Temperature dependence of photoelectron angular distribution from thin films of chloroaluminum phthalocyanine on MoS₂

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Angle-resolved UV photoelectron spectra were measured for thin films of chloroaluminum phthalocyanine deposited on cleaved MoS₂ surfaces. The take-off angle (θ) dependence of the photoelectron intensity of the highest π band showed a remarkable sharpening upon cooling the film, indicating that thermal excitation of molecular vibrations gives a considerable broadening of the photoelectron angular distribution. The θ dependence observed at ~120 K agrees well with that calculated.

Keywords: organic thin film; angle-resolved photoelectron spectroscopy; UPS; chloroaluminum phthalocyanine.

1. Introduction

Quantitative analysis of the photoelectron angular distribution provides a detailed origin of the observed photoelectron band, as well as the geometrical structures of thin films and their surfaces. The use of linearly polarized synchrotron radiation in angle-resolved UV photoelectron spectroscopy (ARUPS) greatly simplifies the analysis of observed spectra since the photoionization channel can be selected by the experimental geometry, including the polarization direction of the incidence photon. Furthermore, for the study of organic thin films ARUPS is very powerful since it causes less radiation damage of the thin films than other surface-sensitive techniques using electron beams. Despite such an advantage of ARUPS, it has not been used to investigate the geometrical structure of functional organic thin films because of a difficulty in analysing the ARUPS intensities.

We recently succeeded in analysing ARUPS intensities from thin films of large organic molecules using the independent atomic center (Hasegawa *et al.*, 1993; Ueno *et al.*, 1993) and single-scattering approximations (Ueno, 1996; Hasegawa *et al.*, 1996; Ueno, Kitamura *et al.*, 1997) combined with molecular orbital calculations (IAC/MO and SS/MO), and determined the molecular orientation of bis(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole), C₄H₄S₆N₄ (BTQBT), and some phthalocyanines on HOPG graphite and MoS₂ surfaces. However, we found that the calculated angular distribution often showed considerable

disagreement with that observed, which was observed at room temperature, and thus we expect that the thermal excitation of the molecular vibrations affects the angular distribution.

We performed ARUPS measurements on thin films of chloroaluminum phthalocyanine (ClAlPc) deposited on cleaved MoS₂ surfaces in order to study the effect of sample temperature on the take-off angle (θ) dependence of the photoelectron intensity. In this paper we will show that the θ dependence of the HOMO (highest occupied molecular orbital) band intensity observed at ~120 K is much sharper than that observed at room temperature and agrees more with that calculated.

2. Experimental

ARUPS measurements were carried out at the beamline BL8B2 of the UVSOR facility at the Institute for Molecular Science. Details of the ARUPS apparatus are described elsewhere (Ueno *et al.*, 1990; Ueno, Kitamura *et al.*, 1997). The take-off angle (θ) dependencies of photoelectrons were measured at normal incidence (incidence angle of photons $\alpha = 0°$) with photon energy 40 eV. Experimental parameters are shown in Fig. 1, together with the molecular structure.

All measurements were carried out under an ultrahigh vacuum of 10^{-10} torr.

Commercially obtained ClAlPc was purified by three sublimations in an Ar gas stream of ~0.1 torr, followed by an additional two sublimations in a high vacuum of 10^{-5} torr. The ultrathin film of 8 Å thickness (*ca* two monolayers) was prepared in the preparation chamber by vacuum evaporation onto cleaved MoS₂ surfaces kept at ~170 K, followed by annealing at room temperature for 12 h and at ~380 K for 8 h. The pressure of the preparation chamber during the film deposition was 10^{-9} torr. The film thickness was monitored with a quartz thickness monitor by assuming that the molecular sticking coefficients are the same for the surfaces of MoS₂ and the thickness monitor. The deposition rate was ~1.8 Å min⁻¹.

The LEED pattern of the annealed film, which was measured after the ARUPS measurements, indicated that the film consists of well ordered square lattices, similar to previous results (Aoki *et al.*, 1995).
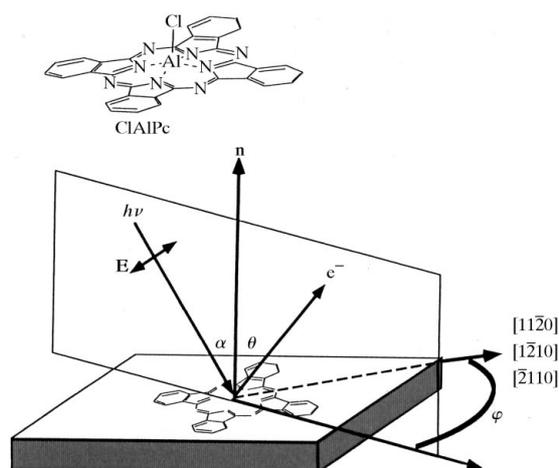
Figure 1
Molecular structure of chloroaluminum phthalocyanine and experimental parameters of the ARUPS.

3. Results and discussion

Fig. 2 shows an example of the θ dependence of the ARUPS spectrum measured at room temperature for the 8 Å film annealed at 380 K for 8 h; the substrate spectrum is also shown. These spectra are in good agreement with previously reported results (Aoki *et al.*, 1995). Feature A at the binding energy $\sim$5.6 eV originates from the HOMO band and consists of a single π molecular orbital. With an increase in θ, the intensities of the HOMO band A first increase, reach a maximum at $\sim$36° and then decrease at larger θ. Fig. 3 shows the θ dependencies of the HOMO band intensity for the as-deposited film (measured at $\sim$120 K), after annealing at room temperature for 12 h (measured at room temperature) and at 380 K for 8 h (also measured at room temperature). The θ dependence becomes sharp as a result of the annealing. This sharpening is ascribed to a change in the molecular orientation from tilt to flat-lying. On the other hand, it was also found from high-resolution electron energy loss spectroscopy, HREELS (Azuma *et al.*, 1998), low-energy electron transmission spectroscopy, LEET (Ueno, Azuma *et al.*, 1997), and Penning ionization electron spectroscopy, PIES (Azuma *et al.*, 1998), that the flat-lying orientation is completed by annealing at 370 K for 3 h, indicating that the film annealed at 380 K for 8 h consists of flat-lying molecules. Here we point out, however, that the θ dependence for the film annealed at 380 K is still broader than
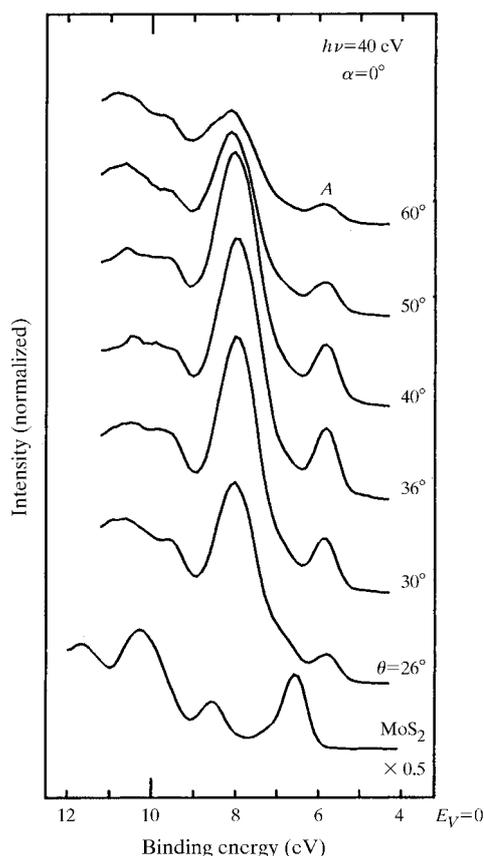
that for the monolayer film with a flat-lying molecular orientation (Aoki *et al.*, 1995).

In Fig. 3 the θ dependence for the film annealed at 380 K for 8 h, which was measured at a sample temperature of 120 K, is also compared. Upon cooling the annealed film at 120 K, the θ dependence becomes markedly sharper and especially the intensity in the larger θ region decreases. It is considered that this sharpening of the θ dependence can be ascribed to the reduction of the thermal excitation of molecular vibrations at lower temperature.

In Fig. 3 we further show the calculated θ dependence of the HOMO band intensity for comparison, where the calculations were carried out with the SS/MO approximation using MNDO wavefunctions of the HOMO state for a flat-lying orientation of the molecule. In the calculation an azimuthal disorder of the molecules was assumed, since the LEED indicated that the molecules form three-directional domains on the MoS_2 surface due to the sixfold symmetry of the substrate surface. Such multiple molecular orientations in general make the θ dependence insensitive to the azimuthal orientation of the molecule (Ueno, Kitamura *et al.*, 1997). It is clearly seen that the calculated θ dependence shows better agreement with that measured at 120 K than at room temperature. This finding indicates that the disagreement between the calculated angular distribution and that measured at room temperature originates from the broadening of the angular distribution due to the thermal excitation of molecular vibrations. Such a broadening of the photoelectron angular distribution at room temperature was observed for

Figure 2
The take-off angle (θ) dependence of ARUPS of the 380 K annealed chloroaluminum phthalocyanine thin film (8 Å thick, double layers) on MoS_2. The spectra were measured at room temperature. The incidence angle, α, of the photon is 0°, and $h\nu$ = 40 eV. The substrate spectrum is also shown.
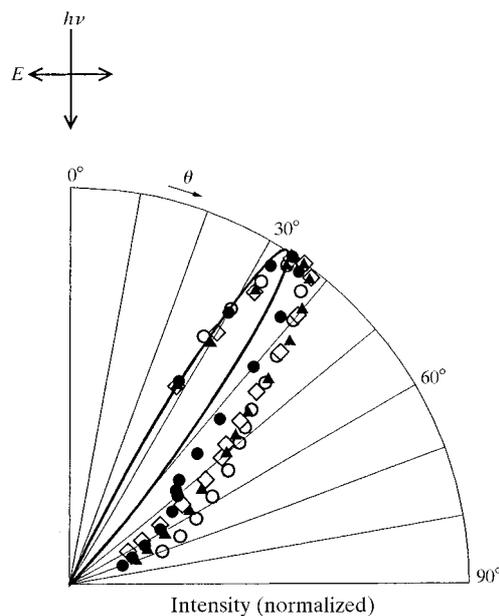
Figure 3
The take-off angle (θ) dependencies of the HOMO band intensity for chloroaluminum phthalocyanine thin film (8 Å thick, double layers) on MoS_2. ○ As-grown film deposited on MoS_2 kept at $\sim$170 K (measured at 120 K). ▲ After annealing at room temperature for 12 h (measured at room temperature). ◇ After annealing at 380 K for 8 h (measured at room temperature). ● After annealing at 380 K for 8 h (measured at 120 K). The calculated angular distribution is shown by a solid curve. The calculations were performed for a flat-lying molecular orientation with rotational disorder. The incidence angle, α, of photons is 0° and $h\nu$ = 40 eV.

multilayer films. This is probably because the intermolecular interaction in the multilayer is weaker than the molecule/substrate interaction.

From these results, we can confirm that the molecules lie flat on the MoS_2 surface and point out that the photoelectron angular distribution from functional organic thin films is broadened considerably by the thermal excitation of molecular vibrations.

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