

## Electronic Properties and Chemistry of 3,4,9,10- Perylenetetracarboxylic dianhydride (PTCDA) upon Mg Deposition

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Metal/organic/semiconductor hybrid structures may have a technological impact on the development of the high frequency Schottky diodes for telecommunications. The main parameters, which determine the operating range of a Schottky diode are the critical frequency and the operating voltage, both being determined by the properties of the organic/semiconductor and metal/organic interfaces. The operating voltage of such devices is closely related with the effective transport barrier heights at the interfaces. An understanding of the mechanisms responsible for the modification of the barrier height can be achieved by a detailed investigation of the electronic properties at the interface.

We present a detailed study of the interface formation between PTCDA (see Figure 1) and Mg using high resolution PES and NEXAFS

The organic layer is evaporated onto the sulphur passivated GaAs substrates followed by Mg evaporation with the thicknesses monitored by a quartz microbalance. The experiments were performed at the Russian-German beamline at Bessy II using the MUSTANG spectroscopy chamber. The photoelectron spectra as well as the NEXAFS spectra were detected with a PHOIBOS 150 (SPECS) analyser. The C1s NEXAFS raw data were divided by the current of the incident X-ray beam, background subtracted and normalized to the absorption step at 315eV photon energy.

The evolution of the C1s, O1s and Mg 2p core levels as a function of Mg coverage on PTCDA is shown in Figures 2(a)-(c). The C1s core level of the bare PTCDA consists of two main components. The high binding energy component (C<sub>2</sub>) corresponds to the anhydride group while the low binding

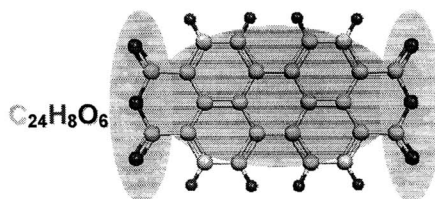


Figure 1. Molecular structure of 3,4,9,10-Perylene tetracarboxylic-dianhydride

energy component ( $C_1$ ) corresponds to the perylene core. More over, this peak has a clear asymmetry due to the different carbon environments within the aromatic system. For the  $O_{1s}$  core level the two components stem from different oxygen environment within the carboxylic group,  $O=C$  ( $O_2$ ) and  $C-O-C$  ( $O_1$ ), respectively.

At low Mg coverage (0.1nm) the intensity of  $C_1$ ,  $C_2$ ,  $O_1$  and  $O_2$  components decreases significantly compared to the spectrum of bare PTCDA. The  $Mg_{2p}$  signal consists of a single high BE component. These observations are consistent with a strong chemical interaction between Mg and the carboxylic group of PTCDA resulting in either Mg-oxide complexes or Mg attached to the molecule. The perylene core of the PTCDA molecule retains its original structure as can be seen from the  $C_1$  component which remains unchanged except for an energy shift of about 0.7eV towards lower BE. This shift can be attributed to a metal-induced polarization. At low coverage reacted molecules are surrounded mostly by unreacted ones experiencing strong polarization resulting in a decrease in binding energy.

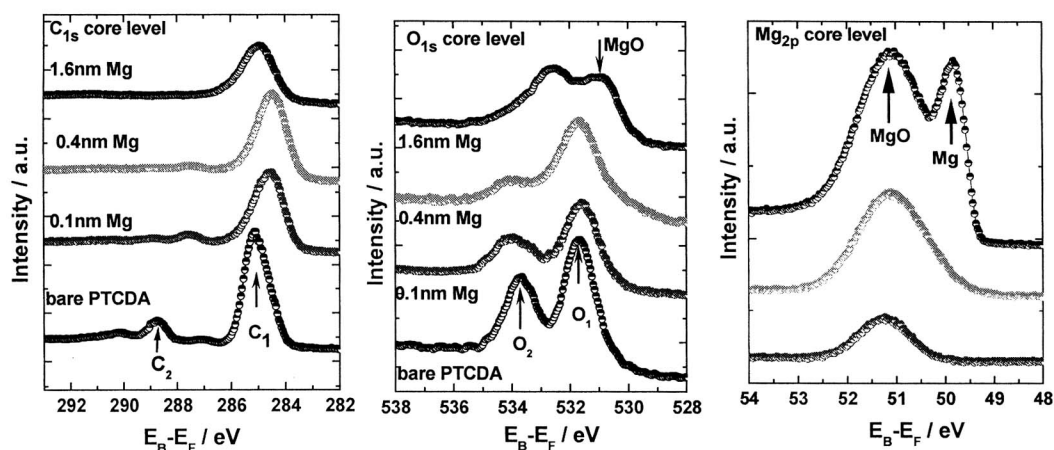


Figure 2. (a)  $C_{1s}$ , (b)  $O_{1s}$  and (c)  $Mg_{2p}$  core levels as a function of Mg coverage on PTCDA

With increasing the Mg coverage (0.4nm) the  $C_2$  and  $O_2$  components are decreasing significantly in intensity. Moreover, this observation is accompanied by the increase in intensity of the  $Mg_{2p}$  core level.  $C_1$ , on the other hand, increases in intensity. We interpret this observed signal changes as a redistribution of charges in the molecule,

or in other words, as an increase in electron density on the perylene core due to the reduction of charge in the carboxylic group.

For coverage above 1.6nm of Mg, the C<sub>2</sub> component of the C1s core level vanishes and a new component in O1s core level being attributed to Mg-O complex arises. This observation may support the idea of formation of Mg-O complex detached from the molecule. The shift towards higher BE energy of the C<sub>1</sub> component may correspond to metal-induced polarization. When a large fraction of PTCDA is reacted the polarization decreases and the core level shifts back towards high BE. Moreover, a metallic Mg 2p component appears indicating that the chemical reaction is limited to the first few layers.

Figure 3 presents high-resolution C1s-NEXAFS measurements as a function of Mg coverage. With the first layer of Mg drastic changes are observed that can be interpreted as a partial occupation of the lowest unoccupied molecular orbital. These changes continue for high Mg thicknesses, the peaks corresponding to  $\pi^*$  transition start to be diminished, this indicates a change in the structure of the molecule.

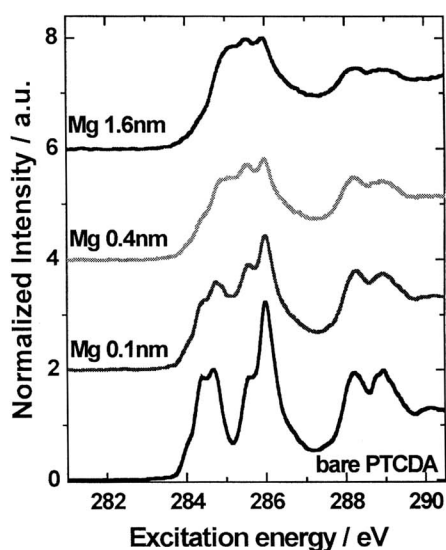


Figure 3. C1s NEXAFS - fine structure region measured as a function of Mg coverage on PTCDA

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