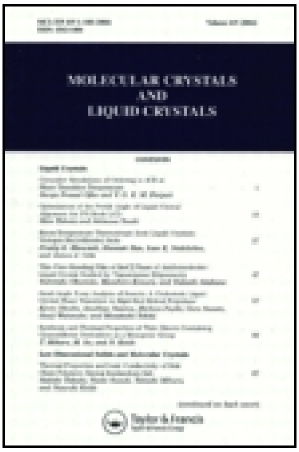

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Observation of Outermost Surface Layers of Phthalocyanine Ultra-Thin Films by Penning Ionization Electron Spectroscopy: Chloroaluminium Phthalocyanine on MoS_2

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Version of record first published: 24 Sep 2006.

To cite this article: Masaru Aoki , Shigeru Masuda , Yuichi Einaga , Koji Kamiya , Nobuo Ueno & Yoshiya Harada (1995): Observation of Outermost Surface Layers of Phthalocyanine Ultra-Thin Films by Penning Ionization Electron Spectroscopy: Chloroaluminium Phthalocyanine on MoS_2 , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 217-222

To link to this article: http://dx.doi.org/10.1080/10587259508033997

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 217–222
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OBSERVATION OF OUTERMOST SURFACE LAYERS OF PHTHALOCYANINE ULTRA-THIN FILMS BY PENNING IONIZATION ELECTRON SPECTROSCOPY
: CHLOROALMINIUM PHTHALOCYANINE ON MoS_2

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ABSTRACT Using Penning ionization electron spectroscopy, which provides information on the local distribution of the individual orbitals exposed outside the outermost surface layer, ultra-thin films (1 to several monolayers) of chloroaluminium phthalocyanine were characterized during layer-by-layer vacuum deposition onto an MoS_2 substrate and the change in the molecular orientation was sensitively detected.

1. INTRODUCTION

Recently considerable effort has been made to obtain molecular electronic devices using organic films.[1] In order to accomplish the purpose we must control the orientation of molecules in the films as well as the film thickness at the molecular level. In this work we have taken up chloroalminium phthalocyanine (ClAlPc) as a model compound of a functional organic molecule and studied the change in the electronic structure and molecular arrangement of the film during layer-by-layer deposition onto a surface of an MoS_2 single crystal by Penning ionization electron spectroscopy.

In Penning ionization electron spectroscopy, the kinetic energy of electrons ejected by collisions between target T and metastable atoms A* is analyzed;

$$T + A^* \rightarrow T^+ + A + e^-, \qquad e^- \text{ for energy analysis.}$$

In contrast to other electron spectroscopies such as photoelectron spectroscopy, Auger electron spectroscopy, and electron impact spectroscopy, which probe an average character of several top layers, Penning ionization electron spectroscopy is selectively sensitive to the outermost surface layer because metastable atoms do not penetrate into inner layers. Furthermore, the orbital of the target molecule extending outside the surface interacts more easily with the metastable atom and gives a stronger band in the Penning ionization spectrum (PIES).[2-5] Thus, the analysis of the relative intensity of PIES provides information on the geometrical orientation of molecules in the outermost layer.

In our earlier work we have studied the structure of ClAlPc films on graphite (cleavage plane) by Penning ionization electron spectroscopy.[6] In this case molecules are oriented flat to the substrate with the chlorine atom protruding outside at one monolayer and they are gradually tilted in subsequent layers with increasing film thickness. In this paper we extend our work to ClAlPc films deposited on MoS_2. Since the outermost surface of an MoS_2 crystal consists of sulfur atoms with trigonal arrangement, the interaction between the ClAlPc molecule and the substrate is much different from the case of the graphite substrate with hexagonal network of carbon atoms. Therefore, the molecular orientation of ClAlPc films on MoS_2 during layer-by-layer deposition is expected to be quite different from that on graphite.

2. EXPERIMENTAL

The details of the experimental apparatus have been described elsewhere.[2] The PIES and UPS (ultraviolet photoelectron spectra) were measured by an ultra-high vacuum (base pressure 10^{-10} Torr) electron spectrometer. Helium metastable atoms He* (2^1S, 20.62 eV and 2^3S, 19.82 eV) were produced by impact of 80 eV electrons. The 2^1S atoms were quenched by a Helium discharge lamp. The excitation source for UPS is the Helium resonance line (21.22 eV) produced by dc discharge using pure Helium gas. A 180° hemispherical-type analyzer was used for electron energy analysis with an energy resolution of about 0.2 eV. The sample of ClAlPc was commercially obtained and purified by vacuum sublimation. The MoS_2 sample is a natural 2H-MoS_2 crystal. For preparing a clean substrate, it was cleaved in air before fixing in the preparation chamber and then heated at about 350° C for 10 h under ultra-high vacuum. The deposited amount of ClAlPc was monitored with a quartz oscillator calibrated in advance. The films of 0.5, 1, 2, 3, 5 and 10 MLE (monolayer equivalence) were prepared onto the substrate held at room temperature. Here the amount of 1 MLE is defined in such that closely packed molecules with their molecular planes parallel to the substrate plane just form a monolayer.

3. RESULTS AND DISCUSSION

Figures 1 and 2 shows the He I UPS and He*(2^3S) PIES of ClAlPc films prepared on the MoS_2 substrate at room temperature. The spectra of the substrate are also shown. In the UPS, MoS_2 peaks (S_1 and S_2) appear up to 3 MLE, showing that photons penetrate through ClAlPc layers and interact with the substrate. In Fig.1 the UPS of ClAlPc have six bands denoted by A-F. By reference to our previous work[6], bands A-F are assigned as follows. Band A is related to π (ring) orbitals, which are mainly distributed along the skeleton of the inner porphine-like ring. Bands B and E are correlated to molecular orbitals with large contribution from the outer four benzene rings [some π (ring) orbitals are also responsible to band B]. Band F can be ascribed to σ orbitals, being located in the high IP region. Finally, bands C and D can be assigned to the nonbonding orbitals of the chlorine atom, Cl($n_{\parallel}$) and Cl($n_{\perp}$), which are distributed parallel and perpendicular to the molecular plane. In Fig.2 PIES shows five bands A-D and F. Further, at 1 MLE the substrate peak S_3 is seen. Therefore, the substrate is not completely covered at room temperature at 1

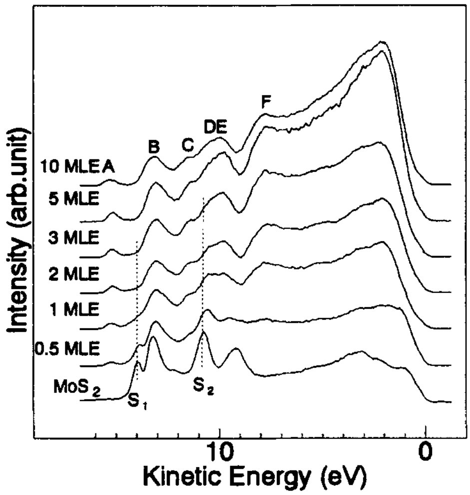

Figure 1 Change in the He I UPS of ClAlPc layers deposited on a MoS_2 cleavage plane held at room temperature with increasing coverage.

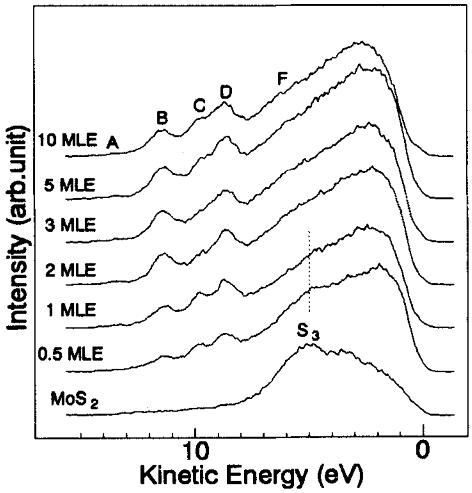

Figure 2 Change in the He*(2^3S) PIES of ClAlPc layers deposited on a MoS_2 cleavage plane held at room temperature with increasing coverage.

MLE. Further discussion on Fig.2 will be given later.

Figure 3 and 4 shows the He I UPS and He* (2^3S) PIES of ClAlPc films heated up to 100 ℃ and measured at the same temperature after preparing at room temperature. In Fig.3 UPS do not change much after the temperature change and show little information on the orientation of molecules in the films. In contrast, the PIES show considerable change (Fig.4). For example, at 1 MLE the substrate peak is almost missing. Since just 1 MLE of ClAlPc shields the MoS_2 substrate from metastable beams, we can conclude that molecules lie flat in the 1 MLE film with their molecular planes oriented parallel to the MoS_2 cleavage plane. Further, the relative intensity of the PIES is seen to change remarkably as a function of the film thickness, while that of UPS scarcely changes (cf. Fig.3). These spectral changes are account for as follows. At 1 MLE ClAlPc molecules are arranged flat to the substrate with chlorine atoms protruding outside the film. When a He* atom approaches a ClAlPc molecule deposited as shown in Fig.5, it effectively interacts with the Cl($n_{\parallel}$), Cl($n_{\perp}$) and π (benzene) orbitals exposed outside, giving stronger bands in the spectrum, while the π (ring) and σ orbitals shielded by the Cl and π (benzene) orbitals show weaker bands. This is the reason why bands B, C and D are intense and bands A and F are

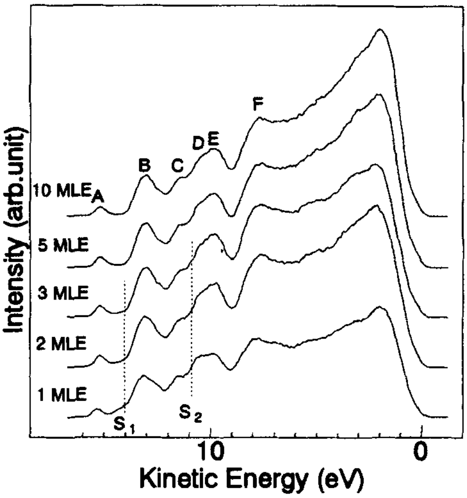

Figure 3 Change in the He I UPS of ClAlPc layers deposited on MoS_2 cleavage plane with increasing coverage. The films were heated up to 100℃ after preparing at room temperature.

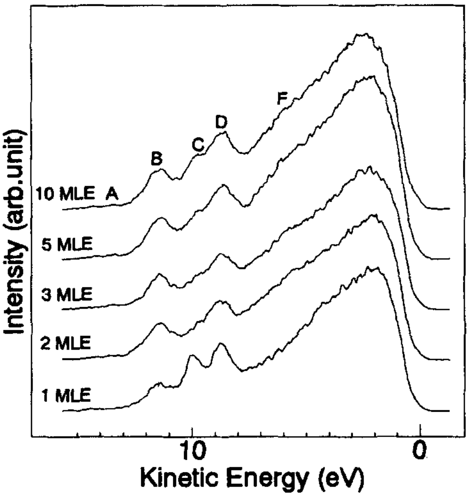

Figure 4 Change in the He*(2^3S) PIES of ClAlPc layers deposited on MoS_2 cleavage plane with increasing coverage. The films were heated up to 100℃ after preparing at room temperature.

scarcely seen at 1 MLE in Fig.4. At 2 MLE the relative band intensity of the PIES clearly changes compared to that of 1 MLE; bands C and D become weaker, while bands A and F appear and band B becomes stronger. This spectral change shows that ClAlPc molecules are tilted in the second layer with chlorine atoms mainly directed to the substrate. As shown in Fig.6, in this case, Cl orbitals corresponding to bands C and D [especially the Cl($n_{\parallel}$) related to band C] are shielded by phthalocyanine rings, and the π (ring) and the σ orbitals correlated to bands A and F are exposed outside compared to the case of the 1 MLE film. The enhancement of band B may be due to the fact that the contribution of π (ring) orbitals partly responsible to band B become greater at the second layer. In Fig.4 we can see that during layer-by-layer deposition bands C and D gradually become stronger and bands A and B weaker compared to the case of 2 MLE. This indicates that the number of molecules with the Cl atom directed to the substrate decreases at the outermost layer with increasing film thickness (see Fig.7).

Now we return to discuss the PIES of the films at room temperature. At 1 MLE the substrate peak S_3 is seen as described before and bands C and D

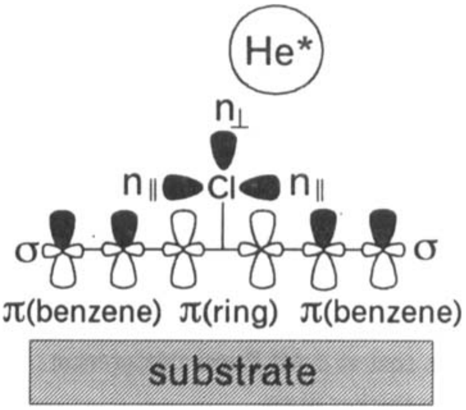

Figure 5 Schematic diagram of a ClAlPc molecule deposited flat on a MoS_2 substrate interacting with a metastable atom. The point of orbitals causing strong interaction are hatched.

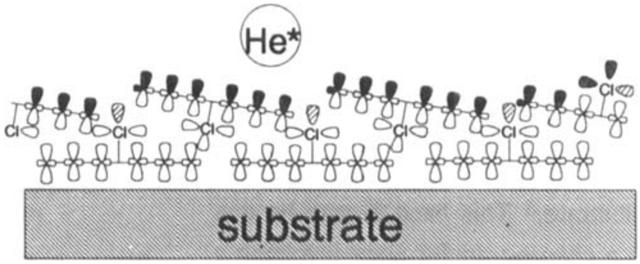

Figure 6 Schematic diagram of ClAlPc molecules tilted at the second layer interacting with a metastable atom.

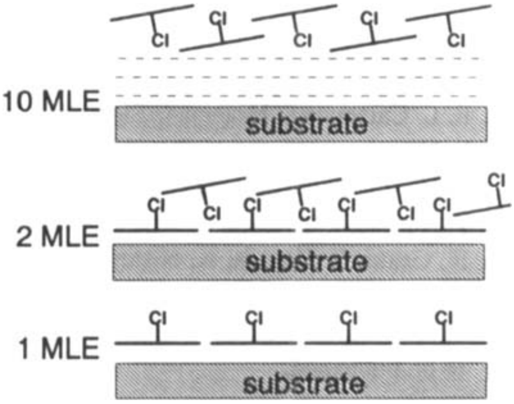

Figure 7 Schematic diagram showing the change in the molecular orientation of the outermost layer with increasing film thickness.

are rather weak (Fig.2). This means that molecules are randomly oriented on the substrate causing lower coverage and loss in the intensity of the Cl lone-pair bands. Upon heating this 1 MLE film to 100℃, molecules are oriented flat to the substrate with Cl atoms protruding outside, as described above (Fig.4). This flat orientation is considered to be more stable on the MoS_2 substrate, because the spectrum shows almost no change after recooling the substrate to room temperature. In Fig.2 the relative intensity of the PIES dose not change much with increasing film thickness. Therefore, random orientations similar to that at 1 MLE are also present in the thicker films.

Figure 8 shows a higher E_k region of He*(2^3S)PIES of ClAlPc films heated up to 100℃ after preparing at room temperature. In the figure a small band X is seen at higher E_k (lower IP) than the top band A. The corresponding band is not observed in the UPS as well as in the PIES of ClAlPc on the graphite substrate.[6] This band X may be due to a charge-transfer state involving a π (ring) orbital. The details will be described elsewhere.

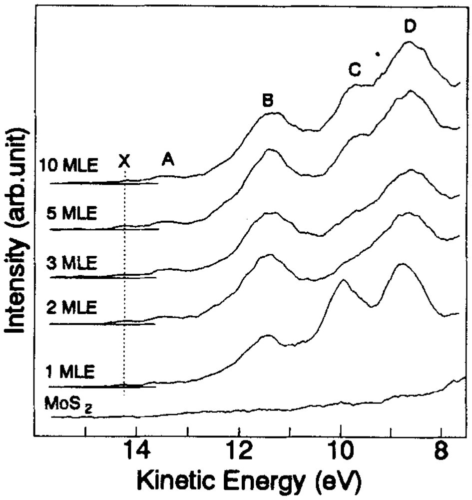

Figure 8 Higher E_k region He*(2^3S) PIES of ClAlPc films heated up to 100℃ after preparing at room temperature.

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