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Photoelectron Angular Distribution of Thin Films of Copper Phthalocyanine on MoS_2 Surfaces: Quantitative Determination of Molecular Orientation

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PHOTOELECTRON ANGULAR DISTRIBUTION OF THIN FILMS OF COPPER PHTHALOCYANINE ON MoS_2 SURFACES: QUANTITATIVE DETERMINATION OF MOLECULAR ORIENTATION

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Abstract The angle-resolved ultraviolet photoelectron spectra of ultrathin films of copper phthalocyanine (CuPc) on an MoS_2 substrate were measured using synchrotron radiation. The azimuthal angle dependence of the photoelectron intensity was analyzed using independent-atomic-center approximation combined with molecular orbital calculation. The results indicate that CuPc molecules lie flat on the substrate and that the film grows epitaxially with respect to the three equivalent directions of the MoS_2 surface.

INTRODUCTION

The determination of the molecular orientation in thin films of functional organic molecules is of fundamental importance, since the surface structure of the substrate affects the molecular orientation to give a new intermolecular interaction. Therefore, the determination of the molecular orientation with respect to the surface crystal axes of the substrate is greatly required.

The angular distribution of photoelectrons from thin films of organic crystals involves information on the molecular orientation in the film as well as on the electronic state. Therefore, the quantitative analysis of the photoelectron angular distribution gives detailed information on the molecular orientation in ultrathin films of functional organic molecules. Further an advantage of the angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) in determining the molecular orientation is that it introduces less radiation damage into functional organic films in comparison with other surface sensitive techniques using electron beams. Many ARUPS experiments have been performed in order to obtain detailed information on the electronic states and orientation of molecules.[1] However, the quantitative analysis of the photoelectron angular distribution

of thin films of large organic molecules is usually difficult, and no quantitative analysis has been performed after the challenging work by Permien *et al.*.[2] Recently, we have found that the angular distributions calculated by the independent-atomic-center (IAC) approximation combined with molecular orbital calculation agree excellently with observed ones for thin films of BTQBT [3] and metal-free phthalocyanine (H_2Pc) [4] on MoS_2 surfaces, and succeeded in determining the tilt angles of these molecules.

In the present study, we measured ARUPS spectra of copper phthalocyanine (CuPc) thin films deposited on MoS_2 surfaces with synchrotron radiation, and determined the molecular orientation, namely both polar (tilt angle) and azimuthal (in-surface-plane) orientations, by the quantitative analysis of the observed angular distribution using the IAC method.

EXPERIMENTS

ARUPS measurements were performed at the beam line BL8B2 of the UVSOR at Institute for Molecular Science.[5] The synchrotron radiation was monochromatized by a plane-grating monochromator. The photoelectron spectra were recorded under the total resolution of about 0.2eV. The experimental parameters in ARUPS measurements are shown in Fig. 1. The electric vector of photons and the momentum vector of photoelectrons are on a plane perpendicular to the substrate surface. The azimuthal angle (ϕ) dependence of photoelectron spectra was measured at normal incidence [incident angle of photon(α)=0°] with the photon energy of 40eV.

Commercially obtained CuPc was purified three times by sublimation in Ar gas stream of about 0.1 Torr and twice by sublimation in a high vacuum of 10^{-5} Torr. The MoS_2 substrates were cleaved under an ultrahigh vacuum of $\sim 4\times10^{-10}$ Torr in the main chamber. The thin films of 6 Å thickness were prepared on the substrate by vacuum evaporation under 10^{-8}-10^{-9} Torr. The sample was then transferred to the measurement chamber for *in situ* ARUPS measurements. The film thickness was estimated with a quartz thickness monitor by assuming that the density of the CuPc film is the same as that of the single crystal (α form).[6] The deposition rate was smaller

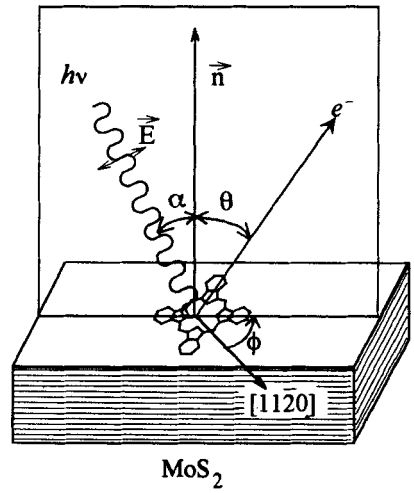

FIGURE 1 Experimental parameters in ARUPS. Azimuthal angle ϕ is the angle between the $[11\bar{2}0]$ direction of the MoS_2 crystal and the plane on which the electric vector of photons and the momentum vector of photoelectrons exist.

than 1 Å/min. The freshness of the cleaved MoS_2 surface was confirmed by ARUPS and low energy electron diffraction (LEED) measurements before the film deposition. Further the direction of the surface crystal axes of the MoS_2 substrate was determined by LEED measurements. The azimuthal angle ϕ is measured from the $[11\bar{2}0]$ direction of the MoS_2 crystal obtained by LEED measurements.

RESULTS and DISCUSSION

Figure 2 compares the ARUPS spectrum of a thin film of CuPc on the MoS_2 substrate and the calculated density-of-states (DOS) of H_2Pc. The DOS was obtained by Gaussian broadening (0.3eV) of molecular energy levels. The calculated binding energies were contracted to 80% and shifted to align the peak positions to experimental ones. Since the observed ARUPS of the CuPc thin film shows a good agreement with the calculated DOS of the H_2Pc molecule, it is considered that the first band A in the ARUPS spectrum of the CuPc thin film originates in the highest occupied molecular orbital (HOMO), which is due to a single π molecular orbital located at the porphine-like ring. Further we found that the photoelectron spectra of CuPc correspond well to those of H_2Pc [4] in the lower binding energy. We, therefore, calculated the photoelectron angular distribution using the wave function of the HOMO of an oriented H_2Pc molecule which can be considered as a model of the HOMO of CuPc. Another important point in Fig 2 is that the HOMO band (peak A) is well separated from the higher binding energy peaks, and therefore the intensity of the HOMO band is not influenced by those of the higher binding energy peaks.

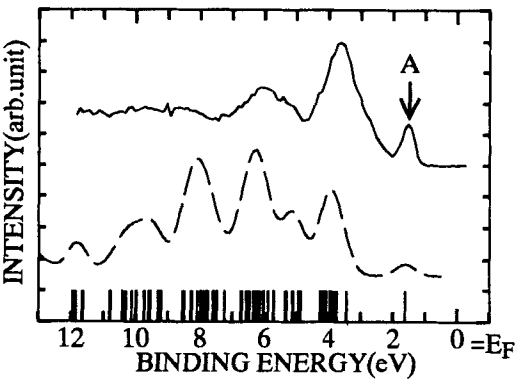

FIGURE 2 Comparison of the photoelectron spectrum (hv=40eV, α=0°,θ=30°) of a CuPc thin film (6 Å) on the MoS_2 surface (———) and the density-of-state (DOS) of valence bands of H_2Pc (— — —). The DOS was obtained by MNDO molecular orbital calculation with Gaussian broadening. The vertical lines at the bottom represent the calculated molecular orbital energies.

Figure 3 displays the ϕ dependence of the ARUPS spectrum of a thin film (6 Å) of the CuPc on the MoS_2 substrate in the low binding energy region from 0 to 3eV, where the intensity is normalized to the incident photon flux. The first peak A is not affected by photoelectrons from the MoS_2 substrate. Although the position of peak A is independent

of the azimuthal angle ϕ of the sample, its intensity shows apparent ϕ dependence. The dependence is plotted in Fig. 4. The experimental sweep range of the azimuthal angle ϕ is about 105° (from −40° to 66°) because it is limited by the sample rotation mechanism. Two large maxima at $\phi \approx -7°$ and 56° and one small maximum at $\phi \approx 23°$ are clearly seen. This strong ϕ dependence can be ascribed to an epitaxial growth of CuPc on the MoS_2 substrate.

We carried out quantitative analysis of the ϕ dependence of the photoelectron intensity of the HOMO band to determine the molecular orientation. The theoretical model in calculating the photoelectron angular distribution with the IAC approximation was described in previous papers.[3,4] The radial matrix element and phase shift for the carbon 2pz atomic orbital are those for hv=40.8 eV tabulated by Goldberg *et al.*,[7] and the corresponding values for the nitrogen 2pz were averaged ones of those for the carbon 2pz and oxygen 2pz atomic orbitals as in the previous calculations.[3,4] The molecular azimuthal angle ϕ_S and the inclination angle β at which the molecular plane is inclined to the substrate surface are introduced for the calculation of the ϕ dependence of the photoelectron intensity. Figure 5 illustrates the origin of ϕ_S. The calculated ϕ_S dependence of the HOMO band intensity for $\beta=0°$ is displayed in Fig. 5, where the corresponding molecular orientation is also shown. In the calculation we summed up six ϕ-dependencies corresponding to the six

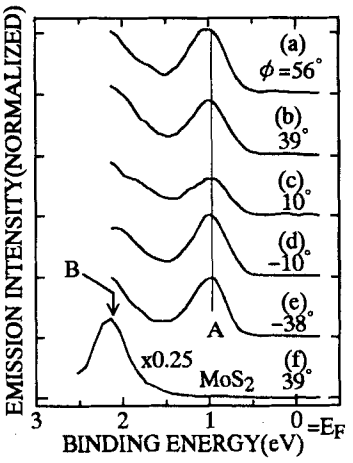

FIGURE 3 Azimuthal angle ϕ dependence of the ARUPS spectrum (hv=40eV, $\alpha=0°$,$\theta=30°$) of the CuPc thin film (6 Å) on the MoS_2 substrate (a)-(e). The ARUPS spectrum of the MoS_2 substrate (f) is also shown for comparison. The peak B for the MoS_2 substrate moves to the left for different azimuthal angles ϕ.

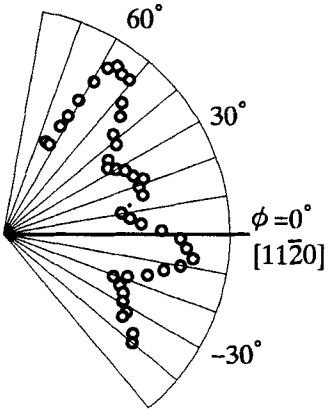

FIGURE 4 Azimuthal angle ϕ dependence of the HOMO band intensity (hv=40eV, $\alpha=0°$, $\theta=36°$) of the CuPc thin film (6 Å) on the MoS_2 substrate.

hold symmetry of the MoS_2 surface. It is seen that there are six large maixma and six small ones in the ϕ_s dependence.

For the determination of the CuPc molecular orientation in the ultrathin film on the MoS_2 surface, we compared the observed results with the calculated ϕ dependencies for various β. The best agreement between the calculated and observed ϕ dependencies was obtained for $\beta=0^\circ$ and $\phi_s=\phi-7^\circ$ as shown in Fig. 6, where the experimental results are shown by extending the observed ϕ range ($-40^\circ<\phi<66^\circ$) to $0^\circ<\phi<360^\circ$ on the basis of the 6 hold crystal symmetry of the MoS_2 substrate. The calculated results for other values of β little agree with the observed ones. From these results it is concluded that the CuPc molecules lie flat ($\beta=0^\circ$) on the substrate and that the film grows epitaxially with respect to the three equivalent directions of the MoS_2 surface. Furthermore the analysis of the take-off angle θ dependence of the photoelectron intensity of the HOMO band gave the flat orientation of CuPc molecules. As the summary, three configurations of the molecular orientation on the MoS_2 substrate are displayed in Fig.7. It is notable that the symmetry axes of the CuPc molecule are not parallel to the crystal axes of MoS_2. More detailed results will be published in the near future.

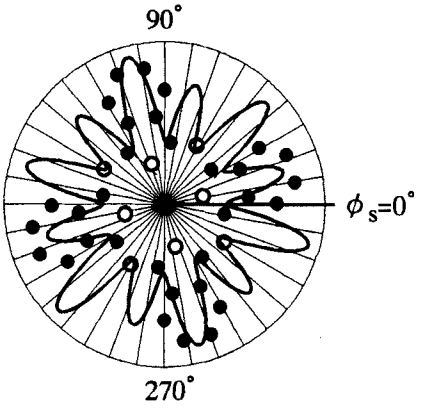

FIGURE 5 The calculated ϕ_s dependence (——) of the photoelectron intensity of the HOMO band of oriented H_2Pc. The molecular orientation of CuPc which gives the ϕ dependence is also shown. The symbols ● and ○ represent the position of the carbon and nitrogen atom, respectively.

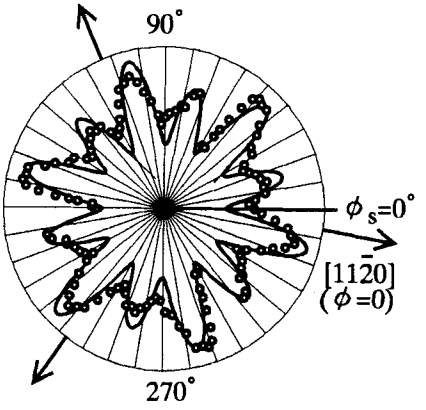

FIGURE 6 Comparison of the calculated (——) and observed (○) ϕ dependencies. Three arrows indicate the direction of the three equivalent crystal axes of the MoS_2 surface.

CONCLUSION

We measured the azimuthal angle (ϕ) dependence of the photoelectron intensity of

the HOMO band for the CuPc molecule in an ultrathin film deposited on the MoS_2 single crystal surface. From the comparison between the observed and calculated ϕ dependencies, we found that CuPc molecules lie flat on the MoS_2 surface. Further by comparing the results of LEED measurements of the MoS_2 substrate and those of ARUPS, it is found that the symmetry axes of the CuPc molecule are not parallel to the surface crystal axes of the MoS_2 substrate.

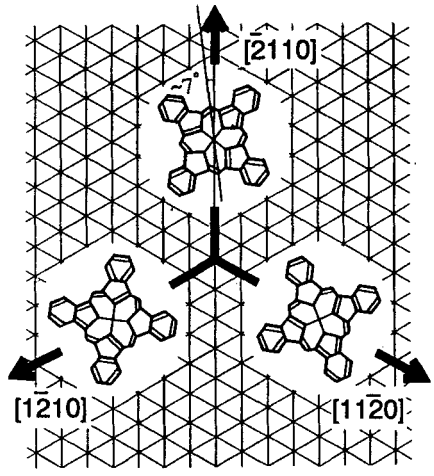

FIGURE 7 Orientation of CuPc molecules on the MoS_2 substrate. Three arrows represent the three equivalent crystal axes of the MoS_2 surface. The molecular plane is parallel to the MoS_2 surface.

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