VI-L Ultraviolet Photoelectron Spectroscopy on Organic Thin Films Using Synchrotron Radiation

The electronic structure and molecular orientation of organic thin films were investigated by angle-resolved UPS with synchrotron radiation. Furthermore corresponding spectroscopies, such as low energy electron transmission spectroscopy, electron energy loss spectroscopy and Penning ionization electron spectroscopy were used in investigating the electronic states of the thin films.

VI-L-1 Origin of Photoemission Intensity Oscillation of C_{60}

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The photon-energy dependences of photoemission intensities of C_{60} were quantitatively calculated by the single-scattering approximation for the final state and the ab initio molecular orbital calculation for the initial state. The calculated results agreed well with the measured intenslty oscillation in the photon-energy range of $h\nu$ = 18–110 eV. The calculation by the plane-wave approximation for the final state also gave similar oscillations, which suggests that the oscillations are independent of the accuracy of the final state. These results indicated that the oscillations originate from the interference of photoelectron waves emanating from the 60 carbon atoms, *i.e.*, the multicentered photoemission with the phase difference of each wave. Further, the analytical calculation with a simplified spherical shell-like initial state revealed that the sphelcal structure of C_{60} molecule and its large radius dominate the oscillations.

VI-L-2 Pennìng Ionization Electron Spectroscopy on Self-Assembled Monolayer of 1-Mercapto-8-Bromooctane on Au(111)

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Penning ionization electron spectroscopy (PIES) and ultraviolet photoelectron spectroscopy (UPS) were used to charactenze self-assembled monolayers (SAMs) of 1-mercapto-8-bromooctane adsorbed on Au(lll)from aqueous solution. The analysis of the relative band intensity of Penning spectrum indicates that the molecule stand up right to the substrate surface at room temperature. Upon heating, the molecule becomes tilted in the layer.

VI-L-3 Thickness-Dependent Orientation of the Pendant Phenyl Group at the Surface of Polystyrene Thin Films

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This paper reports on experimental evidence showing that the take-off angle dependence of the photoelectron intensity from the top n band of a polystyrene thin film, onginating from the pendant phenyl group, depends on the film thickness. The result indicates that the orientation of the phenyl group at the film surface changes with the film thickness. Theoretical analysis of the observed angular distribution using the single scattennng approximation combined with molecular orbital calculation (SS/MO) showed that the phenyl groups at the film surface become perpendicular oriented for a thicker film. The present finding suggests the possibility that thc surface property of a thin film of a pendant group polymer can be controlled by changing the film thickness.

VI-L-4 Structure of Copper- and H_2-phthalocyanine Thin Films on MoS_2 Studied by Angle Resolved Ultraviolet Photoelectron Spectroscopy and Low Energy Electron Diffraction

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Angle-resolved ultraviolet photoelectron spectra (ARUPS) of copper phthalocyanine (CuPc) and metal-free phthalocyanine (H_2Pc) films (thickness from monolayer to 50-80 Å) on cleaved MoS_2 substrates were measured using monochromatic synchrotron radiation. Observed take-off angle (θ) and azimuthal angle (ϕ) dependencies of the top π band intensity were analyzed quantitatively by the single-scattering approximation theory combined with molecular orbital calculations. The analysis indicated that the molecules lie ffat on the MoS_2 surface in monolayer films of CuPc and H_2Pc. The azimuthal orientation of the molecules (angle between molecular axis and surface crystal axis of MoS_2), was found to be about –7°, –37°, or –67° for both monolayer films of CuPc and H_2Pc. In the azimuthal orientation, the analyses indicated that there are only molecules with conterclockwise rotation, although both clockwise and counterclockwise rotations are expected. From the low energy electron diffraction, the two-dimensional lattice stsucture of the monolayer film was obtained. On the basis of these two kinds of experimental results, the full structure of the monolayer film, the two dimensional lattice and the molecular orientation at the lattice points, was determined. Furthermore, for the thick films it is found from the analyses of ARUPS that CuPc and H_2Pc molecules tilt about 10° from the surface plane.

VI-L-5 Electronic Structure of Poly(1,10-phenanthroline-3,8-diyl) and Its K-doped State Studied by Photoelectron Spectroscopy

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Ultaviolet photoelectron spectra were measured using synchrotron radiation for thin films of poly(1,10-phenanthroline-3,8-diyl) (PPhen) and its potassium-doped state. Upon potassium doping of PPhen, two new states, which could be assigned to bipolaron bands, appear in the originally empty energy gap. The electronic structure of the neural and potassium-doped states was theoretically analyzed using single-scattering approximation combined with semiempirical molecular orbital calculations.

VI-L-6 A Differential Thermal Analysis and Ultraviolet Photoemission Study on Surface Freezing of n-Alkanes

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The surface-freezing effect of pentacontane (*n*-$C_{50}H_{102}$) and tetratetracontane (*n*-$C_{44}H_{90}$) films evaporated on a copper substrate has been investigated by differential thermal analysis (DTA) simultaneously with measurements of surface-specific ultraviolet (UV) photoemission. Two anomalies in the DTA curve were observed near the bulk melting temperature, one of which has been attributed to bulk melting. Since the temperature dependence of the surface-specific UV photoemission measurement showed a corresponding stepwise increase and decrease in the photoemission current at the two anomalies observed in the DTA, we have concluded that the other phase transition peak originates from surface freezing.

VI-L-7 Angle-Resolved UPS Studies of Organic Thin Films

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This paper describes recent progress of angle-resolved photoelectron spectroscopy using synchrotron radiation (SR-ARUPS) on organic thin films. SR-ARUPS has been growing to a new surface analysis technique which can offer concrete information on the molecular orientation at the film surface as well as on the origin of the electronic structure, both of which are important in understanding functions of organic thin films. Some examples of the experimental determination of the molecular orientation by SR-ARUPS are shown for epitaxial ultrathin films of phthalocyanines and bis(l,2,5-thiadiazolo)-*p*-quinobis (1,3-dithiole) (BTQBT). The orientation of pendant naphthalene groups at the surface of thin film of poly(2-vinyl-naphthalene) is also shown, where the comparison between the results obtained by SR-ARUPS and near edge X-ray absorption fine structure (EXAFS) spectroscopy is made in order to understand an advantage of SR-ARUPS. Furthermore, it is pointed out by showing the result on C_{60} thin film that the multicentered photoemission dominates the photoelectron intensity of thin films of large organic molecules.