# Growth of Metal-Phthalocyanine on GaAs(001): an NEXAFS study

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**Abstract**

Organic semiconductors molecules are often employed as a thin film interlayer to improve electronic and optoelectronic devices. The characterisation of the interface is thus important to understand the physical properties between the organic thin film and the inorganic semiconductor substrate. Also the orientation of the molecules within the film can be of importance. Two molecules, SnPc and MgPc, are studied on argon sputtered GaAs(001)-1×6 using a surface sensitive synchrotron-based technique, Near Edge X-Ray Absorption Fine Structure (NEXAFS). With NEXAFS, the orientation of the molecule is investigated. It is shown that these two molecules have different orientations in thick films, e.g. SnPc lying close to flat to the surface whereas MgPc is 'standing up'. At the monolayer level, however, the SnPc spectra are unchanged, while the MgPc spectra show an orientation reversal. The spectra are discussed with respect to bulk crystalline strucures.

Keywords: Phthalocyanine, GaAs, NEXAFS, semiconductor, organic

## 1. Introduction

Organic semiconductors are being widely introduced in the fabrication of hybrid electronic devices [1, 2]. Thin organic films are often used as adayers or interlayers in multilayer devices. The internal structure of organic thin films can have a significant role on the properties of the film and thus in the final device. A good example is lead phthalocyanine, which exhibits a conductivity several order of magnitude higher for the monoclinic crystalline form compared to the triclinic phase [3, 4]. It has been shown that using SnPc as an interlayer between the inorganic semiconductor and the metal in a Schottky diode can considerably improve the device [1, 5]. The internal

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structure of the film can also affect other properties, i.e. reduction or increase of charge carriers, optical properties (different absorption for different crystalline phases). Thus it is important to understand the growth and structure of such films.

In this work, thin films of two metal phthalocyanines, MgPc and SnPc ($MC_{32}H_{16}N_8$), are deposited on the GaAs(001)-1x6 surface. Metal phthalocyanines are symmetrical macrocycle molecules exhibiting aromatic behaviour due to the delocalised electron density of the π-bonds above and below the plane of the molecule. MgPc is a planar molecule whereas SnPc adopts a shuttlecock shape due to steric effect [6]. They are thermally stable and can form well ordered crystalline structures with high purity [7, 8].

This work investigates thin and intermediate thickness layers to probe the influence of the substrate on the first few layers of the organic thin film. The orientation of the molecules within the thin film is investigated by probing the intensity of the NEXAFS π and σ resonances as a function of the polarisation vector of the light; in this case the focus is on the π orbitals which are perpendicular to the plane of the molecule.

## 2. Experimental

NEXAFS experiments were performed on beamline 1.1 (bending magnet) at the Daresbury synchrotron radiation source. Total and partial electron yield NEXAFS spectra were taken at the nitrogen 1s edge. The variable angle α is the angle of incidence of the photon beam relative to the surface normal which is equivalent to the angle between the E-vector and the surface. An important factor is the degree of polarisation of the light, which is estimated to be 85%. NEXAFS normalisation is a two-step process and is described in more detail elsewhere [9].

n-type GaAs(001) substrates supplied by Freiberger Compound Materials, were prepared by argon sputtering with a beam energy of 500 eV and annealing at 770 K. A 1×6 LEED pattern was observed.

The organic molecules were firstly purified in UHV by degassing for several hours at just under evaporation temperature. MgPc and SnPc thin films were deposited by organic molecular beam deposition (OMBD) using a Knudsen cell with an evaporation rate of 1 Å $min^{-1}$. The deposition rate was monitored using a quartz microbalance assuming unity sticking coefficient.

## 3. **Results and discussion**

### 3.1. MgPc

Figure 1 (left panel) shows the N1s edge NEXAFS for a 60 Å layer of MgPc deposited on the GaAs(001)-1×6 surface. The π* features are enhanced for low angles of incidence indicating that the molecules lie close to perpendicular to the surface. The evolution of resonance intensities for 60 Å and 3 Å layers are shown in the right panel. The best fit for the 60 Å layer is for an average molecular tilt angle of 65°. For a 3 Å layer the best angle for the fit is 45°.

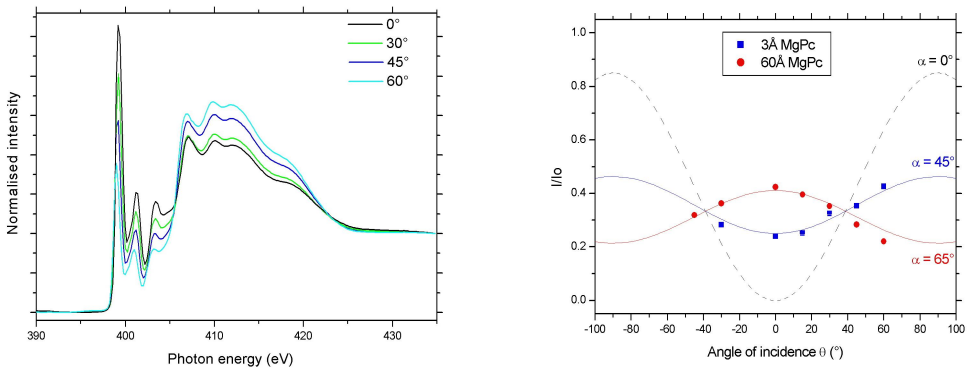


Fig. 1. Left: Normalised NEXAFS spectra at the N1s absorption edge for a thick MgPc film (60Å) deposited on the GaAs(001)-1×6 surface. Spectra were taken in total and partial yield mode. Right: Evolution of the π* peak intensities versus the angle of incidence for a thick MgPc film (60Å) deposited on the GaAs(001)-1×6 surface. Expected curves for molecule tilt angles of 0°, 45° and 65° are plotted along side the original data assuming a polarisation factor of 0.85.

Planar phthalocyanines such as MgPc have two main crystalline structures, the α and the β forms. They differ in angle of the molecular plane with respect to the stacking b-axis. For the α-form this angle is 25° to 30° and 45° to 48° for the β form. The intensities of the π* features indicate that the plane of the molecules has an angle of 65° with the surface of the substrates. This corresponds to an α-form stacking with the b-axis parallel to the substrate.

For an equivalent 3 Å deposit (approximately one monolayer), the plane of the molecule has a tilt angle of 45° with the surface of the surface. For a 1 Å layer deposited on Ge(001) this angle was found to be 25° [9], that is, tending to the α-form stacking with the b-axis perpendicular to the substrate.. The result here may represent a difference in interaction but it can also be explained by the possibility that a slightly thicker layer was deposited on GaAs. In this case the molecules in the second layer are already starting to lift off the surface thus increasing the average angle of tilt. Thus

there is a change in the molecular orientation in the first few layers where the molecules rearrange themselves into the α-form crystalline structure with the b-axis parallel to the surface of the substrate.

### 3.2. SnPc

Figure 2 (left panels) shows N1s edge NEXAFS for thin and thick adlayers (3 Å and 40 Å) of SnPc deposited on GaAs(001)-1×6 and the evolution of the π* peak intensity versus the angle of incidence (right panels). The resonance intensities of the NEXAFS spectra clearly show that the π* features are strongly reduced at low angles meaning that the plane of the molecule is roughly parallel to the surface. For the 3 Å and 40 Å, the evolution of the π* peak intensity is best fitted assuming, in both cases, an average molecular tilt angle of 25°.

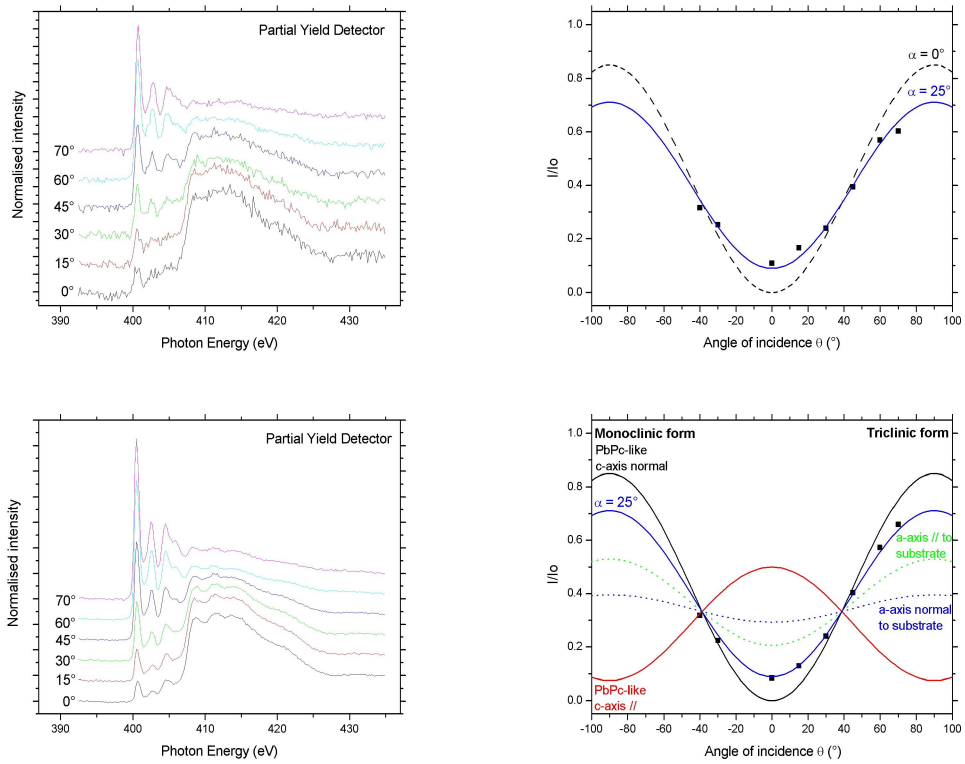


Fig. 2. Left: Normalised NEXAFS spectra at the N1s absorption edge for a 3 Å (top) and a 40 Å (bottom) SnPc film deposited on the GaAs(001)-1×6 surface. Spectra were taken using a partial yield detector. Right: Evolution of the π* peak intensities versus the angle of incidence. Expected models for molecule tilt angles of 0° and 25° are plotted along side the original data assuming a polarisation factor of 0.85.

The best fit for a 3 Å layer is for an angle of tilt of 25°, which indicates that the molecules are not lying exactly flat on the surface. This picture is very similar to that of MgPc on Ge(001). For the SnPc 40 Å layer, the analysis will be made with respect to known crystalline structures. The most reported form for SnPc is the triclinic form [6]. To our knowledge there is only one reference to the monoclinic form [10]. The curves representing the different bulk crystalline forms are plotted alongside the data. For the triclinic form, two extreme orientations are shown for the crystallographic a-axis parallel and perpendicular to the substrate, the green and blue dashed lines respectively. The sole mention of a monoclinic form is not specific but two possibilities can be considered. The first possibility is a PbPc-like monoclinic form [3]. In this case, curves for two extreme orientations are plotted in which the c-axis is parallel and perpendicular to the substrate, the red and black full lines, respectively - the orientation with the c-axis perpendicular to the substrate is equivalent to all the molecules lying flat on the surface (i.e. $\alpha$=0°). The second possibility is a MgPc-like monoclinic form.

It is clear that the range of the triclinic curves cannot accommodate the data. The range of curves for the PbPc-like monoclinic form would place the data close to the case of the c-axis normal to the substrate (black line). A tilt of 25° of the stacking c-axis would accommodate the data as would a polycrystalline mixture in which this form is dominant. Finally, a MgPc-like monoclinic $\alpha$-form would also fit. These are indistinguishable.

Similar NEXAFS results have been observed for SnPc molecules on passivated semiconductor substrates [8] and on Ge(001) [9] suggesting that the adlayer orientation for a thick film of SnPc is largely independent of substrate type.

### 3.3. Discussion

In both cases, the spectra for thin and thick layers are very similar (polarisation-dependences apart) indicating little changes in the unoccupied states upon deposition. This is indicative of a weak interaction between the first layer and the substrate. This is in agreement with photoemission work [11].

For a monolayer, both SnPc and MgPc are lying close to flat to the surface. LEED and STM studies of PbPc and CuPc on other substrates tend to report completely flat structures [12-14]. However, these NEXAFS data suggest that a degree of tilt is always involved. Of course, admixing of opposing structures can create this result.

If the molecules show the same orientation for monolayers, they clearly differ for thicker films:
- MgPc grows in the $\alpha$-form but with its b-axis parallel to the surface. In this case the plane of the molecule makes an angle of 65° with the surface of the substrate. This

involves a reorientation of the molecules in the first few layers. This means that the stacking axis is parallel to the surface. The π orbitals of adjacent molecules will overlap in the plane parallel to the surface thus the charge mobilities should be enhanced in that plane

- For SnPc, there are different possible interpretations as to the crystalline form adopted. A pure triclinic form can be excluded. For a PbPc-like monoclinic form, the data is closer to the case with the c-axis normal to the substrate. The presence of another crystalline form or a tilt of 25° of the stacking c-axis of the PbPc-like monoclinic form would accommodate the data. Equally, a MgPc-like monoclinic α-form would also be possible.

## 4. Conclusions

Two metal phthalocyanines have been deposited on GaAs(001)-1×6 substrates. NEXAFS spectra show that there is no redistribution of the unoccupied states upon deposition indicating that the molecule is still intact, confirming that the interaction between the substrates is weak. Furthermore NEXAFS allowed the orientation of the molecules within the film to be determined. At a monolayer level, both molecules are lying close to flat on the surface. For thicker films, results suggest that the molecular orientation is independent of the substrate and each molecule exhibits a different molecular orientation. MgPc grows in the α-form with its b-axis parallel to the surface, which involves a reorientation of the molecules in the first few layers. For SnPc, PbPc-like monoclinic crystallites with the c-axis normal to the substrate is an approximate interpretation. However, the presence of other crystalline forms or a tilt of 25° of the stacking c-axis for this structure would fully accommodate the data. Equally, a MgPc-like monoclinic α-form is possible. MgPc shows a higher degree of orientation which could be more suitable for the fabrication of hybrid devices. However due to the flipping of the molecules in the first few layers, the characteristics of such a device could be highly dependent on the interlayer film thickness.

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