

Angle-resolved UV photoelectron spectra (UPS) of thin films of perylene-3,4,9,10-tetracarboxylic dianhydride on MoS₂

Yasushi Azuma,^{a*} Takehiko Hasebe,^a Takayuki Miyamae,^{a,b} Koji K. Okudaira,^b Yoshiya Harada,^c Kazuhiko Seki,^d Eizi Morikawa,^e Volker Saile^e and Nobuo Ueno^{b,c}

^aGraduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan, ^bInstitute for Molecular Science, Okazaki 444-8585, Japan, ^cDepartment of Materials Science, Faculty of Engineering, Chiba University, Inage, Chiba 263-8522, Japan, ^dDepartment of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-8602, Japan, and ^eThe J. Bennett Johnston Sr Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, LA 70803, USA.
E-mail: azuma@msnu0145.tech.chiba-u.ac.jp

(Received 4 August 1997; accepted 14 November 1997)

Angle-resolved UV photoelectron spectra (ARUPS) were measured for thin films of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) deposited on cleaved MoS₂ surfaces. The take-off angle (θ) dependence of the photoelectron intensity of the highest π band showed a sharp maximum at $\theta = 32\text{--}34^\circ$. A spectral feature of the binding energy at ~ 8.9 eV, which is believed to originate from a π state, showed a remarkably different θ dependence from that of the π band. A quantitative analysis of the observed θ dependencies clearly indicates that (a) the feature at ~ 8.9 eV originates from the oxygen $2p$ non-bonding states and (b) the molecules lie flat on the substrate surface.

Keywords: organic thin films; angle-resolved UV photoelectron spectroscopy; UPS; perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA).

1. Introduction

The angular distribution of photoelectrons in principle involves information on the initial-state wavefunction and thus the quantitative analysis of the angular distribution provides a detailed origin of the observed photoelectron band, as well as the geometrical structures of thin films and their surfaces. We recently successfully analysed ARUPS intensities from thin films of large organic molecules using the independent atomic center (Hasegawa *et al.*, 1993; Ueno *et al.*, 1993) and single-scattering approximations (Ueno, 1996; Hasegawa *et al.*, 1996; Ueno *et al.*, 1997) combined with molecular orbital calculations (IAC/MO and SS/MO), and determined the molecular orientation of bis(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole), C₄H₄S₆N₄ (BTQ-BT), and some phthalocyanines on HOPG graphite and MoS₂ surfaces.

The archetypal organic semiconductor perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) has recently gained increasing

interest as a promising material for organic devices, since the molecules form excellent ordered multilayers of high stability (Forrest *et al.*, 1994; Schmidt, Schuerlain *et al.*, 1995, and references therein; Schmidt, Chau *et al.*, 1995). Furthermore, it was reported that thin films of PTCDA provide new band-gap states due to the reaction at the interface between the film and the substrate or over-layer materials such as GaAs, In, Al, Ti and Sn (Hirose *et al.*, 1994, 1996). The reaction between the molecule and metal atoms was considered to occur at the C=O groups in the molecule (Hirose *et al.*, 1996). Although it is of great importance to investigate the pristine valence states originating from the C=O groups in order to understand the gap-state formation at the interface, there seems to be no experimental work which shows the location of the valence band due to the C=O groups.

In the present study we performed ARUPS and low-energy electron diffraction (LEED) measurements on thin films of PTCDA deposited on cleaved MoS₂ surfaces in order to characterize the valence states originating from the C=O groups. Furthermore, our interest was also on the quantitative molecular orientation which affects the electronic structure of the interface. In this paper we report the results of the quantitative analysis of the take-off angle (θ) dependence of the ARUPS spectra using the SS/MO approximation (Ueno, 1996; Hasegawa *et al.*, 1996; Ueno *et al.*, 1997) from *ab initio* (STO-6G) molecular orbital calculations. From the analysis we could undoubtedly assign the photoelectron band originating from oxygen $2p$ non-bonding orbitals (n_o) of the C=O groups and experimentally determined that the tilt angle between the molecular plane and the surface is 0° .

2. Experimental

ARUPS measurements were carried out at the beamline BL8B2 of the UVSOR at the Institute for Molecular Science. Details of the ARUPS apparatus are described elsewhere (Ueno *et al.*, 1990, 1997). The take-off angle (θ) dependencies of photoelectrons were measured at normal incidence (incidence angle of photons $\alpha = 0^\circ$) with photon energy 40 eV. Experimental parameters are shown in Fig. 1, together with the molecular structure. The sample azimuthal angle (φ) was measured from one of the three

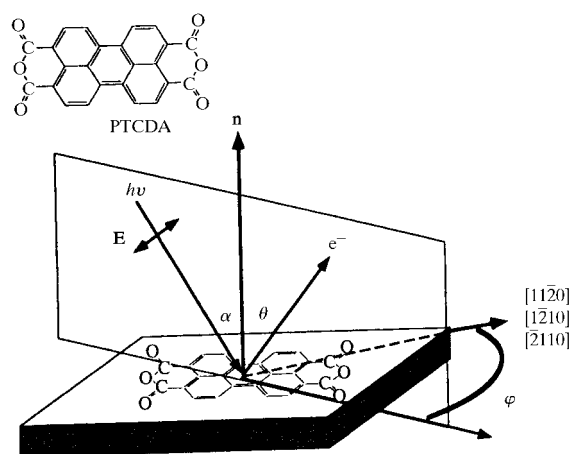


Figure 1 Molecular structure of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and experimental parameters of the ARUPS.

equivalent surface crystal axes ($[1\bar{1}20]$, $[1\bar{2}10]$ and $[\bar{2}110]$) of the MoS_2 surface. As described later, however, the value of φ is not important in the analysis of the present θ dependence of photoelectron intensity due to the multiple azimuthal orientation of the molecules.

All measurements were carried out under an ultrahigh vacuum of 10^{-10} torr.

Commercially obtained PTCDA was purified by three sublimations in an Ar gas stream of ~ 0.1 torr, followed by an additional two sublimations in a high vacuum of 10^{-5} torr. The ultrathin films were prepared in the preparation chamber by vacuum evaporation onto MoS_2 surfaces obtained by *in situ* cleavage. The pressure of the preparation chamber during the film deposition was 10^{-9} torr and the temperature of the substrate was kept at room temperature. The film thickness was monitored with a quartz thickness monitor, assuming the molecular sticking coefficients are the same for surfaces of MoS_2 and the thickness monitor. The deposition rate was smaller than 1 \AA min^{-1} .

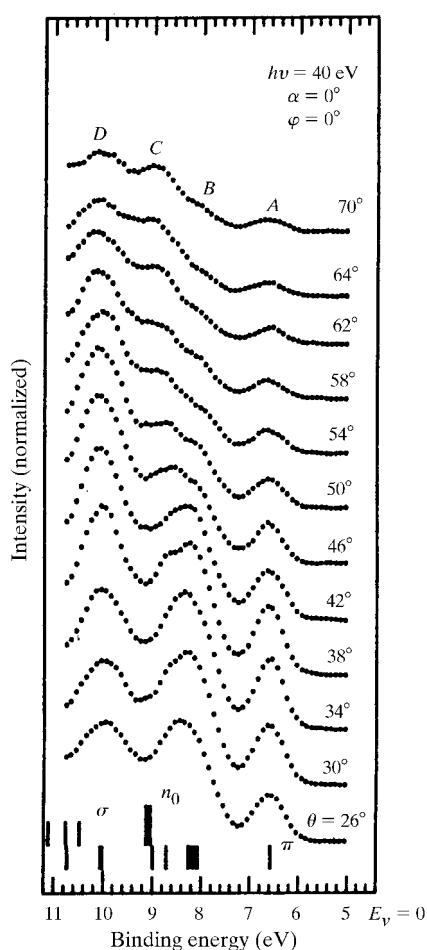


Figure 2

The take-off angle (θ) dependence of the ARUPS of a PTCDA film (42 Å thick) on MoS_2 at $h\nu = 40 \text{ eV}$ and normal incidence (incidence angle of photons $\alpha = 0^\circ$). The intensity is normalized to the incidence photon flux. The energy levels calculated using the *ab initio* (STO-6G) method are shown by vertical bars, where longer bars indicate oxygen $2p$ non-bonding states (n_o). The binding energy scale of the calculated results was contracted by 0.68 and shifted by 2.35 eV in order to fit the energy positions between observed and calculated results for the HOMO (feature A) and n_o states at C=O groups (feature C).

3. Results and discussion

The LEED of PTCDA thin films on the MoS_2 substrates showed no film-thickness dependence for the pristine films of 1.4–42 Å thickness. The diffraction spots of $(n, 0)$ and $(0, n)$, where n is an odd number, were not observed because of the existence of a glide-reflection symmetry in this system. From analysis of the LEED patterns we concluded that PTCDA forms a two-dimensional rectangular unit cell with dimensions $b_1 = 13.8$ and $b_2 = 21.2 \text{ \AA}$, with two molecules. Two domains of the PTCDA lattice exist with the rotation angle $R = \pm 12.5^\circ$, with respect to each surface crystal axis of the substrate. The results agree well with those reported by Schmidt, Schuerlein *et al.* (1995), and references therein. Thus, owing to the sixfold symmetry of the substrate surface, the film consists of six-directional domains of these two-dimensional lattices and at the center of each rectangular lattice there is a molecule with a different azimuthal orientation from that at the corner.

Fig. 2 shows the θ dependence of the ARUPS of the 42 Å film for the binding energy range 5–11 eV, where the energy levels calculated using the *ab initio* (STO-6G) method are also shown. Four features, A–D, depending on the value of θ are clearly seen. These spectra are in good agreement with results previously reported (Karl & Sato, 1992; Hirose *et al.*, 1994, 1996), considering that the reported results were not obtained by ARUPS. The observed top feature A, at the binding energy $\sim 6.6 \text{ eV}$, should originate from the HOMO (highest occupied molecular orbital) and consists of a single π molecular orbital. With an increase in θ , it is seen that the intensities of features A, B and D first increase, reach a maximum at ~ 34 , 34 and 46° , respectively, and then decrease at larger θ . On the other hand, it is clearly seen that feature C at $\sim 8.9 \text{ eV}$ appears only at a larger value of θ . Hirose *et al.* (1994, 1996) ascribed the photoemission peak, which corresponds to the present feature C, to the π_3 state. Band A originates from the HOMO of π character and, therefore, feature C should not originate from the valence state of π character since the difference in these θ dependencies is reflected in the wavefunctions of the initial states. θ dependence similar to this spectrum was also observed for a 1.4 Å thick film.

Fig. 3 shows a comparison between the observed and calculated θ dependencies of the photoelectron intensities at features

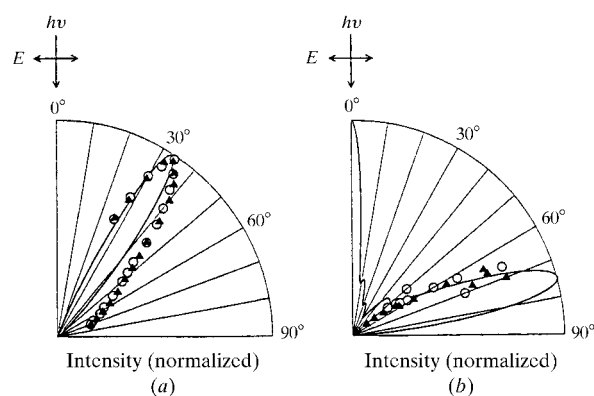


Figure 3

Comparison between observed and calculated θ dependencies of the photoelectron intensities for (a) HOMO (π) and (b) n_o (C=O) bands with the SS/MO. \circ Experimental results for the 42 Å film on MoS_2 at $\varphi = 0^\circ$. \blacktriangle Experimental results for the 1.4 Å thick film on MoS_2 at $\varphi = +4^\circ$. The calculations were performed for a flat-lying molecular orientation with rotational disorder. The incidence angle of photons α is 0° and $h\nu = 40 \text{ eV}$.

A and C , where the calculations were carried out using the SS/MO approximation with STO-6G wavefunctions of the HOMO and n_o states at C=O groups for a flat-lying orientation of the molecule. In Fig. 3 the experimental results for the 1.4 Å film are also shown, together with those for the 42 Å film. As there are four n_o (C=O) states near the energy position of the observed feature C , we sum the θ dependencies from the four n_o states. Furthermore, in the calculation an azimuthal disorder of the molecules was assumed, since the LEED indicated that the molecules on MoS₂ show at least 12 different orientations and such multiple molecular orientations, in general, make the θ dependence insensitive to the experimental value of φ (Ueno *et al.*, 1997). It is clearly seen that the calculated angular distributions for the HOMO and n_o states show remarkable differences and they respectively agree well with those observed. From these comparisons we conclude that (i) the molecules lie flat and (ii) the observed feature C originates from the n_o states at the C=O groups.

The authors would like to thank Dr M. Aoki and the staff of the UVSOR facility at the Institute for Molecular Science for their support during ARUPS experiments. This work was supported by the Joint Study Program (1995–1996) of the Institute for Molecular Science and in part by Grant-in-Aids for

Scientific Research from the Ministry of Education, Science, Sports and Culture (grant nos. 08455004 and 09044134).

References

- Forrest, S. R., Burrows, P. E., Haskal, E. I. & So, F. F. (1994). *Phys. Rev. B*, **49**, 11309–11314.
- Karl, N. & Sato, N. (1992). *Mol. Cryst. Liq. Cryst.* **218**, 79–84.
- Hasegawa, S., Inokuchi, H., Seki, K. & Ueno, N. (1996). *J. Electron Spectrosc. Relat. Phenom.* **78**, 391–396.
- Hasegawa, S., Tanaka, S., Yamashita, Y., Inokuchi, H., Fujimoto, H., Kamiya, K., Seki, K. & Ueno, N. (1993). *Phys. Rev. B*, **48**, 2596–2600.
- Hirose, Y., Chen, W., Haskal, E. I., Forrest, S. R. & Kahn, A. (1994). *Appl. Phys. Lett.* **64**, 3482–3485.
- Hirose, Y., Kahn, A., Aristov, V., Soukiassian, P., Bulovic, V. & Forrest, S. R. (1996). *Phys. Rev. B*, **54**, 13748–13758.
- Schmidt, A., Chau, L.-K., Valencia, V. S. & Armstrong, N. R. (1995). *Chem. Mater.* **7**, 657–662.
- Schmidt, A., Schuerlein, T. J., Collins, G. E. & Armstrong, N. R. (1995). *J. Phys. Chem.* **99**, 11770–11779.
- Ueno, N. (1996). *J. Electron Spectrosc. Relat. Phenom.* **78**, 345–350.
- Ueno, N., Kitamura, A., Okudaira, K. K., Miyamae, T., Harada, Y., Hasegawa, S., Ishii, H., Inokuchi, H., Fujikawa, T., Miyazaki, T. & Seki, K. (1997). *J. Chem. Phys.* **107**, 2079–2088.
- Ueno, N., Seki, K., Sato, N., Fujimoto, H., Kuramochi, T., Sugita, K. & Inokuchi, H. (1990). *Phys. Rev. B*, **41**, 1176–1183.
- Ueno, N., Suzuki, K., Hasegawa, S., Kamiya, K., Seki, K. & Inokuchi, H. (1993). *J. Chem. Phys.* **99**, 7169–7174.