

IX-T Study of Electronic Structure of Organic Thin Film and Organic/Inorganic Interface

Organic semiconductors have attracted much interest due to their highly potential, flexibility, electronic and optical properties, and their considerable promise in molecular device technologies. To clarify the electronic properties at the organic/organic and organic/metal interface, various characterization techniques such as high-resolution ultraviolet photoemission spectroscopy (UPS) and near-edge x-ray absorption fine structure (NEXAFS) have been performed for organic thin film systems, because origin of the energy position, band shape and band width of UPS spectra are keys to understand the interface properties such as the energy level alignment at the interface, intermolecular or molecule-substrate interactions, and carrier transfer/transport process. Especially, vibronic coupling and lifetime of a hole created in the highest occupied molecular orbital (HOMO) state in the organic thin film play a crucial role in the hole transport through the film and the electron injection from an electrode to the ionized molecule. The HOMO band in UPS spectra in principle involves such information about the hole, and thus offers a variety of key information that is necessary to unravel fundamental mechanism in carrier dynamics in organic devices.

IX-T-1 Deep Insight into a Valence Hole in Organic Semiconductors: High-Resolution Ultraviolet Photoemission Study

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We have succeeded to observe a very sharp highest occupied molecular orbital (HOMO) band for oriented thin films of various phthalocyanines prepared on graphite *via* high-resolution ultraviolet photoelectron spectroscopy. Hole-vibration couplings can be resolved even for films of large π -conjugated molecules. The fine structure would give us lots information on “hidden” properties in organic-based devices, such as molecular-vibration related carrier dynamics, intermolecular interaction, and molecule-substrate interaction. Moreover, it was found that the observed binding energy position is much affected by inhomogeneity of the film with different molecular orientations, leading to a broadening of the HOMO bandwidth.

IX-T-2 UPS Fine Structures of Highest Occupied Band in Vanadyl-Phthalocyanine Ultrathin Film

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Ultraviolet photoelectron spectra were measured for vanadyl phthalocyanine (VOPc) ultrathin films prepared on graphite to study effects of the molecular orientation and the electric dipole layer on the organic electronic states. VOPc has a permanent electric dipole perpendicular to the molecular plane, hence a well-defined electric dipole layer could be intentionally prepared by using the oriented monolayer. The observed binding-energy difference of the highest occupied molecular orbital (HOMO) bands between the oriented monolayer

and the double layer was found to agree with the vacuum level shift, leading to a conclusion that the molecular energy level with respect to the substrate Fermi level is changed when the molecule is in the electric dipole layer.

IX-T-3 Fine Structure of the Highest Occupied Band in OTi-Phthalocyanine Monolayer

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Ultraviolet photoelectron spectra were measured for ultrathin films of OTi-phthalocyanine (OTiPc), which has an electric dipole perpendicular to the molecular plane, prepared on highly oriented pyrolytic graphite in order to study effects of the molecular orientation and the electric dipole layer on the organic electronic states. For the as-grown films, the observed highest occupied molecular orbital (HOMO) band consists of two prominent peaks that can be assigned to different molecular orientations. For the oriented monolayer obtained by annealing the as-grown film, we detected a very sharp HOMO band at 290 K. The binding-energy (E_B) difference between the HOMO bands of the as-grown and annealed films was found to agree with the shift in the vacuum level. For the oriented monolayer, the observed sharp HOMO band involves at least four components that are ascribed to the coupling between the HOMO hole and the molecular vibration. Upon cooling the sample to 95 K, the HOMO bandwidth became sharper than that at 290 K. From the peak fitting using Voigt function, additional components are expected in the HOMO band at 95 K. Moreover, we detected the E_B shift in the HOMO band for the oriented monolayer upon cooling, which can be originated from decrease in the HOMO-hole screening due to the change in the film structure and/or the molecule-substrate interaction.

IX-T-4 Hole/Vibration Coupling of the Highest Occupied Band in Pentacene Thin Film

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The hole-vibration coupling of the highest occupied state in pentacene thin films on graphite is studied by high-resolution ultraviolet photoelectron spectroscopy. Vibration satellites in the film show a take-off-angle dependence, indicating that the Frank-Condon principle is not strictly satisfied in this system. They are more intense than in the gas phase and the vibrational energy in the film is slightly lower than that in the gas phase. This demonstrates that the reorganization energy in pentacene thin films is slightly larger than that estimated from the photoelectron spectrum of free pentacene molecules. Furthermore, it is pointed out that the electron hopping in the low-temperature film may occur in the femtosecond scale before the electronic polarization of the surrounding medium is completed.

IX-T-5 Quantitative Analysis of Photoelectron Angular Distribution of a Single Domain Organic Monolayer Film: NTCDA on GeS(001)

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Angle-resolved photoelectron spectra were measured for a single-crystal monolayer film of naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA) prepared on a cleaved GeS(001) surface using synchrotron radiation. The observed photoelectron angular distributions were analyzed by a calculation using the single-scattering approximation combined with molecular orbital calculation. With the help of the low-energy electron diffraction pattern, the structure of the NTCDA monolayer on GeS(001) was estimated quantitatively.

IX-T-6 UPS Study of VUV-Photodegradation of Polytetrafluoroethylene (PTFE) Ultrathin Film by Using Synchrotron Radiation

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The VUV-photodegradation of polytetrafluoroethylene (PTFE) ultra-thin film was studied by ultraviolet photoelectron spectroscopy and quadrupole mass

spectrometry. These results were compared with the previous photodegradation studies of the polyvinylidene fluoride (PVDF) and polyethylene (PE). Generation of new peak, π -band originated from the C=C bond, was observed in the low binding energy region of the UPS spectra in both PVDF and PE during the photodegradation. In contrast, no new peak generation was observed in the UPS of the photodegraded PTFE. Mass spectrometry analysis also suggested that the C=C bond generation is not a major mechanism in the VUV photodegradation of PTFE.

IX-T-7 Site-Specific Ion Desorption of Fluorinated Phthalocyanine Studied with Electron-Ion Coincidence Spectroscopy

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Auger electron photo-ion coincidence (AEPICO) and Auger spectra of fluorinated copper phthalocyanine (F₁₆CuPc) were observed to study the mechanism of the site-specific ion desorption. From the photon energy dependence of Auger electron spectra at fluorine (F) K-edge region, it is found that the spectator-Auger shift at $h\nu = 691.4$ eV is about 2 eV. To estimate the contribution of spectator-Auger component to the Auger spectra, the difference Auger spectra were obtained by subtracting the Auger spectrum above F 1s ionization energy from observed Auger spectra. AEPICO yield spectra for F⁺ at $h\nu = 691.4$ eV gives a large intensity at $E_{\text{kin}} = 650$ eV. The electron kinetic energy position of this intense F⁺ AEPICO peak agrees with that of the difference Auger spectra, indicating that the most probable mechanism for F⁺ ion desorption induced by the transition from F_{1s} to $\sigma(\text{C-F})^*$ is the spectator-Auger-stimulated ion desorption.

IX-T-8 Polarized Near-Edge X-Ray-Absorption Fine Structure Spectroscopy of C₆₀-Functionalized 11-Amino-1-Undecane Thiol Self-Assembled Monolayer: Molecular Orientation and Evidence for C₆₀ Aggregation

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Near-edge x-ray-absorption fine structure (NEXAFS) spectroscopy was adopted to probe the unoccupied electronic states of C₆₀ anchored onto an organized assembly of 11-amino-1-undecane thiol on Au(111). The polarization dependence of the intensity of π^* resonance associated with C₆₀ π network revealed the self-assembled monolayer (SAM) system to be oriented with an average molecular tilt angle of 57° with respect to the surface normal. Invoking the absence of solid-state band

dispersion effects and in comparison to solid C₆₀ and/or 1-ML C₆₀/Au(111), the electronic structure of the resulting assembly was found dominated by spectral position shift and linewidth and intensity changes of the lowest unoccupied molecular orbital (LUMO), LUMO +1, and LUMO+2 orbitals. The latter implied hybridization between N *P_z* of -NH₂ group of thiolate SAM and π levels of C₆₀, resulting in a nucleophilic addition with a change in the symmetry of C₆₀ from *I_h* to *C₁* in the SAM. Occurrence of a new feature at 285.3 eV in the NEXAFS spectrum, assigned previously to π^* graphitic LUMO, signified the formation of aggregated clusters, (C₆₀)_{*n*} of C₆₀ monomer. Low tunneling current scanning tunneling microscopy confirmed them to be spherical and stable aggregates with *n* ~ 5.