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Organic Electronics 3 (2002) 73–79

Organic Electronics

www.elsevier.com/locate/orgel

Photoelectron spectroscopic studies of thin PTCDA layers on $TiSe_2$

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Received 15 March 2001; received in revised form 31 January 2002; accepted 31 January 2002

Abstract

Thin films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) grown on $TiSe_2$ have been studied by means of angle-resolved photoelectron spectroscopy and low energy electron diffraction. It was found that PTCDA forms an ordered 3D crystal, commensurate with the chemically inert metallic substrate. Energy shifts in the photoemission spectra are interpreted in terms of screening effects, interface dipoles and band bending in the thin films. The final- and initial state effects have been estimated separately.

PACS®: 61.14.Hg; 61.66.Hq; 71.20.Rv; 79.60.Fr

Keywords: Low energy electron diffraction; Photoelectron spectroscopy; Growth; Organic semiconductor; PTCDA; Titanium diselenide

1. Introduction

Over the last decade conducting and semiconducting organic materials have attracted increasing interest. One reason is the possible incorporation of conducting polymers and organic molecular crystals in optical and electronic devices, such as organic light emitting diodes or solar cells. These devices are expected to be commercially competitive due to low fabrication cost and absence of critical demands for single crystal- or lattice matching substrates. Furthermore, organic chemistry provides possibilities to substitute single atoms or groups of atoms in a given molecule, which opens possibilities to tune the optical and the electronic transport characteristics. Among the drawbacks, in comparison to inorganic materials, the most serious one is instability with respect to elevated temperature. All future applications require solid knowledge about the organic materials of interest.

The molecule 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) has been in the researchers' field of vision for some time and thin films of PTCDA have become favourite models for spectroscopic investigations. The electronic structure of PTCDA is fairly well known [1], and the layered growth of the planar molecules makes it possible to prepare fairly well-ordered thin films of PTCDA on different substrates. On weakly interacting

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1566-1199/02/$ - see front matter
PII: S1566-1199(02)00035-6

substrates the quadrupole moment of the PTCDA molecules tends to order them in an in-plane herringbone structure [2].

We have previously investigated the electronic and structural properties of PTCDA layers on Si(1 1 1):H, which is an extremely passive semiconductor surface [3]. In the present study we have chosen $TiSe_2$ as a substrate. It is a layered compound that is semimetallic at room temperature [4] and with very weakly interacting layer planes, which means that a surface that is obtained by cleavage should be non-reactive. Since previous studies of metal/PTCDA junctions involving traditionally inert metals like Ag have revealed reacted interfaces [1], the $TiSe_2$/PTCDA combination provides an attractive alternative from this point of view.

2. Experimental

The experiments include angle-resolved photoelectron spectroscopy (ARUPS) and low energy electron diffraction (LEED). The measurements were performed in UHV ($\approx 1.5 \times 10^{-8}$ Pa). For the photoemission studies we used a VG ADES 400 spectrometer, operated at an energy resolution of 0.1–0.2 eV, and the excitation was made with HeI (21.2 eV) and HeII (40.8 eV) resonance lines. Since the HeI and HeII spectra are qualitatively very similar, except for a more pronounced background in HeI, only HeII spectra are presented here. For the LEED experiments an apparatus with three grid optics was used, and the beam current was <1 μA. The $TiSe_2$ crystal was glued with silver epoxy on a transferable sample holder. On the front side a lever was glued, to be knocked off for cleaving the crystal. The cleaved $TiSe_2$ surface is Se-terminated with a hexagonal unit cell with $a = 3.54$ Å [5]. In a preparation chamber connected with the analysis chamber the PTCDA was evaporated from an aluminium oxide crucible at an estimated temperature of 250 °C. A quartz crystal oscillator, mounted next to the substrate, was used to monitor the amount of deposited PTCDA. The deposition rate was about 3 Å (i.e. 1 monolayer (ML)) per minute. During growth the substrate was kept at room temperature.

3. Results and discussion

3.1. LEED

The cleaved $TiSe_2$ substrate showed a good quality LEED pattern without any sign of surface reconstruction, and the photoemission spectra were in good agreement with previously published data [6,7]. In particular a clear Fermi level onset was observed at an emission angle of 30° (Ti 3d band), confirming the metallic character. After evaporation of PTCDA a new LEED pattern appeared, similar to that observed on PTCDA/MoS_2 [8]. An image of the LEED pattern together with a schematic drawing is displayed in Fig. 1, where the electron energy was ~13 eV and the PTCDA coverage was approximately 2 ML. The pattern shows that PTCDA grows in ordered domains with six equivalent orientations relative to the substrate. For each in-plane symmetry direction of the substrate there are two domains, rotated ±8.9° with respect to each direction. The spots in the two inner circles in the LEED pattern, corresponding to (0,1) and (1,0) diffracted beams, are not visible due to the glide plane symmetry in this herringbone structure. From the substrate and the PTCDA LEED patterns, we can calculate that the overlayer has a nearly orthogonal unit cell 19.7 × 12.4 Å (244 Å^2), related to the substrate by a superstructure matrix,

$$\begin{bmatrix} a' \\ b' \end{bmatrix}_{\mathrm{PTCDA}} = \begin{bmatrix} 6 & -1 \\ -3/2 & 4 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}_{\mathrm{TiSe_2}}.$$

The rational numbers in the matrix show a commensurate relation between overlayer and substrate. As a consequence of the commensurability some (2,1) diffraction spots from different domains coincide, as indicated in Fig. 1. Thus only 18 such reflections are seen instead of 24. From the LEED pattern we conclude that each PTCDA domain is in registry with the substrate as indicated in Fig. 2.

The pattern was visible even for films thicker than 100 Å, although less sharp and with a higher background. This fact together with the photoemission results discussed below, implies that ordered growth is maintained far beyond monolayer coverage. By comparison of photoemission spectra recorded before and after the LEED studies, we

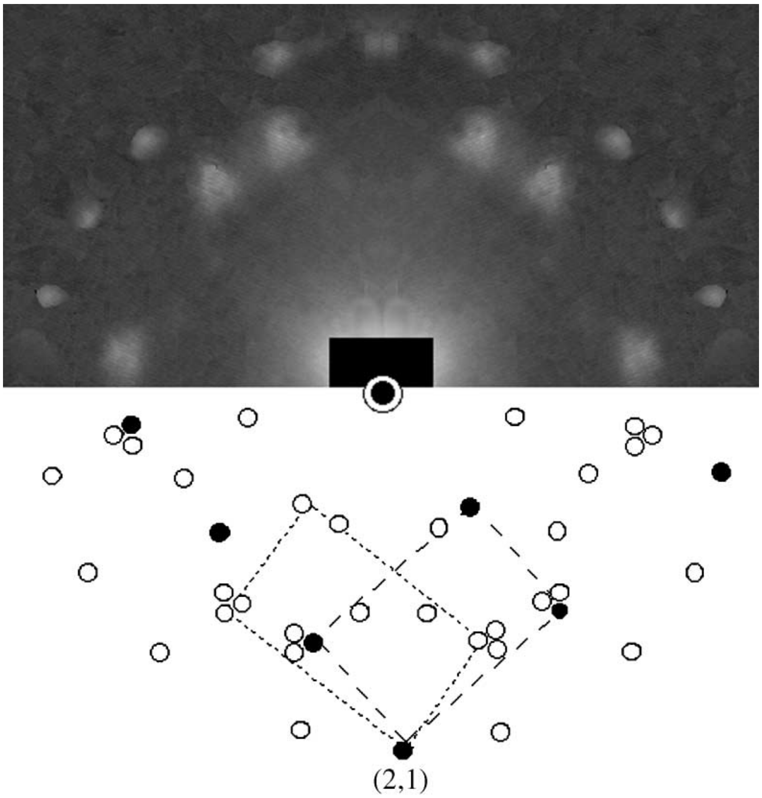

Fig. 1. A photograph (top) and a schematic drawing (bottom) of the PTCDA/TiSe$_2$ LEED pattern. The energy of the electron beam was ~13 eV and the thickness of the PTCDA film was approximately 2 ML. The diffraction spots of one domain orientation are enhanced for clarity.

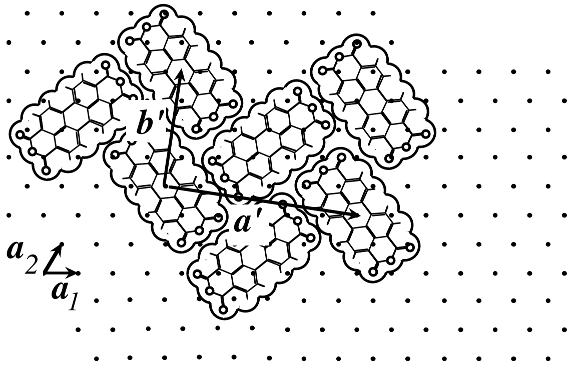

Fig. 2. Schematic drawing of the real space geometry in one of the six symmetry-equivalent domains of PTCDA molecules situated on the TiSe$_2$ surface.

found that the LEED beam did not deteriorate the layers.

3.2. UPS

The intensity of the photoemission spectra from the PTCDA films has a pronounced angular dependence, as is shown in Fig. 3. This is due to the directional characteristics of the molecular orbitals and shows that the molecular structure is well-ordered. Peak “p” has a maximum in intensity at approximately 30° emission angle (defined as the angle between the surface normal and the direction of emitted electrons), in agreement with [9], indicating that the molecules are lying flat on the surface. There is also a small (60 meV), but clear shift of the HOMO orbital towards higher binding energies with increasing emission angle from 0° to 30°. A similar shift has been observed earlier for PTCDA on hydrogen-passivated Si(1 1 1), in which case a layered growth was reported [10].

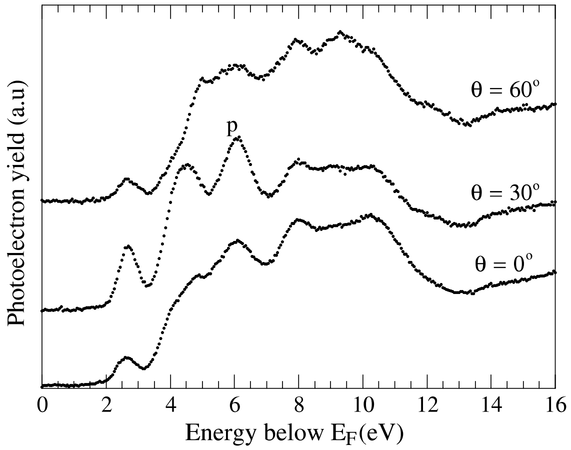

Fig. 3. Angular-resolved photoemission spectra from a 100 Å thick layer of PTCDA on $TiSe_2$ at different emission angles θ (plotted with vertical offsets for clarity). The photon energy was 40.8 eV and the angle of incidence 45°.

This angular dependence is interpreted as a surface effect where holes created in the topmost layer are less screened than holes created in underlying layers. According to [9], the direct emission at 60° emission angle is very weak and the intensity of the HOMO peak is here largely due to scattered electrons from deeper layers. Thus, the relative contribution from the surface layer cannot be expected to increase in the "normal" way at large emission angles.

A series of photoemission spectra (photon energy 40.8 eV) from increasingly thicker PTCDA layers on $TiSe_2$ are shown in Fig. 4. As pointed out in previous studies [1], the two peaks with highest kinetic energy (smallest binding energy) are associated with molecular orbitals located on the perylene core of the PTCDA molecule, and the lower lying peaks are connected with orbitals concentrated on the anhydride groups. The HOMO level is located approximately 1.8 eV below the Fermi level for 1 ML coverage. To remove substrate contributions in the 1 and 2 ML spectra, the substrate spectrum was subtracted with a scaling factor adjusted to remove the Fermi level step in the difference spectra. We see that with increasing coverage the spectra appear to shift towards higher binding energy, and the features become narrower. The shift is illustrated in Fig. 5(a) where the kinetic energy relative the vacuum level of the most prominent peak in the valence band (marked "p" in Fig. 4) is plotted as a function of the number of deposited molecular layers. The final shift of the spectrum is approximately 0.8 eV. Uniformity of the grown layers was estimated from the attenuation of substrate-related emission. At 21 eV kinetic energy (relative the E_F) we obtained a mean free path of approximately 15 Å in the thickness range up to approximately 20 Å (6 ML). This value is consistent with tabulated mean free path data for semiconductors [11]. The fact that the peaks become narrower with increasing thickness directly suggests that the probed region becomes electronically more uniform. The thickness range over which this uniformity is approached and the attenuation of the substrate signal indicates that the PTCDA does not form tall islands, but follows a

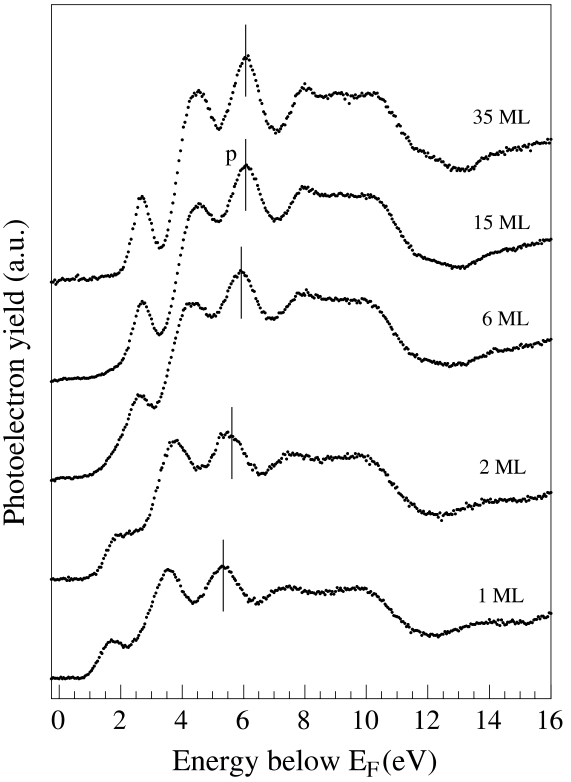

Fig. 4. Thickness dependence of angular-resolved photoemission spectra from PTCDA on a $TiSe_2$ substrate (plotted with vertical offsets for clarity). The photon energy was 40.8 eV, the angle of incidence 45°, and the emission angle 30°.

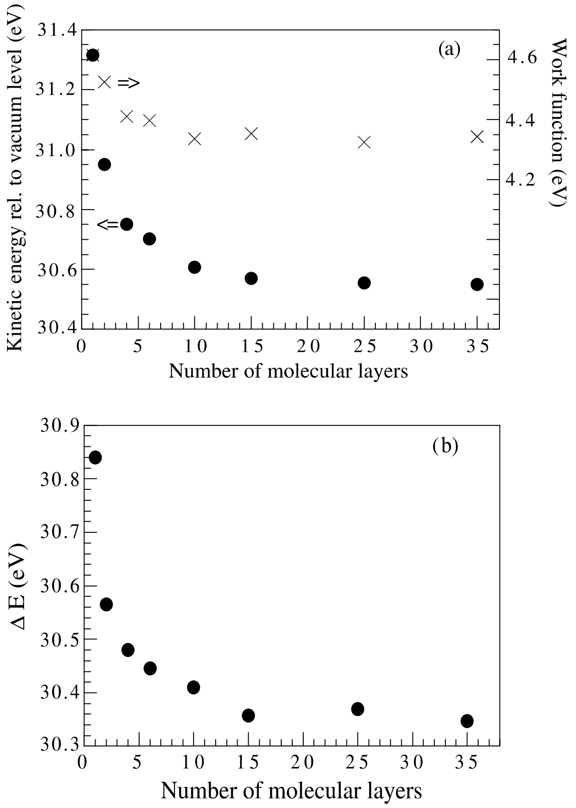

Fig. 5. (a) The kinetic energy of peak "p" from the PTCDA/ $TiSe_2$ photoemission spectrum shown in Fig. 4 (•), and the work function (×), as a function of the number of molecular layers. (b) The difference in energy (ΔE) between the peak marked "p" in the valence band spectra (Fig. 4) and the work function cut-off.

layer by layer growth mode yielding ordered domains with quite uniform height. We thus conclude that the subsequent layers are inequivalent, and therefore give rise to a gradual shift of the spectra. This shows up most clearly in the 2 ML spectrum, where peak "p" reveals a clear shoulder and the minimum following the HOMO peak is completely filled due to simultaneous emission from the first two layers. Peaks in the 1 ML spectrum are probably also broadened due to non-ideal layer-by-layer growth and possibly also due to substrate-induced polarisation. Upon thermal desorption at 250 °C it is found by UPS that the first layer remains on the substrate surface. This suggests that the bonding between the first PTCDA layer and the substrate is stronger than that between the subsequent PTCDA layers. However, the photoemission spectra from the first layer are qualitatively the same as spectra from thicker films. No additional features are found in the monolayer spectra that would indicate covalent bonding between the first layer and the substrate, as e.g. in the case of PTCDA/Ag [1]. We therefore conclude that a strong physisorption occurs for the first monolayer of PTCDA on $TiSe_2$.

Shifts in photoelectron spectra from semiconductors can be caused by different effects associated with changes in the initial or final states of the photoemission process. The former include the development of an interface dipole, band bending and photovoltaic shifts. The latter reflect changes in the response of the medium to the excited photohole state. Assignment of experimentally observed shifts to these specific mechanisms can be achieved by various complementary observations. A photovoltaic effect (i.e. the occurrence of photon-induced reduction of band bending), for instance, can be identified via its sensitivity to sample temperature and excitation rate (light intensity). In the present case no dependence on light intensity could be observed (the intensity was varied one order of magnitude), which implies that photovoltaic effects can be ignored. This is also a reasonable conclusion considering that the layers are extremely thin. In order to distinguish other electrostatic initial state effects from final state effects, we examined how the work function changed with layer thickness. Assuming a rigid electronic structure in the overlayer during the growth process, and that the surface geometry remains the same, the work function changes reflect the combined effects of all electrostatic shifts in the initial state. Considering the local character of the electron states in PTCDA, these assumptions appear to be justified. Thus, the difference between the observed shifts and the changes in the work function should be assigned to final state effects. The work function of $TiSe_2$ has been measured to be 5.4 eV while for thick layers of PTCDA we find a value of approximately 4.3 eV. In Fig. 5(b) we represent the difference in the magnitude of the shifts by the energy separation (ΔE) between the peak marked "p" in the valence band spectra

(Fig. 4) and the low energy cut-off (taken from spectra where a −5 V bias has been applied to the sample). We see that the PTCDA spectra shift by ca. 0.5 eV relative to the cut-off energy as the film thickness is increased from 1 to 35 ML. The shift of peak p (0.8 eV, Fig. 5(a)) is approximately 0.5 eV larger than the work function difference between the thinnest (1 ML) and thickest (35 ML) coverages of PTCDA (0.3 eV). We thus conclude that 0.5 eV of the total 0.8 eV shift of the spectrum is to be attributed to final state relaxation. The direction of the shift is such that the binding energy appears to increase with increasing layer thickness. In analogy with shifts reported earlier for Xe layers on Pd [12], and also treated in model calculations [13], we ascribe the effects observed here to a decreasing metal-induced screening of the photohole as the location of the hole is moved away from the substrate-overlayer interface.

The thickness range over which the screening effect is observed is very similar in the present case to that reported for Xe/Pd, but the present shift is about 50% smaller (0.5 vs. 1.1 eV). The lower value can be understood as an effect of an efficient intramolecular screening. In PTCDA there is a large difference between the in-plane and out-of-plane dielectric constant ε, with a value of 4.5 in-plane and as low as 1.9 perpendicular to the molecular planes [16]. The effective dielectric constant relevant to final state screening must be dominated by the higher in-plane value while the bulk ε in Xe used in [12] is 2.25. One should note, however, that the strong excitonic effects, that for instance are manifested in a large difference between the optical and transport band gaps [14], show that the local screening in PTCDA is relatively poor. The possibility of final state-induced shifts in organic thin films on metal substrates has also been considered in previous studies [15], but the actual magnitude of this contribution to the observed shifts was not discussed. Subtracting the final state relaxation effect (0.5 eV) from the total shift of the spectra (0.8 eV) leaves 0.3 eV that is ascribed to band bending which is assumed to develop parallel with the work function change. We use the difference between the work function of the clean substrate and of the substrate covered by 1 ML PTCDA to estimate the interface dipole and get a value of approximately 0.8 eV (5.4–4.6 eV), which seems reasonable [15].

4. Summary

PTCDA forms a well-ordered 3D crystal on $TiSe_2$ (at least up to 30 ML). The in-plane structure of the PTCDA has a 2D coincident orientation with respect to the substrate. A strong angular dependence has been observed for the intensities of the PTCDA peaks in UPS, corroborating the assumption of an ordered PTCDA structure. Also small systematic energy shifts of the HOMO peak were observed for different emission angles as an effect of varying probing depth.

The interface dipole between $TiSe_2$ and PTCDA is estimated to 0.8 eV, and a further electrostatic shift of 0.3 eV due to band bending has been separately estimated for thick overlayers. A spectral energy shift of 0.5 eV is observed with increasing overlayer thickness, the origin of which is ascribed to final state screening effects.

Acknowledgements

We would like to thank Prof. F. Lévy for providing the $TiSe_2$ crystals and Dr. H. Starnberg for valuable discussions. We are also grateful to Prof. N. Karl for many valuable comments. The work is supported by the Swedish Natural Science Research Council.

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