

Different approaches to adjusting band offsets at intermolecular interfaces

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Abstract

We show that at the hetero-molecular interface, the molecular band offsets can be modified by either adjusting the dopant or dopant concentration of one or both molecular layers or by changing the dipole orientation at the intermolecular interface. Photoemission studies reveal the changes in electronic structure and diode devices exhibit conduction properties that are altered in response to changes to the molecular band offsets. As a demonstration, thin film copper phthalocyanine to crystalline ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene) heterojunction diodes, without additional dopants, are compared with doped polyaniline layers on the crystalline ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene).

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1. Introduction

The addition of ligands, doping or alloying necessary for significant chemical shifts of the valence band results in significant changes in the molecular orbitals (in molecules) and band structure (in solids) and can obscure changes in the valence band due to simple charge addition or subtraction. With insulators, doping can lead to a number of interesting complications. Changes in electron localization can lead to dramatic changes in photoemission screening [1] and, as a consequence, photoemission final state effects rather than initial state chemical shifts can dominate the valence band [2]. For wide band gap insulators, doping can lead to the formation of a density of states in the gap (Hubbard bands). These new bands can appear well away from the Fermi level (both above and below the Fermi level) as a result of the on site correlation

energies. These Hubbard bands have been observed with the alkali metal doping of a number of molecular systems with a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [1,3,4]. If the molecular orbitals are sufficiently delocalized, organic conductors provide an avenue for the direct investigation of systematic shifts of the valence and conduction band states as a result of charge transfer.

The role of interface dipoles in heterojunction devices using semiconducting organics (as basic constituent for organic electronics applications) resides on two key issues: charge injection and the molecular band offsets. For many large molecular adlayers, including a number of organic and metal-organic species, the energy level alignment (of the adsorbate) is dependent upon the interfacial electronic structure and the interfacial dipole layer, as has been readily demonstrated for many large molecules [5–7], including the metal phthalocyanines [8]. Charge injection and the dipoles at the electrode interface are surprisingly complex [9] because of interface chemistry. At the interface between the two organic layers, the expected weaker chemical interactions permit better understanding of the molecular band offsets, in spite of usually

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limited understanding of the interface structure. This weak interaction between the metal phthalocyanines and an organic polymer substrate should, in fact, be weaker than the interactions observed at insulating substrate, where the latter interactions are seen to be less strong than for a conducting substrate [10].

The obvious way to control interface dipoles is to use a semiconducting ferroelectric thin films. Organic ferroelectrics are among the best candidates for such studies as with such systems band bending is minimized and one can ensure compositional control of the interface. Organic ferroelectrics have been exploited as components in heterojunction devices, in particular using the better known [11] copolymers of the ferroelectric copolymer poly(vinylidene fluoride with trifluoroethylene) (P(VDF-TrFE)). Organic heterojunction diodes [12,13] and transistors [14,15] have been fabricated with the crystalline ferroelectric P(VDF-TrFE). As the copolymer poly(vinylidene fluoride with trifluoroethylene) is a ferroelectric, transistors, both fully organic heterojunctions [14,15] and hybrid heterojunctions with an inorganic SiO₂ buffer layer integrated state gate over silicon [16,17], 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.

Here we show how it is possible to design heterojunction devices involving organic thin films, of interface electronic properties tunable through doping or voltage control of interface dipoles. We present the reasoning leading to the choice of adequate organic films compatible with (inverse) photoemission studies (or ultra-high vacuum compatible). Such experimental techniques provide insight into the density of states around the Fermi level, and indicate how doping can allow tuning of the semiconducting properties. We present electrical characteristics of the basic device for applications, namely a heterojunction diode, as a confirmation of the expected and desired properties for use in organic electronics applications.

2. Some background on the organic semiconductors compared

Both polyaniline [12,18–21] and copper phthalocyanine (CuPc) thin films [8,13,22–27] (schematically illustrated in Fig. 5) can be produced by vapor deposition compatible with ultrahigh vacuum photoemission. These films can be grown very thin (100 Å or less) and are free of solvent contamination. Such films exhibit a perpendicular resistance of only a few ohms at temperatures as low as 4 K and are thus free of surface charging in photoemission.

Copper phthalocyanine, like polyaniline, is an organic semiconductor and has been used in field effect devices [28,29]. Because of the small, adsorption induced, instantaneous dipole, copper phthalocyanine was chosen [13] for the organic heterostructure with P(VDF-TrFE) as a comparison with polyaniline [12,21] rather than the more conventional organic semiconductors like poly(methoxy(ethyl-hexloxy)-*p*-pheny-

lene-vinylene) (MEH-PPV) [14], or poly(ethyenedioxythiophene)-polystyrene-sulphonic acid (PEDOT-PSS) [15].

Although copper phthalocyanine is considered a planar molecule with no permanent electric dipole [22], the molecular orbital alignment of adsorbed copper phthalocyanine is affected by both interface dipoles [8,13] and molecular orientation [13,22] while interactions or charge transfer influence the highest occupied (HOMO) to lowest unoccupied (LUMO) gap [23]. Indeed, with adsorption on metallic substrates copper phthalocyanine exhibits an electric dipole as the molecular center copper atom is not in the same plane as the surrounding ligand, and adopts a position that is typically closer to the interface [27]. The changes in the copper phthalocyanine orientation and dipole make this metal-organic semiconductor a useful adsorbate for the study of effects of dipole interactions at a heterojunction interface [13]. While high dielectric constant composites of CuPc have been fabricated with P(VDF-TrFE) and like copolymers [30,31], the structures considered here are that of an organic heterojunction in the mesa geometry.

3. Experiment

The polyaniline samples were prepared by vacuum deposition on Au-coated (100 nm) silicon substrates in a preparation chamber vacuum continuous with the spectrometer vacuum systems [12,13]. A SEAS Na getter was used to dope the polyaniline films with sodium, while iodine vapor was used to introduce iodine into the films. The Na 2s to C 1s X-ray photoemission (XPS) intensity ratios show no emission angle dependence following Na deposition, or iodine adsorption indicating the sodium is uniformly distributed in the surface region of vapor deposited polyaniline.

The band positions, relative to the Fermi level, of P(VDF-TrFE) films and pure/doped polyaniline covered P(VDF-TrFE) films, with each polymer about five monolayers thick, were determined through inverse photoemission (IPES) and photoemission (PES), undertaken in the same UHV chamber, as described elsewhere [12,13,20]. The CuPc thin films, of 2 nm thickness and greater, were also evaporated onto Au and P(VDF-TrFE) substrates (the latter also deposited on Au and graphite) in a preparation chamber, vacuum continuous with the spectroscopy ultra-high vacuum (UHV) chamber, at a rate of about 0.2 nm/min [13]. Combined photoemission and inverse photoemission spectra were taken of 2-nm thick CuPc films (nominally five monolayers [28]) and nominally five monolayers thick P(VDF-TrFE) copolymer “bottom” films on graphite (roughly 2–3-nm thick films) and Au(1 1 1).

For the perpendicular transport measurements, mesa structures were fabricated by growing nominally 30 monolayers (about 1.7 nm/monolayer) of P(VDF-TrFE) copolymer films used as substrates for the vapor deposited polyaniline thin films [12,19–21] with polyaniline polymer films about 80 molecules (20 nm) thick, or 2–4 nm of CuPc on 2–3 nm of P(VDF-TrFE). 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. Throughout, the P(VDF-TrFE) thin films were made on Al, Au

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