VI-R Ultraviolet Photoelectron Spectroscopy of Organic Thin Film and Organic/Inorganic Interface

Electronic structures of organic film surface and organic/inorganic interface are expected to play an important role in organic-device properties. We investigated surface structures and energy alignments to clarify their electronic structures using electron spectroscopy such as photoelectron spectroscopy combined with synchrotron radiation and metastable atom electron spectroscopy.

VI-R-1 Pendant Group Orientation of Poly(2-vinylnaphthalene) Thin Film Surface Studied by Near-Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS) and Angle-resolved Ultraviolet Photoelectron Spectroscopy (ARUPS)

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Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy were applied to the investigation of the tilt angles of the naphthalene pendant groups at the surface of poly(2-vinylnaphthalene) thin film. The NEXAFS results indicates that the mean value of tilt angle of naphthalene pendant groups with respect to the polymer surface is about 57°. In contrast to NEXAFS, which provides only an average determination of the tilt angle, ARUPS combined with a sophisticated analysis of photoelectron angular dependence offers more detailed information. Analysis by ARUPS combined with the single-scattering approximation with molecular orbital calculation indicates that the naphthalene pendant groups are tilted randomly at the polymer surface, and that the tilt angle distribution is well described as a three-dimensional isotropic random orientation, which indicates that the majority of the pendant groups is tilted at large angles with respect to the polymer surface.

VI-R-2 Origin of Indium-[perylene3,4,9,10-tetracarboxylic Dianhydride] Interface States Studied by Outermost Surface Spectroscopy Using Metastable Atoms

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[*Phys. Rev. B* **63**, 115204 (2001)]

Metastable atom electron spectra (MAES) and ultraviolet photoelectron spectra (UPS) of indium-[perylene3,4,9,10-tetracarboxylic dianhydride (PTCDA)] system prepared on a MoS_2 single crystal substrate were measured as a function of the In overlayer thickness (ΘIn). As observed by a previous UPS experiment, a new band was observed in the original PTCDA energy gap region even by the MAES which detects the outermost surface selectively (Figure 1). The ΘIn dependence of this new band intensity measured by the MAES gives a maximum at ΘIn ~ 1 Å, suggesting that four In atoms are reacting with one PTCDA molecule at the C=O parts. From the result of the density functional theory (DFT) methods and the enhanced intensity of the new band in the MAES, it was concluded that the new band originates from π state consisting of In 5pz AO’s.

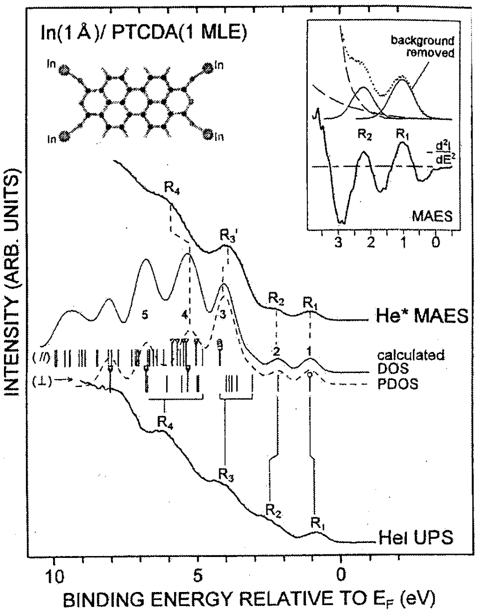

Figure 1. Comparison of the observed He*(2^3S) MAES and He I UPS of the In(1 Å)/PTCDA(1 MLE)/MoS_2 and the calculated results for In_4PTCDA. Bars show calculated MO energy levels obtained by DFT method (B3LYP/LanL2DZ). The Upper and lower bars respectively, indicate $MO_{//}$ and $MO_{\perp}$ states, and bars with circles show states with large contribution of In AO’s (5p,5s). Bars with triangles indicate states with contribution of oxygen AO’s. The calculated DOS is shown by solid curve. The PDOS, which corresponds to partial DOS for $MO_{\perp}$ and four contracted σ states (marked by circles in $MO_{//}$), is shown by a dashed curve. These DOS’s were observed by 0.7 eV Gaussian broadening of MO’s. Negative of the second derivative of the MAES ($-d^2I/dE^2$) and the MAES after background removal is shown in inset, in order to show the enhanced intensity of band R_1 than band R_2. Molecular structure of the reaction product, In_4PTCDA, is also shown.

VI-R-3 Surface Images of SiO_2/Si(100) Pattern using Electron Emission Microscopy with Metastable Atoms, Photons and Low-Energy Electrons

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The surface images of a SiO_2 pattern on Si(100) was observed by three types of electron emission microscopies, *i.e.*, metastable electron emission microscopy (MEEM) with metastable he, photoelectron emission microscopy (PEEM) and low-energy electron emission microscopy (LEEM). Among these, MEEM gave the most diffused image at the pattern edges of the SiO_2 region. Furthermore, it is found that the difference in MEEM, LEEM, and PEEM images can provide new information on the spatial distribution of surface electronic state. By comparing MEEM, LEEM, and PEEM images, it is expected that we can obtain local information on surface electronic states in more detail

VI-R-4 Ultraviolet Photoelectron Spectra of Metallofullerenes, Two Ca@C_{82} Isomers

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Ultraviolet photoelectron spectra (UPS) of two Ca@C_{82} isomers (III and IV) were measured with a synchrotron radiation light source. Figure 1 shows these photoelectron spectra obtained with 20 eV excitation energy. The photoelectron onset energies of isomer III and IV were 0.7 eV and 0.8 eV below the Fermi level, respectively, which indicates their semiconductive nature. When the excitation energy is tuned, spectral intensity changes as other fullerenes have shown. Their upper valence band (0–5 eV) spectra are different from those of other metallofullerenes such as La@C_{82}, Sc@C_{82} and Gd@C_{82} as well as those of empty C_{82} but their lower valence band spectra (below 5 eV) are almost identical. Comparison between the UPS and *ab initio* calculation assuming transfer of two electrons from encapsulated calcium atom to the cage (*i.e.* Ca^{+2}@C_{82}^{2-}) suggests C_2(c) geometry for isomer III and C_s for isomer IV.

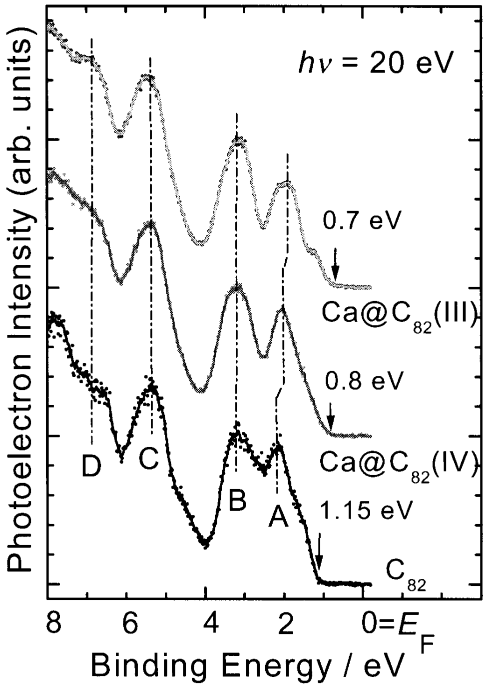

Figure 1. UPS spectra of two Ca@C_{82} isomers and C_{82}.

VI-R-5 Chemical Reaction at the NTCDA/Metal Interfaces

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Planar π-stacking organic molecules have been shown to be excellent model compounds for studying the growth and optoelectronic properties of organic semiconducting thin films on metal substrates.[1)] In this study, we investigated the bonding of 1,4,5,8-naphthalene-tetracaboxylicacid-dianhydride (NTCDA) on Au and In by ultra-violet photoemission spectroscopy (UPS). Figures 1 and 2 show the valence band of NTCDA on Au and In, respectively, as a function of the amount of NTCDA deposition. The structures due to the highest occupied molecular orbital (HOMO) of NTCDA are seen even at low coverage on Au. However, the spectra of NTCDA deposited on Al are quite different from those on Au even at 50 Å. Taking into account the results of AES measurements, it is considered that NTCDA molecules are weakly bonded to Au substrate through the HOMO, on the other hand, a strong chemical bond between In and the anhydride group of NTCDA is formed and results in the diffusion of In atoms into NTCDA films.

Reference

1) Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic and S. R. Forrest, *Phys. Rev. B* **54**, 13748 (1996).

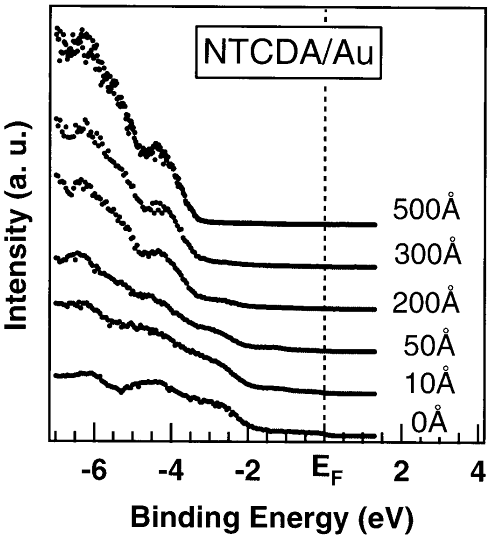

Figure 1. Valence band UPS spectra for NTCDA on Au.

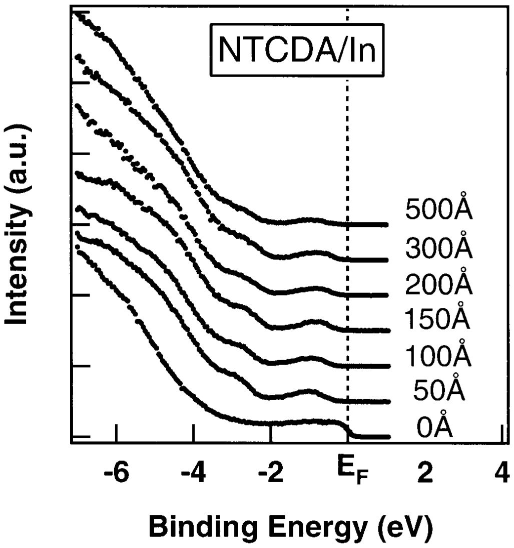

Figure 2. Valence band UPS spectra for NTCDA on In.