Controlled $p$-doping of zinc phthalocyanine by coevaporation with tetrafluorotetracyanoquinodimethane: A direct and inverse photoemission study

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$P$-doping of zinc phthalocyanine (ZnPc) with tetrafluorotetracyanoquinodimethane ($F_4$-TCNQ) is investigated with ultraviolet and x-ray photoemission spectroscopy, inverse photoemission spectroscopy, and in situ current–voltage ($I–V$) measurements. The electron affinity of $F_4$-TCNQ (5.24 eV) is found to be equal, within experimental error, to the ionization energy of ZnPc (5.28 eV), consistent with efficient host-to-dopant electron transfer. As a result, the Fermi level in doped ZnPc drops from near midgap to 0.18 eV above the leading edge of the highest occupied molecular orbital and a narrow space-charge layer (~32 Å) is formed at the interface with the Au substrate. In situ $I–V$ measurements show a seven orders of magnitude doping-induced increase in hole current.

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Electrical doping is beginning to be perceived as a means to improve the efficiency of organic devices by enhancing charge carrier injection and lowering drive voltages. Activity on doping is accelerating, yet the majority of these studies remain at the phenomenological level. Few studies have addressed the fundamental doping mechanisms in molecular films. Blochwitz et al. have reported the investigation via ultraviolet photoemission spectroscopy (UPS) of zinc phthalocyanine (ZnPc) doped with the molecular acceptor tetrafluorotetracyanoquinodimethane ($F_4$-TCNQ). The present letter extends this work and reports a study of the electronic structure of films of ZnPc and $F_4$-TCNQ molecules by UPS, inverse photoemission spectroscopy (IPES), x-ray photoemission spectroscopy (XPS) and in situ current–voltage ($I–V$) measurements. A comparative study of the ionization energy and electron affinity of ZnPc and $F_4$-TCNQ is presented. The results confirm that doping occurs via charge transfer from the highest occupied molecular orbital (HOMO) of the host molecule to the lowest unoccupied molecular orbital (LUMO) of the guest molecule. The Fermi level ($E_F$) drops by nearly half of the ZnPc band gap toward the HOMO upon doping, in agreement with the result of Blochwitz et al. Finally, the diffusion of the dopant molecule throughout the molecular film is investigated.

All experiments are performed in ultrahigh vacuum (UHV). The substrates are Si(100) wafers precoated with ~200 Å of chromium and 800 Å of gold (Au). ZnPc (Sigma-Aldrich) is purified via three cycles of gradient sublimation, placed in an evaporation cell in the preparation chamber (base pressure $2 \times 10^{-10}$ Torr), and outgassed. $F_4$-TCNQ (Sigma-Aldrich) is only outgassed in UHV before use. The two organic sources are protected from cross contamination by tantalum shields in contact with a cold finger. The deposition rates are monitored with a quartz-crystal microbalance, assuming a bulk density of 1.5 g/cm$^3$ for the two materials.

The electronic properties of the pure organic compounds are measured in separate experiments on 100-Å-thick films. A fresh 300 Å Au layer is first deposited prior to the deposition of the organic film. ZnPc is deposited at room temperature, while $F_4$-TCNQ is deposited on the substrate cooled to $-20 ^\circ$C to improve the sticking coefficient. All the measurements are done at room temperature. UPS (He I, 21.22 eV and He II, 40.8 eV) is used first to determine the energy position of the HOMO of the organic film with respect to the $E_F$, measured separately on the Au surface, and of the onset of photoemission, which yields the position of the vacuum level $E_{\text{vac}}$ of the film. The ionization energy of the condensed film is defined as the energy difference between $E_{\text{vac}}$ and the leading edge of the HOMO. IPES is used to determine the electron affinity, defined as the energy difference between the vacuum level and the leading edge of the LUMO. The IPES electron beam current density is $\sim 5 \times 10^{-6}$ A/cm$^2$. Spectra are collected from several points on the sample and averaged. The energy scales of the UPS and IPES spectra are aligned by matching the Fermi energies obtained from the Au substrate. The resolutions of the UPS and IPES measurements are 0.15 and 0.45 eV, respectively.

The doped layers are made by coevaporation of ZnPc and $F_4$-TCNQ. The molar doping ratio is set at 0.3% and 3%, close to the ratio used in a recently reported low-voltage light-emitting device. The $I–V$ measurements are collected in situ at room temperature on Au/ZnPc/Au structures consisting of a 400 Å Au metal base, a 3000 Å ZnPc film (undoped or doped), and 350 Å top Au electrodes evaporated through a shadow mask. Doping for the $I–V$ measurements is limited to 0.3% because the current in 3% doped ZnPc is excessively large for our experimental set up. Finally, XPS (Al $K\alpha$ photon line, 1486.6 eV) is performed to investigate dopant diffusion in the ZnPc film.

The energy of the molecular levels of ZnPc and $F_4$-TCNQ determined by UPS and IPES are summarized in Fig. 1. Both compounds display excellent stability under...
photon and electron irradiation for UPS and IPES data collection times in excess of 30 min. The ionization energy of ZnPc is 5.28 eV, in good agreement with the value reported by Blochwitz et al., and the electron affinity is 3.34 eV. The leading edges of the ZnPc HOMO and LUMO are at 0.90 eV below and 1.04 eV above \( E_F \), respectively. The near-midgap \( E_F \) position confirms the intrinsic character of the undoped host film. The ionization energy and electron affinity of \( F_4 \)-TCNQ are 8.34 and 5.24 eV, respectively. These very high values underscore the exceptionally strong acceptor character of the \( F_4 \)-TCNQ molecule. The leading edges of the HOMO and LUMO are at 2.76 eV below and 0.34 eV above \( E_F \), respectively. In that regard, the determination of the position of \( E_F \) vs HOMO and LUMO brings the important question of equilibrium under electron spectroscopy in molecular films. In the present case and for ZnPc, equilibrium is checked following the experiment by depositing a Au layer (15–20 Å) on top of the 100 Å organic film, and verifying that the corresponding Fermi edge and the edge measured on the Au substrate are indeed aligned.

The relevance of the molecular level energies given above in terms of doping levels is another important question. The photoemission process in the condensed ZnPc film leaves a ZnPc cation surrounded by polarized molecules, equivalent to a ZnPc molecule occupied by a hole in the doped matrix. Conversely, the IPES process in \( F_4 \)-TCNQ leaves a molecular anion surrounded by polarized molecules, equivalent to an ionized \( p \)-type impurity. Neglecting the (small) energy associated with lattice relaxation, which switches on too slowly to be included in UPS and IPES, and assuming similar polarization energies in the two molecular solids, the measured HOMO and LUMO levels can indeed be considered as relevant for the estimation of a charge transfer from one molecule to the other. The ZnPc ionization energy (5.28 eV) and \( F_4 \)-TCNQ electron affinity (5.24 eV) are equal within the experimental error, and show, therefore, that the transfer of an electron from the HOMO of the host molecule to the LUMO of the dopant molecule is energetically favorable.

The electronic structure of the undoped ZnPc/Au interface measured by UPS is shown in Fig. 2(a). The diagram results from the analysis of spectra (not shown here) recorded for thicknesses of ZnPc ranging from 0 to 128 Å on the metal surface. The sign of the 0.76 eV interface dipole barrier suggests a (partial) electron transfer from the organic material to the metal. Alternatively, a decrease in the metal work function, resulting from the adsorbed molecules compressing the tail of the electronic wave function at the metal surface, has also been invoked to explain this type of dipole. The molecular levels are flat away from the interface, consistent with most organic-on-metal interfaces investigated to date. \( E_F \) is near midgap at 0.90 eV above the leading edge of ZnPc HOMO, consistent with the fact that ZnPc is basically intrinsic.

The electronic structure of the ZnPc:3%\( F_4 \)-TCNQ/Au interface is shown in Fig. 2(b). The dopant concentration is assumed to be constant throughout the ZnPc film. The interface dipole is reduced by nearly 0.3 eV with respect to the undoped interface. The strong electron attraction by acceptor \( F_4 \)-TCNQ molecules present at the interface increases electron retention at the interface and counters an eventual electron transfer from the organic to the metal. By the same token, it limits an eventual decrease of the metal work function. The UPS spectra show a 0.5–0.6 eV shift of the valence band toward lower binding energy, consistent with the fact that ZnPc is 5.28 eV closer to the HOMO level than in undoped ZnPc, consistent with efficient \( p \)-type doping. Assuming a dielectric constant \( \varepsilon = 3 \) in the organic film, a charge transfer ratio between host and dopant molecules equal to 1 (Ref. 3) and a standard electrostatic model, the depletion width is estimated at 20 Å, which is in fair agreement with
the experimental estimation. The ionization potential of the doped film (5.24 eV) is equal to that of the undoped film within experimental error, suggesting that the growth modes are similar despite the incorporation of the dopant molecules.

The hole injection barriers are 0.90 and 0.8 eV for the undoped and 0.3% doped films (also investigated via UPS) deposited on Au, respectively. This difference, like the one observed with the interface dipole, could come from an increase in electron density at the doped interface with respect to the undoped interface due to the acceptor molecules. This increase reduces the dipole and raises the energy levels of the organic material with respect to the metal $E_F$. The room-temperature $I$–$V$ characteristics measured for Au/ZnPc/Au and Au/ZnPc:0.3%F$_4$-TCNQ/Au are shown in Fig. 3. The current, which corresponds to holes injected from the bottom electrode, is almost seven orders of magnitude larger for doped ZnPc. This difference cannot be explained by the difference in barrier heights. It is the result of doping and increase in film conductivity and tunneling via tunneling. Which of the two dominates is, however, still unclear. The conductivity of the undoped film, assuming space-charge-limited current, is calculated to be $10^{-9}$ S/cm, comparable to a previously reported value. The current through the doped film may still be injection limited, since the conductivity of ZnPc:0.2%F$_4$-TCNQ is reported to be around $10^{-4}$ S/cm.3

Diffusion of dopants in semiconductors is a common problem. To investigate this point with ZnPc, ZnPc(200 Å)/F$_4$-TCNQ(100 Å)/Au structures are grown on Au cooled to $-20^\circ$C. The intensity of the F(1$s$) core level measured at the top of the ZnPc film as a function of time is shown in Fig. 4. Seven minutes after the deposition of the ZnPc film, the F(1$s$) core level is barely visible. Its intensity increases dramatically as the sample warms up to room temperature, while the Zn(2$p$) signal (not shown here) remains unchanged throughout the experiment. The small dopant molecules appear, therefore, to diffuse throughout the host matrix, a situation that does not bode well for device engineering aimed, for example, at interface doping to improve carrier injection without affecting the bulk of the film. In the present case, the diffusion of the dopant molecules could be enhanced by the columnar structure of the ZnPc film. The ability to stop the diffusion is demonstrated with the insertion of a 16-Å-thick Au layer between the F$_4$-TCNQ film and the ZnPc film. In this case, the F(1$s$) core level remains undetected throughout a 4 h experiment and for a ZnPc thickness of only 40 Å. Diffusion can, therefore, be drastically limited, and future investigations will need to focus on more practical interlayers, e.g., amorphous organic films, as well as on the design of larger dopant molecules with smaller diffusion constants.

In summary, we have shown that $p$-type doping of ZnPc with F$_4$-TCNQ results from an efficient charge transfer due to an excellent match between host ionization energy and dopant electron affinity. The Fermi level in ZnPc:3%F$_4$-TCNQ is 0.18 eV above the HOMO level, indicating strong $p$-type character. Doping results in the formation of a narrow space-charge region (<32 Å) at the ZnPc/Au interface. In situ transport measurements show an increase by seven orders of magnitude in current injected in Au/ZnPc:0.3%F$_4$-TCNQ/Au structures due to doping-induced increase in film conductivity and tunneling through the interface barrier. Finally, the dopant molecules are found to diffuse through the host matrix.

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