

Interaction between metals and organic films

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The injection of carriers into organic molecular semiconductors is a key to the operation of organic based devices. In most cases, top metal electrodes are fabricated by evaporating metals onto organic films through a shadow mask. The resulting carrier injection is determined by the chemical and electronic properties at metal/organic interfaces. Despite the technological importance, however, only a few investigations have focused on metal-on-organic interfaces. In this study, near-edge x-ray absorption fine structure (NEXAFS) is employed to investigate chemical interaction upon deposition of various metals on organic films of two different perylene derivatives, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI). The molecular structures of PTCDA and DiMe-PTCDI are shown in Figure 1.

Organic films of ~ 20 nm thickness were grown on S-passivated GaAs(100) surfaces via organic molecular beam deposition in an ultrahigh vacuum chamber and serve as substrates for the subsequent metal deposition. Ag and In were evaporated from Knudsen cells while Cs was evaporated from a dispenser. The thickness of the organic films as well as the metal layers was controlled using a quartz microbalance in the vicinity of the sample. During the evaporation the substrate was kept at room temperature. The fine structure in C-K, N-K, and O-K absorption edges was measured using the PM1 monochromator at BESSY II. The spectra were recorded in the total electron yield (TEY) mode. For the normalization spectra of a Ag film of 100 nm thickness were taken and used as reference spectra.

Figure 2 shows NEXAFS spectra of the C K-shell absorption taken for 20 nm PTCDA films and for subsequent metal deposition on the PTCDA films. The spectra were taken at two different angles of incidence with respect to the substrate surface normal. The spectra corresponding to the 20 nm PTCDA film are characterized by sharp structures in the low photon energy region due to transitions from core levels to unoccupied π^* orbitals, followed by broad features due to transition to σ^* orbitals in continuum states. Peak C1 and C2 can be assigned to transitions from the C atoms in the perylene core into the LUMO and LUMO+1 states, respectively, while transitions involving the anhydride group contribute to peak C3 in the C K-edge spectra [1].

The evaporation of Ag on the 20 nm PTCDA film does not change the lineshape, the relative

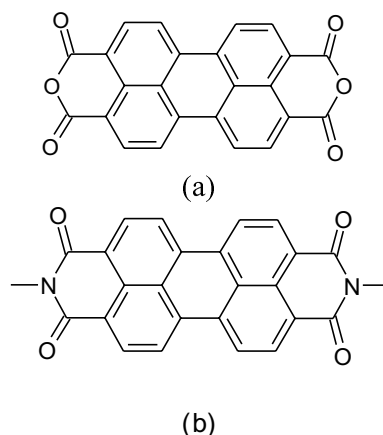


Figure 1. Molecular structure of (a) PTCDA and (b) DiMe-PTCDI.

intensities, as well as the angular dependence. This indicates the formation of an unreactive Ag/PTCDA interface, which is in good agreement with the synchrotron photoemission study by Hirose *et al.* [2].

The situation is different when Cs and In are evaporated on the PTCDA film. Changes in the spectra are apparent in the spectra at 70° , indicating that predominantly transitions to π^* orbitals are influenced by the metal deposition. Upon Cs deposition, all the π^* resonance peaks become broadened, the intensity of C1 and C2 orbitals decreases, the energy position of C3 slightly shifts towards higher photon energy. The spectral change indicates that there is a charge transfer between the Cs atoms and the PTCDA molecules. More dramatic changes are observed upon In deposition. Upon 0.3 nm In deposition, peak C1 completely disappears and a decrease in intensity and a broadening of the peak width are observed. Similar behavior is observed in the O K-edge NEXAFS spectra. Thus, it can be seen that the degree of the charge transfer between the metals and the PTCDA molecules is in the order of Ag (negligible) < Cs < In, and the spectral changes can be understood according to the rate of the charge transfer.

From an element and functional-group analysis of the NEXAFS spectra, the charge transfer mechanism between metals and organic molecules can also be deduced. The survival of the peaks corresponding to the π^* orbitals of the carboxylic C atoms, the absence of strong shifts or new features and the negligible dependence of peak intensities on the metal thickness indicate that the interaction between metals and PTCDA molecules is not accompanied by a covalent bond formation [3]. It is known that a reaction of metals with π^* -conjugated molecules form organometallic-complexes, resulting in cationic metal states, like Cs^+ and In^{3+} [4]. The cationic metal is bound to the entire π^* -electron system of the ring, not forming a covalent bond at a

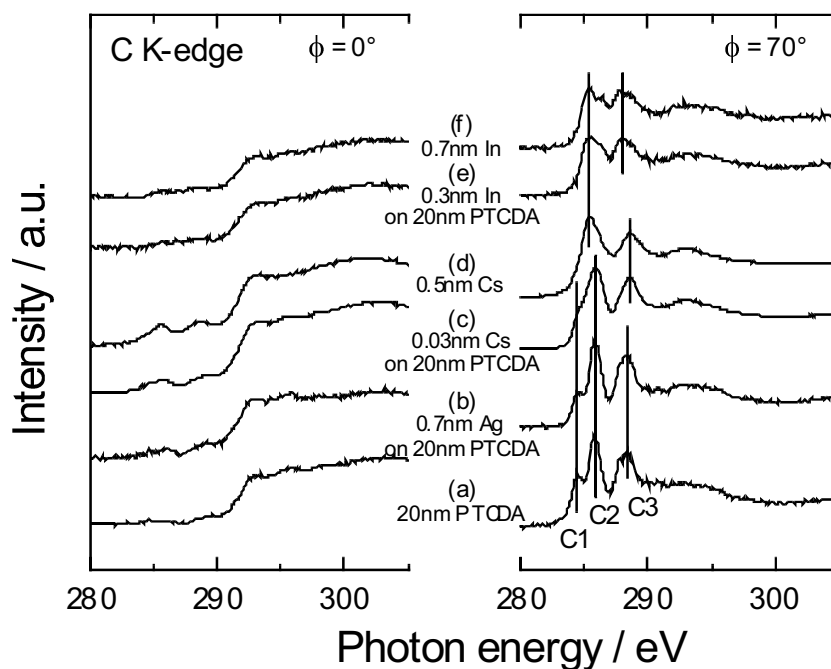


Figure 2. C K-edge NEXAFS spectra at two different (0 and 70°) angles between the incident photon beam and the surface normal for (a) PTCDA film of 20 nm thickness, (b) 0.7 nm Ag deposited on 20 nm PTCDA film, (c) 0.03 nm, (d) 0.5 nm Cs deposited on 20 nm PTCDA film, and (e) 0.3 nm, (f) 0.7 nm In on 20 nm PTCDA film.

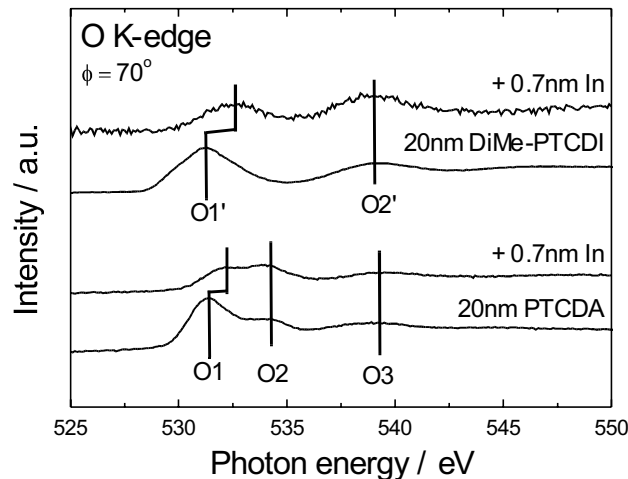


Figure 3. O K-edge NEXAFS spectra for 0.7 nm In deposited on PTCDA and DiMe-PTCDI films 20 nm thickness.

certain molecular site. Wherever in the molecule the charge transfer occurs, the charge should consequently be redistributed over the molecules. Since, as in the case of the highest occupied molecular orbital in the photoemission spectra, the low lying π^* orbitals are most susceptible to any charge redistribution, pronounced changes in the spectra occur in peaks corresponding to transition to the π^* orbitals.

Figure 3 shows O K-edge NEXAFS spectra upon deposition of In on the PTCDA and DiMe-PTCDI films. A main feature in the spectra is that the shift of peaks (O1 and O1') which arise from excitation of carboxylic O atoms to LUMO is bigger for In deposition on the DiMe-PTCDI film. This indicates that stronger charge transfer occurs between In and DiMe-PTCDI than between In and PTCDA. Comparing the molecular structure of the two molecules (Figure 1), it can be deduced that an additional charge transfer occurs via the dimethyl pendant group in the DiMe-PTCDI molecule.

In this report, the chemical interaction upon the deposition of various metals on the PTCDA and DiMe-PTCDI films was investigated using NEXAFS. The charge transfer between metal atoms and organic molecules is found to strongly depend on type of metal and organic molecular structure. The results show that NEXAFS is a suitable tool to probe the degree of the charge transfer.

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