

Chemistry of Metal/Organic Interfaces Revealed by High Resolution Photoemission Spectroscopy

Spectroscopy

G. Gavrilu, M.Gorgoi, D.R.T Zahn

Institut für Physik, Technische Universität Chemnitz, D-09107, Chemnitz, Germany

W. Braun

BESSY GmbH, Albert-Einstein-Straße 15, D-12489 Berlin, Germany.

The chemical and electronic properties of interfaces in organic devices are decisive for charge carrier injection and transport. Metal/organic interfaces can undergo complex and spatially extended chemical interaction. We present here an overview of a detailed study of the interface formation between perylene derivatives (i.e. PTCDA and PTCDI) and low work function metals (i.e. Mg and In). The aim of this study is to understand whether a variation of the molecular structure by different functional endgroups result in different interface properties. The differences are explored via high resolution photoemission spectroscopy followed by a peak fitting procedure of the core levels as a function of metal deposition.

The organic layers were evaporated onto sulphur passivated GaAs substrates followed by metal evaporation with thicknesses monitored by a quartz microbalance. The experiments were performed at the Russian-German beamline at BESSY II using the MUSTANG experimental station. The photoelectron spectra were detected with a PHOIBOS 150 (SPECS) analyser.

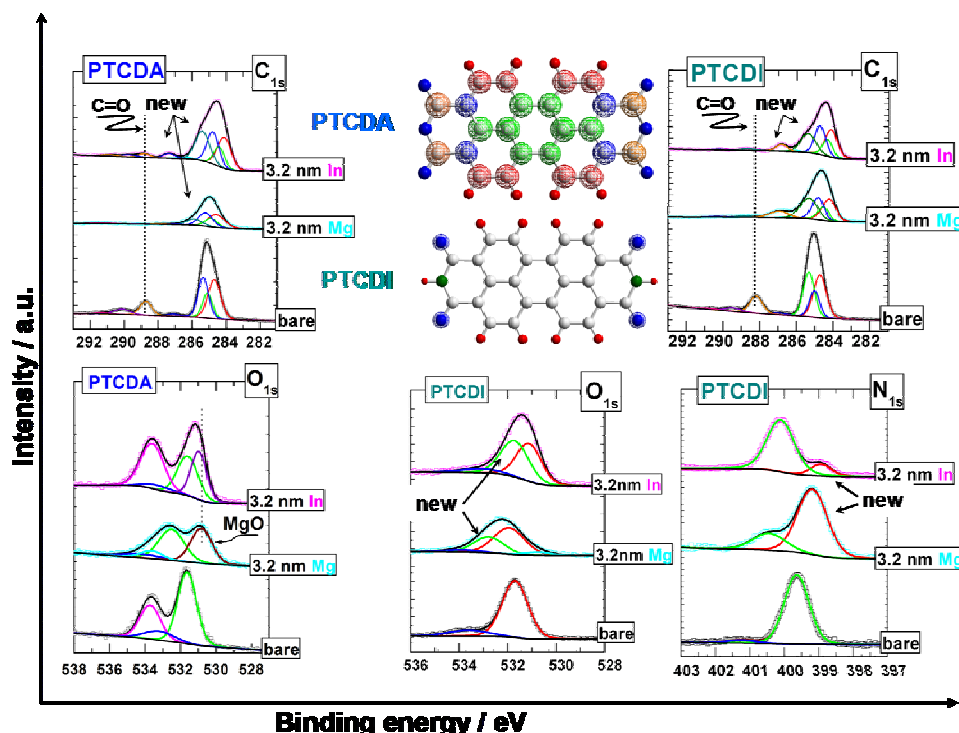


Fig.1. Contribution of the individual peaks to the overall intensities of the C_{1s}, O_{1s} and N_{1s} for bare organic and upon 3.2nm of metal deposition. The individual components for the C_{1s} of PTCDA are assigned according to the colour coding.

Fig.1. shows the C_{1s}, O_{1s} and N_{1s} spectra of about 15nm of PTCDA (left) and PTCDI (middle+right). The C_{1s} spectra consist of two well separated features. The main peak with maxima at about 285.3 eV is resulting from different carbon atoms of the aromatic part while the second peak situated at 288.9 eV and 288.3 eV stems from the carbon atoms of the anhydride and imide

endgroups, respectively. The O_{1s} spectra of PTCDA exhibit a double peak structures with energy separation of about 2.0eV. The low energy peak results from the carboxylic oxygen atoms (C=O) while the high energy peak is derived from the central oxygen atoms (C-O-C). In PTCDI this central atom is replaced by a NH group thus the O_{1s} spectrum will exhibit only the carboxylic contribution.

Strong changes are observed in all the core level emission spectra after 3.2 nm metal deposition. These changes include binding energy shifts, which differ for the various core levels and metals, and appearance of new components. We can conclude that each metal/organic interface has a distinct chemisorptive nature.

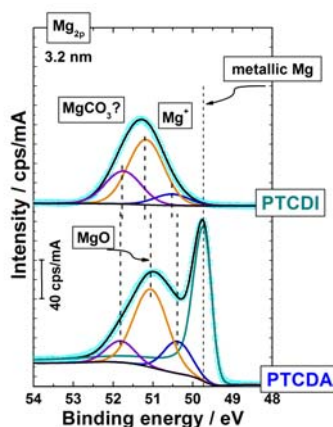


Fig.2. The individual components of Mg_{2p} core level emission at a thickness of 3.2nm on the two distinctive perylenes.

Mg case: In the C_{1s} and O_{1s} spectra of Fig. 1 for the molecules new components are present. In the PTCDA case we observe the following: vanishing of the C=O component, new component at a lower binding energy, and a ratio of the peaks 8:12:4. In the O_{1s} spectra the C-O-C peak vanishes and a new component corresponding to MgO is present. Presence of MgO is observed in the Mg_{2p} core level as well (see Fig.2). These findings are consistent with a strong chemical interaction between Mg and the single bonded oxygen atoms of PTCDA, resulting in MgO detached from the molecule. In the PTCDI case Mg affects again the side group of the molecule (imide group). The new components in the C_{1s} , O_{1s} , N_{1s} and Mg_{2p} spectra indicate that Mg is likely to be involved in “bridging” the carboxylic oxygen with the nitrogen. The main differences between the two molecules are that the oxidation (MgO

formation) prevents diffusion of Mg into the organic film. Strong metallic Mg components are observed beyond 1.6nm Mg coverage onto PTCDA while for PTCDI the metallic component only appears at thicknesses larger than 33 nm. In both cases the perylene core retains its aromatic structure.

In case: In the C_{1s} and O_{1s} spectra of Fig. 1 the changes in the core levels upon In deposition are very similar for PTCDA and PTCDI. The changes observed strongly indicate that In atoms are placed in the neighbourhood of the aromatic rings and/or of the carboxylic oxygen atoms. The new components present in all the core level spectra, including In_{4d} (see Fig.3.) are related with an electron transfer from the metal to the π electron system of the molecule. Again large differences are observed in the degree of the diffusion of the In metal into the organic film.

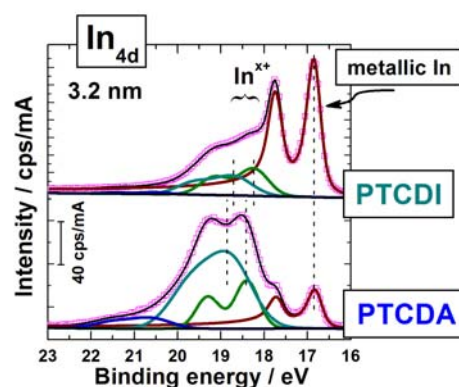


Fig.3. The individual components of In_{4d} core level emission at a thickness of 3.2nm on the two distinctive perylenes.

Acknowledgements

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