High resolution photoemission spectroscopy: Evidence for strong chemical interaction between Mg and 3,4,9,10-perylene-tetracarboxylic dianhydride

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The interface formation between Mg and 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) was investigated by high resolution soft x-ray photoemission spectroscopy. The interface chemistry was obtained after fitting the core level spectra as a function of Mg thickness. At the initial stage of deposition, a strong chemical interaction between Mg and the single bonded oxygen atoms of PTCDA is observed leading to the formation of MgO and a modified organic molecule. Based on the experimental evidence, the molecular structure of the modified molecule is proposed. Moreover, the changes observed in the measured C\textsubscript{1s} core level spectra are supported by density functional theory calculations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2356305]

The interface formation between metals and organic semiconductors is a key factor in nearly all aspects related to the performance of the organic based devices. The charge carrier injection process is mainly controlled by the energy level alignment at the interfaces, and this can be dramatically affected by the chemistry at the interfaces.

3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) is a model prototype for large \pi-conjugated molecules, belongs to the perylene derivative family and is a planar molecule that consists of two electron-withdrawing anhydride (O—C—O—C) groups attached to the opposite ends of a perylene core (for structure see Fig. 1). Prepared as a highly ordered thin film, it is a potentially useful n-channel material in organic field effect transistors\textsuperscript{1} and hybrid Ag/PTCDA/GaAs\textsuperscript{2} junctions.

Studies of Ag, Au, Al, Ti, Sn, and In (Ref. 3) depositions onto PTCDA layers revealed that reactive metals such as Al, Ti, Sn, and In react with the anhydride groups giving rise to electronic states in the band gap. These “chemically induced” gap states strongly affects the conductivity by allowing charge carriers to tunnel through the junction in sharp contrast with the blocking character typically observed in junctions made by nonreactive noble metals. Still there is a lack of information specifically discussing the chemistry of the interface.

Soft x-ray photoemission spectroscopy (SXPS) is a technique with high sensitivity to the changes of the chemical environment and charge redistribution. High resolution SXPS measurements together with sophisticated core level line shape analysis can deliver a deeper insight into the physics and chemistry at metal/organic interfaces.

Here, we report high resolution SXPS investigations of Mg adsorption on PTCDA, with the metal thickness ranging from the submonolayer regime to thick metallic overlayers. The chemical properties of this interface were obtained after fitting the C\textsubscript{1s}, O\textsubscript{1s}, and Mg\textsubscript{2p} core level emission spectra as a function of Mg thickness. Strong chemical interaction between Mg and the anhydride groups, in particular, with the center oxygens, takes place leading to the formation of MgO and a modified molecule.

The organic layer was grown onto sulfur-passivated GaAs(100) substrates by organic molecular beam deposition in an ultrahigh vacuum chamber with 1×10\textsuperscript{-10} mbar base pressure. The passivation procedure of the GaAs substrate is described elsewhere.\textsuperscript{2} The molecular material was obtained from Syntec GmbH Woflen and prepurified by double sublimation prior to deposition by thermal evaporation. The organic material and the metal were evaporated from Knudsen cells kept at 280 °C for PTCDA and at 375 °C for Mg. The organic films were deposited at a rate of approximately 0.2 nm/min up to a total thickness of 15 nm followed by metal evaporation at a rate of about 2 nm/min. The thicknesses were monitored by a quartz microbalance. The experiments were performed at the Russian-German beamline at BESSY using the MUSTANG experimental station, equipped with a PHOIBOS 150 (SPECS GmbH) electron energy analyzer. The overall experimental resolution was 70 meV for the Mg\textsubscript{2p}, 85 meV for the C\textsubscript{1s}, and 140 meV for the O\textsubscript{1s} data for photon energies of 100, 355, and 585 eV, respectively.

Figure 1(a) displays the C\textsubscript{1s} core level spectra for bare PTCDA and after different Mg coverages. The C\textsubscript{1s} spectra show complex peak structures. The contribution of the individual carbon sites is evidenced by a careful fit and assigned according to the color coding [see left side of Fig. 1(a)]. The three components having smaller intensities are also present and they are attributed to shake-up satellites. The area ratio of the peaks are in good agreement with the expected values (8:4:8:4) when the shake-up areas are taken into account. Together with the bare C\textsubscript{1s} core level, the results of the curve fit analysis for three different Mg thicknesses are displayed in the same figure. The main lines (C—H, C—C, C—C═O, and C═O) were curve fitted with Voigt profiles with a constant Lorentzian linewidth of 80 meV and variable width for the Gaussian contribution.

For all Mg thicknesses, strong changes in the core level spectra are apparent when compared to the spectrum of bare PTCDA. These changes include binding energy shifts, which
are significantly different for the various atoms, and the appearance of new features.

The nature of the reaction can be followed in more detail in Fig. 1(b), where the evolution of intensity and relative area resulting from the peak fitting analysis is presented. Upon deposition of 0.2 nm Mg all the components of the C1s core level are significantly decreased in intensity. The strongest decrease is observed for the high binding energy (BE) components indicating that the presence of Mg predominantly affects the carboxylic carbon (C==O) or side of the molecule. Moreover, in the C1s core level, two new components at 285.35 eV (C1) and 287.45 eV (C2) evolve on the low BE site of the C==O component. Component C1 is present in the spectrum up to thicknesses larger than 13 nm, while component C2 is significantly diminished and vanishes at thicknesses above 3.2 nm. This component indicates that at the initial stage of the reaction, some molecules are in a higher oxidation state because of the formation of new bonds. Nevertheless, it is important to notice that if we integrate the area of these two peaks and calculate the total area, we find that this is very close to the stoichiometric ratio of 5:1 between the perylene ring (20) and functional group carbon atoms (4). Therefore, the C1 and C2 structures can be attributed to intermediate phases derived from the carboxylic carbon at 289.5 eV.

In the low BE region, the spectra of C1s show mainly the same spectral features for all Mg coverages but with drastically different intensities and significant broadening. After the initial decrease in intensity upon deposition of 0.2 nm Mg, the intensity of the aromatic carbon slightly increases at coverage of 0.4 nm. We interpret the signal changes observed as a result of a redistribution of charges in the molecule. For thicknesses larger than 0.8 nm, no significant changes are observed except for the attenuation of the intensity of all components as a function of Mg coverage. Moreover, the area ratio of the C1s peaks in the perylene core remains constant above 0.8 nm Mg thicknesses.

The remaining $\pi \rightarrow \pi^*$ shake-up satellites in the C1s spectra, [see left of Fig. 1(a)], reveal that the organic component preserves its aromatic structure. Therefore, one main finding from the C1s fit analysis is that the modified organic molecule consists of the same number of carbon atoms as in PTCDA.

The evolution of the O1s and Mg2p spectra as a function of Mg thickness is presented in Figs. 2(a) and 2(b), respectively. The evolution of the intensities for different Mg coverages is summarized in Fig. 2(c) for the O1s core level and in Fig. 2(d) for the Mg2p core level. The O1s emission for bare PTCDA consists of two distinct components O==C (low BE) and C–O–C (high BE). The small intensity at higher BE than the O==C component stems from a $\pi \rightarrow \pi^*$ shake-up satellite. The first major change observed in the O1s core level at low Mg coverage (0.2 nm) is the significant decrease in intensity of the O1s components compared to the spectrum of bare PTCDA. The second major change is the shift of the high BE component towards even higher energies. This change is another indication that a chemical interaction occurs and the component predominantly affected is the C–O–C one. At the same coverage of 0.2 nm, the Mg2p signal can be fitted using three components: one component at 50.45 eV (Mg1), one strong component at 51.20 eV (Mg2), and a high BE component at 51.95 eV (Mg3).

However, in the O1s spectra at a coverage of 1.6 nm, corresponding to an equivalent of about 4 ML of Mg, two new strong features, one at a BE of 530.9 eV (O1) and another at 533.4 eV (O2), are present while the C–O–C component has vanished. At the same coverage one more component at 49.8 eV assigned to metallic Mg (Ref. 4) occurs in the Mg2p core level emission.

Literature data analysis5 show that BE values of 51.2 eV for (Mg2p) and 530.6 (O1s) indicate the presence of oxidized magnesium. Similarly, films containing relatively large...
amounts of magnesium hydroxide Mg(OH)$_2$ and/or MgCO$_3$ species are characterized by the appearance of the 51.9±0.4 eV (Mg$_{2p3/2}$) and of the 533.1±0.4 eV peak (O$_{1s}$), respectively. With these details we can easily assign the components Mg$_2$ and O$_1$ to MgO. The Mg$_2$ and O$_2$ components have a fairly broad full width at half maximum (FWHM) indicating a rather undefined environment, and a hydroxide or carboxide environment of magnesium cannot unambiguously be assigned. Consequently, the high binding energy components may be attributed to the absorption of isolated Mg atoms on different sites of the organic layer: near hydrogen atoms or/and between the molecular planes. The component at 50.45 eV, labeled Mg$_{3}$, might be due to a hydrated Mg (1+) or a suboxide species.

At 1.6 nm Mg it seems that the reaction is almost complete. Larger Mg deposition decreases the intensities of the O=C component of the O$_{1s}$ core level and of the Mg$_2$ (MgO) of the Mg$_{2p}$ core level in agreement with the appearance of the strong metallic Mg component. However, the presence of the Mg$_2$ and O$_2$ and their increase as a function of Mg coverage suggest that some of the Mg atoms may still adsorb near hydrogen atoms and/or between the molecular planes. The presence of MgO obviously prevents diffusion of Mg into the organic film. On top of the reacted layer, the morphology of metallic Mg overlayer is islandlike as revealed by the persistence of the C$_{1s}$ main peak of the O$_{1s}$ (O=C) peak as well as of the oxidized Mg up to a coverage of at least 13 nm.

Besides the changes in the spectral line shape, shifts in binding energies were also observed. Initially gradual shifts of ∼0.7 eV for C$_{1s}$, in particular, of the perylene core components, and of ∼+0.25 eV for O$_{1s}$ (C–O–C) are observed. After the reaction is initiated by the presence of Mg the C–O–C bond is strongly affected, most probably broken. Due to these changes the charges will redistribute over the entire molecule but mainly over the perylene core. This hypothesis agrees very well with the increase in intensity of the aromatic carbon at a coverage of 0.4 nm Mg. An additional contribution of screening due to the photogenerated core hole upon deposition of Mg, however, cannot be excluded. At thicknesses larger than 0.8 nm, the C$_{1s}$ and O$_{1s}$ features shift towards higher binding energies by ∼+0.6 and ∼+1 eV, respectively. Above the same thickness (0.8 nm) the C–O–C component vanishes. This is an indication that the reaction between Mg and PTCDa is almost complete with the apparent formation of MgO and a modified organic molecule with different properties than PTCDa. As a result of MgO formation, the C$_{1s}$ and O$_{1s}$ photoemission lines cannot be efficiently screened due to the charge transfer consequently inducing the shift towards higher binding energies. We notice that about the same thickness, the Mg$_3$ component decreases dramatically.

Moreover, the formation of MgO is also supported by the valence band measurements. Figure 3(a) shows the valence band spectra of bare PTCDa (bottom), of 0.8 nm Mg on a 15 nm film of PTCDa (middle), and of the MgO, the latter being measured using a He discharge lamp (21.22 eV) (top). An assignment of the valence band features of pristine PTCDa can be found elsewhere. The individual peak at ∼2.5 eV corresponds to the highest occupied molecular orbital (HOMO) and is distributed over the perylene core, while the feature at ∼6 eV is mainly attributed to the O$_{2p}$ derived molecular orbitals. By comparison with the valence band spectra corresponding to MgO, the change in the HOMO and of the feature at ∼6 eV is explained by the strong intermixing between Mg atoms and the organic material resulting in MgO, charge transfer to the molecule, and a modified organic molecule. Moreover, the formation of MgO is consistent with the delay of the appearance of the density of states at the Fermi level due to metallic Mg.

On the basis of the changes observed in the core levels, the molecular structure of the modified “new” molecule is proposed. The modified molecule consists of two quinone (O=–C–O=) groups attached to the opposite ends of a perylene core. The structure of the new molecule is shown in Fig. 3(b). It is worth mentioning that studies of a similar π-conjugated organic molecule (e.g., acenaphthenquinone) via high resolution XPS were already reported.

Consequently, density functional theory (DFT) calculations for a single molecule using the GAUSSIAN 98 package [B3LYP method, and 6-311-G (d,p) basis set] were applied to the C$_{1s}$ core levels of the pristine PTCDa and of the modified molecule. They are displayed and compared in the Fig. 3(b). The simulated C$_{1s}$ was obtained by Gaussian broadening of each calculated energy position of C$_{1s}$ (vertical bars) with a FWHM of 0.84 eV. The calculated data support the experimental results, namely, the C–O component of the C$_{1s}$ core level shifts towards lower binding energies.

In summary, we have employed high resolution SXPS spectroscopy to study the chemistry and electronic structure of the Mg/PTCDa interface. A detailed analysis of the evolution of C$_{1s}$, O$_{1s}$, and Mg$_{2p}$ core levels indicates a strong chemical interaction between Mg and the single bonded oxygen atoms of PTCDa. The interaction leads to the formation of MgO and a modified organic molecule with different properties than PTCDa. The formation of MgO preferentially occurs in the initial stage of Mg deposition, followed by the accumulation (clustering) of Mg atoms on top of the reacted layer. It appears that the formation of MgO prevents diffusion of Mg into the organic film. Simulations of the C$_{1s}$ core level of the modified molecule also support the measured spectra.

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