

Orientation of Perfluorinated Phthalocyanines: from Ultra-low Coverages on Hydrogen Passivated Silicon to Thick Layers

M. Gorgoi, G. Gavrilă, D.R.T.Zahn

Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

W. Michaelis

IAPC, Universität Bremen, D-28334 Bremen, Germany

D. Schlettwein

Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35392 Gießen, Germany

W. Braun

BESSY GmbH, Albert-Einstein-Str. 15, D-12489 Berlin, Germany

Hybrid devices such as organic light emitting diodes, solar cells or thin film transistors, based on phthalocyanine (Pc) materials and silicon receive special attention nowadays. Pcs have a tendency to form ordered layers, however the growth mode may vary significantly on different substrates [1]. Moreover the first layers near the interface seem to have a structure distinct from the thick films. Consequently the present work was directed towards determining the molecular orientation of phthalocyanine monolayers and thin films using polarization dependent X-ray absorption spectroscopy. The organic materials involved are the copper phthalocyanine (CuPc) and its fluorine derivatives: F₄CuPc and F₁₆CuPc. Hydrogen passivated p-type (111) oriented silicon provided by Siltronic AG with a doping concentration of approximately $1.5 \times 10^{15} \text{ cm}^{-3}$ was used as the substrate. The passivation process consists of a wet chemical etching in a solution containing HF 40%. After the

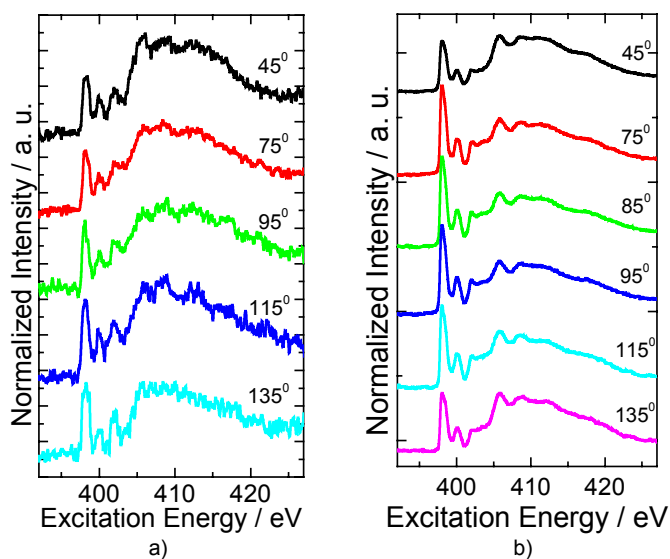


Figure 1. N1s excitation spectra of CuPc 2 monolayers a) and CuPc 20 nm b) as a function of θ the angle of incidence; The lower energy features (398-403 eV) represent the π^* resonances, whereas those features above 403 eV are related to the σ^* resonances.

passivation process the samples were transferred into UHV. All measurements were performed on freshly evaporated organic layers. Their thickness was monitored by a quartz microbalance. The experiments were performed on the MUSTANG spectroscopy chamber at the Russian-German beamline at BESSY II. The NEXAFS spectra were acquired with a PHOIBOS 150 (SPECS) analyzer. The N1s NEXAFS raw data were divided by the spectra of the H-Si(111), background was subtracted and normalized to the absorption step at 425eV photon energy. A series of NEXAFS measurements were performed as a function of thickness and angle of incidence of the synchrotron radiation.

Figure 1 displays the CuPc N1s excitation spectra for 2 monolayers a) and 20 nm thickness b) as a function of the angle of incidence θ (normal incidence $\theta = 90^\circ$) of the synchrotron radiation. The intensity of the π^* (relative to the σ^* one) resonances has a maximum at $\theta=135^\circ$ Fig. 1 a) and $\theta=85^\circ$ Fig.1 b). However, the intensity and features of σ^* resonance are still visible at the given incidence

angles. This suggests the presence of short range ordering in both cases. This behaviour is similar to $F_4\text{CuPc}$ but opposite of $F_{16}\text{CuPc}$ which is rather well ordered.

The quantitative analysis of the NEXAFS excitation spectra for CuPc , $F_4\text{CuPc}$ and $F_{16}\text{CuPc}$ is provided in figure 2. Figure 2 exhibits the normalized resonance intensity of the π^* orbitals as a function of the incidence angle of the synchrotron radiation for the three phthalocyanines. The normalized resonance intensity of the π^* orbitals is fitted [2] and the average tilt-angle for each case is calculated. The 3-fold symmetry of the silicon substrate is lifted by the surface roughness and as a consequence the model used for the fit contains an azimuthal dependence as well.

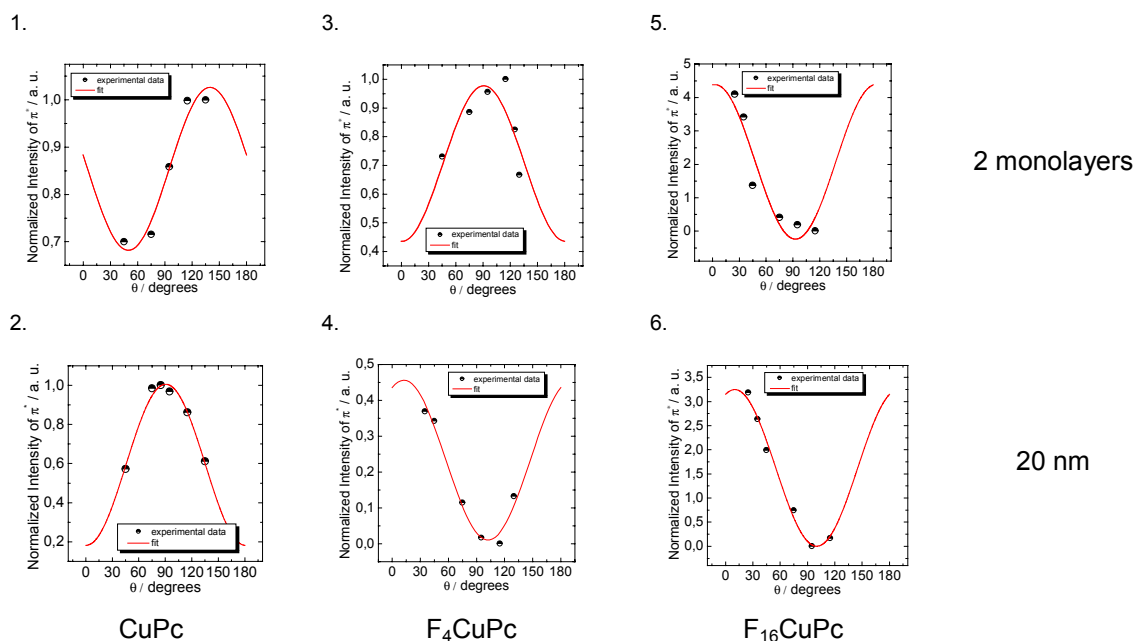


Figure 2. Normalized resonance intensity of the π^* orbitals as a function of the incidence angle θ of the synchrotron radiation – experimental data and fit.

Table 1 summarises the results in terms of tilt angles α and azimuthal angles Φ obtained from the fits as well as the average orientation of the molecules. While CuPc and $F_4\text{CuPc}$ behave in a similar way

	CuPc	$F_4\text{CuPc}$	$F_{16}\text{CuPc}$
2 ML	$\alpha=70^\circ \pm 2^\circ$	$\alpha=90^\circ \pm 3^\circ$	$\alpha=26^\circ \pm 2^\circ$
	$\Phi=108^\circ \pm 3^\circ$ tilted	$\Phi=55^\circ \pm 5^\circ$ standing	$\Phi=84^\circ \pm 5^\circ$ almost lying
20 nm	$\alpha=90^\circ \pm 1^\circ$	$\alpha=60^\circ \pm 2^\circ$	$\alpha=10^\circ \pm 2^\circ$
	$\Phi=45^\circ \pm 2^\circ$ standing	$\Phi=82^\circ \pm 4^\circ$ tilted	$\Phi=0^\circ \pm 0.3^\circ$ lying

in terms of adsorbate geometry with a tilt-angle of the molecular plane higher than 50° , the $F_{16}\text{CuPc}$ molecule behaves differently. Regarding the two measured thicknesses it is important to point out the different molecular orientations found in 2 monolayers and in a thin film of 20 nm for each phthalocyanine. This finding confirms previous results for CuPc [3] and represents a new step in describing the $F_4\text{CuPc}$ and $F_{16}\text{CuPc}$

molecules. The authors acknowledge the BMBF (FK MUSTANG 05KS40C1/3, OS ES3XBA/5) for the financial support and Mike Sperling for his assistance during the beam time.

References

- [1] H. Peisert, T. Schwieger, J. M. Auerhammer, M. Knupfer, M. S. Golden, J. Fink, P. R. Bressler M. Mast, J. Appl. Phys. 90 (2001) 466;
- [2] J. Stöhr, NEXAFS Spectroscopy, Surface Science Series, Springer, 1996.
- [3] K. K. Okudaira, S. Hasegawa, H. Ishii, K. Seki, Y. Harada, N. Ueno, J. Appl. Phys. 85 (1999) 6453;