of rectification at 1–4 eV for these diodes is consistent with the molecular orbital alignment inferred from Fig. 1, with P(VDF-TrFE) acting more n type than CuPc.

A dipole interaction between CuPc and ferroelectric material P(VDF-TrFE) is evident in the electric field controlled p-n diode formed by combining these two molecular thin films together. By biasing the diode by ±15 V, hysteresis is seen in the current versus voltage traces at low bias, as seen in the inset of Fig. 3. Application of bias voltages up to ±15 V is more than sufficient to polarize the ferroelectric P(VDF-TrFE) (Ref. 8) and/or flip the dipole direction of P(VDF-TrFE) or both P(VDF-TrFE) and CuPc thin films of this thickness, so this effect is not entirely unexpected. The dipole interaction could affect the diode properties in several ways, which are difficult to distinguish from these measurements. The local electric field due to the P(VDF-TrFE) could also align the CuPc’s dipoles and either change the molecular orientation(s) or change the molecular dipole alignment(s) at the interface, thus leading to a decrease or increase in the barriers to current. Changes in the barrier height could have dramatic changes in the tunneling current, which cannot be completely excluded, as both organic films are quite thin (to exclude final state effects and charging). Alternatively, changes in dipole orientation or dipole alignment could change the molecular orbital alignment of CuPc relative to P(VDF-TrFE), resulting in an effective change in the “band offsets” and the diode characteristics. In the measurements we have undertaken here both effects of the dipole interactions at the organic molecular interface would be similar and lead to hysteretic effects. Simply switching of the ferroelectric dipoles alone is unlikely, as these hysteretic effects would have been observed in resistive layer structures or prior organic heterojunction diodes, which is not the case.

In summary, dipole interactions between CuPc and P(VDF-TrFE) play a key role in our combined photoemission and inverse photoemission spectra, and such interface dipole interactions may be the origin of the electric field “controlled” diodes fabricated from CuPc and ferroelectric P(VDF-TrFE), the latter being a ferroelectric material with a strong intrinsic (reversible) dipoles. This effect was not seen in P(VDF-TrFE) on polyanieline heterostructures.

This work was supported by the National Science Foundation through Grant Nos. CHE-0415421 and CHE-0650453 and the NSF “QSPINS” MSEC (DMR 0213808). The authors would also like to thank Steve Ducharme for his assistance and support and acknowledge helpful conversations with Evgeny Tsybail and Anthony Caruso.