

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

Organic semiconductors have gained increasing interest because of their highly potential uses in various molecular devices. To clarify the electronic processes at the organic/inorganic 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 the origin of the energy position and the bandwidth 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 transport process. Energy, 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 transport properties in organic devices.

IX-W-1 Impact of an Interface Dipole Layer on Molecular Level Alignment at an Organic-Conductor Interface Studied by UPS

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The effect of an interface dipole layer on the energy level alignment at organic-conductor interfaces is studied on a copper phthalocyanine (CuPc) monolayer/electric dipole layer/graphite system *via* ultraviolet photoemission spectroscopy (UPS) and metastable atom electron spectroscopy (MAES). An oriented monolayer of the OTi-phthalocyanine molecule (OTiPc), which has an electric dipole moment, is grown on graphite to yield a well-defined dipole layer with the vacuum side negatively charged. The CuPc monolayer is sequentially deposited on the dipole layer kept at 123 K. This weakly interacting system made of a very thin organic layer on top of a very thin dipole layer is in thermodynamic equilibrium. The UPS data from the system grown with and without the interface dipole layer show that the binding energy of the highest occupied state of the CuPc monolayer decreases when the dipole layer is inserted. The binding energy shift is in excellent agreement with the increase in vacuum level energy of the graphite substrate upon deposition of the dipole layer. The results show that the Fermi level of the CuPc shifts toward the valence states when the interface dipole layer is inserted.

IX-W-2 HOMO-Band Fine Structure of OTi- and Pb-Phthalocyanine Ultrathin Films: Effects of the Electric Dipole Layer

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Ultraviolet photoelectron spectra were measured for titanyl- and lead-phthalocyanine ultrathin films prepared on graphite in order to study effects of the electric dipole layer on the organic energy levels. Each of these molecules has an electric dipole perpendicular to the molecular plane, and hence a well-defined electric dipole layer could be intentionally prepared by using oriented monolayer of these molecules. For as-grown films the observed highest occupied molecular orbital (HOMO) band consists of many peaks that could be assigned to different molecular orientations/aggregations. For well-oriented monolayer films obtained by annealing the as-grown films, we observed a very sharp HOMO band with two satellites for both molecules as for copper phthalocyanine. Difference of binding energy of HOMO bands between the oriented monolayer and the doublelayer in which molecular dipoles are cancelled was found to agree with the vacuum level shift for both molecules, leading to important conclusions that (1) the molecular energy level with respect to the substrate Fermi level is changed when the molecule is in the dipole-layer and (2) the binding-energy shift corresponds with the vacuum level shift.

IX-W-3 Photoelectron Fine Structures of Uppermost Valence Band for Well-Characterized ClAl-Phthalocyanine Ultrathin Film: UPS and MAES Study

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Metastable atom electron spectroscopy was used to characterize monolayer formation of chloroaluminum phthalocyanine (ClAlPc) prepared on graphite. For as-grown film, molecules form island structure of staggered doublelayers on the substrate. By annealing the film, molecules diffuse to form a uniform monolayer where all the molecules are oriented flat with Cl atom directed to the vacuum. After the confirmation of the oriented monolayer formation, high-resolution ultraviolet photoelectron spectra were measured to study

effects of the molecular orientation on the energy levels. ClAlPc has an electric dipole perpendicular to the molecular plane, hence a well-defined electric dipole layer could be intentionally prepared by using the oriented monolayer. Difference of binding energies of HOMO bands between the oriented monolayer and the doublelayer 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 dipole-layer field.

IX-W-4 Study of Excited States of Fluorinated Copper Phthalocyanine by Inner Shell Excitation

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Near edge X-ray absorption fine structure (NEXAFS) spectra of hexadecafluoro copper phthalocyanine (FCuPc) films (thickness of 50 Å) on MoS₂ substrates were observed near the carbon (C) and fluorine (F) K-edges. From the analysis of the dependence of C and F K-edge NEXAFS spectra on the photon incidence angle (α), the average molecular tilt angle was determined to be 30°. The lowest and second lowest peaks in the F K-edge NEXAFS were assigned to the transition to σ^* . In the ion time-of-flight mass spectra of FCuPc excited by photons near the F K-edge, F⁺, CF⁺, and CF₃⁺ ions were mainly observed. These results indicate that C–C bonds as well as C–F bonds are broken by the photon irradiation. From the analysis of the partial ion yield spectra of F⁺ and CF⁺ near the F K-edge, the lowest and second lowest peaks in the F K-edge NEXAFS spectra could be assigned to transitions to $\sigma(\text{C–F})^*$ and $\sigma(\text{C–C})^*$, respectively.

IX-W-5 Simulation Study of Angle-Resolved Photoemission Spectra and Intramolecular Energy-Band Dispersion of a PTFE Oligomer Film

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Theoretical simulations of the angle-resolved ultraviolet photoemission spectra for the oligomer of poly(tetrafluoroethylene) ((CF₂)_n; PTFE) was performed using the independent-atomic-center (IAC) approximation combined with *ab initio* molecular orbital (MO) calculations. Previously observed normal-emission spectra for the end-on oriented sample (with long-chain axis being perpendicular to the surface) showed the incident photon-energy ($h\nu$) dependence due to the

intramolecular energy-band dispersion along the one-dimensional chain,¹⁾ and the present simulations successfully reproduced this $h\nu$ -dependence of the observed spectra. We employed the experimentally observed helical structure for PTFE oligomers for the simulations. We also calculated the density of states (DOS) for the planar zigzag structure, and examined the changes in the electronic structure due to the difference in the molecular structure by comparing the DOS for the helical and planar zigzag structures. Only little change in the DOS was found between these structures, showing little change of the electronic structure between these conformations. We also evaluated the inner-potential V_0 , which is the parameter defining the energy origin of the free-electron-like final state, and checked the validity of the value of –10 eV estimated in our previous study using the experimentally observed $h\nu$ -dependence of the peak intensity.¹⁾ The estimation of V_0 was performed by pursuing the best agreement between the energy-band dispersion ($E = E(\mathbf{k})$) relation along the chain direction obtained from the simulated spectra and the experimentally deduced one. An excellent agreement in the topmost band was achieved when the assumed inner potential V_0 was set about zero. This value of V_0 is much different from the value of $V_0 = -10$ eV in the previous study, suggesting the invalidity of the previous assumption at the estimation of V_0 from the peak intensity variation with $h\nu$. Using the presently obtained V_0 , we could derive more reliable $E = E(\mathbf{k})$ dispersion relation from the observed ARUPS spectra. The comparison of this newly derived relation gave good agreement with theoretically calculated $E = E(\mathbf{k})$ relations, in contrast to the poor agreement for the previous results with $V_0 = -10$ eV.

Reference

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