Using TEM and XRD to probe crystal orientation in organic thin films grown with OMBD

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Abstract. Correlating X-ray diffraction data with images of lattice fringes obtained in the transmission electron microscope allows diffraction from planes in crystalline materials to be studied from different perspectives. The focus of this work is on the characterisation of thin films of copper phthalocyanine prepared using organic molecular beam deposition. Films grown on silicon have been studied using X-ray diffraction, which identifies that the (100) plane lies parallel to the substrate surface. Films grown on amorphous carbon have been studied using transmission electron microscopy which confirms that the (001) plane is close to perpendicular to the substrate surface. The promotion of a different crystal orientation can be achieved by deposition of copper phthalocyanine on to a film of perylene tetracarboxylic dianhydride. The X-ray diffraction data of these films shows that the (11-2) plane is now parallel to the substrate surface and this is confirmed by the observation of lattice fringes corresponding to the (100) plane in the transmission electron microscope. The information obtained can be used to correctly predict the angles needed to tilt the sample in the transmission electron microscope to observe lattice fringes from both the (100) and (001) planes in the double layer films.

1. Introduction
Organic semiconducting materials can be used for electronic and optoelectronic applications such as transistors and solar cells and, because they are relatively cheap and significantly lighter [1], they could provide an alternative to conventional silicon based semiconductors. These possible applications have driven considerable research in this area. Organic photovoltaic devices are a combination of electron donor and acceptor materials, the interface between which results in the dissociation of excitons (bound electron-hole pairs, formed by the absorption of a photon in the organic layer) [2]. The small, macrocyclic, aromatic molecule copper phthalocyanine (CuPc), has shown to be a good donor layer for photovoltaic devices when combined with fullerene (C_{60}) as an acceptor material [3]. One method used to prepare these organic photovoltaic devices is organic molecular beam deposition (OMBD), which involves the sublimation under vacuum of the source material from a Knudsen cell [4]. The sublimed species is collimated by an aperture into a beam and deposited onto the substrate located above the source. On weakly-interacting substrates (non-chemisorbing), CuPc grows as crystalline grains in the α-phase [5]. The crystal structure of these grains can be probed with X-ray diffraction (XRD) to estimate both crystal phase and texture, i.e. which planes will be lying parallel to the substrate surface. Transmission electron microscopy (TEM) can be used to identify which planes are close to perpendicular to the substrate surface in top views of thinner but otherwise equivalent films grown on carbon coated copper TEM grids, by measuring the interplanar spacing of lattice...
fringes found in the crystalline grains. This information can be correlated with XRD results. The orientation of the crystallographic planes will then indicate molecular orientation. Since charge transport in CuPc is anisotropic with respect to molecular orientation, this information is important when growing films for electronic applications. On weakly-interacting substrates at room temperature, α-CuPc will grow with the molecular plane close to perpendicular to the substrate surface, i.e. the undesirable orientation for electronic applications. The promotion of a more desirable molecular orientation can be achieved by growing the CuPc film on a previously deposited film of perylene tetracarboxylic dianhydride (PTCDA), another small, aromatic molecule. Molecules of PTCDA are known to lie close to parallel to the substrate surface. This will cause the CuPc molecules to be oriented so that the molecular plane is also close to parallel to the substrate surface. This promotion is attributed to the strong π-π interaction that would occur at the interface between these two materials [6].

2. Method
Films of CuPc (395 nm) and CuPc (436 nm) on PTCDA (247 nm) were grown on a Si (100) substrate in a Kurt J. Lesker high vacuum chamber (base pressure about 10⁻⁸ mbar, with a growth rate set at 1 Å/s). Films of CuPc and CuPc on PTCDA were also grown directly onto carbon coated copper TEM grids (Agar) with the same conditions as for the Si substrates but thicknesses set to 50 nm for both CuPc and PTCDA. SEM imaging was performed in a Gemini Leo 1525 microscope with a field emission gun (FEG), operated at an accelerating voltage of 10 kV and a 30 µm aperture. CuPc and CuPc/PTCDA films grown on the silicon substrate were probed with XRD using a Philips PW1700 series diffractometer operated in theta-2-theta using Cu Kα radiation at 40 kV and 40 mA. Each scan was performed from 2θ = 5 - 30° with a step size of 0.033° and a time per step of 99.7 s. All XRD data has been interpreted using the model proposed by Hoshino et al. [5], although this is different from work done by others e.g. Sullivan et al. [6]. The films of CuPc and CuPc/PTCDA that were grown on carbon coated copper TEM grids were examined using a JEOL 2010F with a LaB₆ crystal source and operated at 120 kV. Measurements were obtained using the line profile tool in Gatan’s digital micrograph program.

3. Results

3.1. CuPc Single Layer
The growth of grain structures of CuPc on Si (100) can be observed (figure 1a). XRD data of this film confirms that the film is crystalline, adopting the α-phase model proposed by Hoshino et al. [5] and that diffraction from the (100) plane (at 2θ = 6.9°) is the predominant diffracting plane (figure 2a). Diffraction from this plane means that the orientation of the CuPc molecules will be almost perpendicular to the substrate surface (figure 2b). The presence of peaks at 2θ = 13.7° and 27.7° which arise from diffraction from the (200) and (400) planes also confirms this. Diffraction from other planes (the (001) plane at 2θ = 7.3°, (01-1) at 24.0° and (111) at 26.7°) suggest that the preferred orientation of the film is not perfect, this is attributed to the grains not all having the same growth direction at high thicknesses. The films grown on carbon coated copper TEM grids are thin enough to be transparent to the electron beam. The presence of lattice fringes confirm that the films are crystalline and the distance between these fringes suggests diffraction from the (001) plane, 1.2 nm (figures 2c and d). Diffraction from these planes occurs when they are close to parallel to the electron beam, meaning that the molecules are almost perpendicular to the substrate surface, confirming the XRD data.

3.2. CuPc/PTCDA Double Layer
The grain growth seen in the CuPc single layer cross section appears to be preserved when grown on a film of PTCDA (figure 1b). However, the XRD data suggests a large deviation from the single layer crystallinity. The peak resulting from diffraction from the (100) plane is not present, and a large peak
at 27.5° suggests diffraction from the (11-2) plane (figure 3a). When the (11-2) plane lies parallel to the substrate surface the molecular plane will be almost parallel to the substrate surface (figure 3b).

**Figure 1** a) An SEM image of a 395 nm CuPc film grown on silicon which has been cleaved to reveal a cross section. b) A 436 nm CuPc film grown on a 247 nm PTCDA film on silicon.

**Figure 2** a) XRD from a 395 nm CuPc film grown on Si (100). b) Schematic of X-Ray diffraction occurring on planes parallel to the substrate surface. c) Schematic of electron diffraction occurring on planes more perpendicular to the substrate surface (plane tilt exaggerated for clarity). d) TEM image showing lattice fringes corresponding to diffraction from the (001) plane (1.2 nm) in thinner films grown on carbon coated TEM grids.

**Figure 3** a) XRD from a 436 nm CuPc film grown on 247 nm PTCDA film. The main peak is now due to diffraction from the (11-2) plane which shows that the molecular plane is now nearly parallel to the substrate surface. b) X-ray diffraction schematic. c) Electron beam diffraction schematic when the (11-2) plane is parallel to the substrate surface. d) Fringes corresponding to diffraction from the (100) plane (1.3 nm) visible when the (11-2) plane lies parallel to the substrate surface.
The change in crystal orientation will therefore cause the (100) plane to be close to perpendicular to the substrate surface, and therefore close to parallel to the electron beam when imaging the films grown on carbon coated copper TEM grids. The presence of lattice fringes with a spacing of 1.3 nm confirms that the (100) plane does lie almost parallel to the electron beam, therefore confirming data from the XRD (figures 3c and d). Diffraction patterns of the single and double layer films cannot currently be obtained, this being attributed to the sensitivity of the material to the electron beam and the short time that the fringes exist before being degraded.

On examining the crystal structure of α-CuPc, it can be seen that when the (11-2) plane is parallel to the substrate surface the (100) plane will diffract the electron beam. It can also be seen that it would be possible to bring the both the (100) and the (001) planes to a position where diffraction will occur by tilting the sample 28° and 13° in perpendicular directions, giving rise to lattice fringes from both the (100) and (001) planes that are perpendicular to each other (figure 4).

Figure 4 A CuPc unit cell viewed perpendicular to the (11-2) plane, showing how by tilting the sample crystalline regions can be brought into a position where both the (100) and (001) planes show up as lattice fringes perpendicular to each other in the images.

4. Conclusions
The results show that films of CuPc grown by OMBD form grain structures which are crystalline. For CuPc films grown on silicon substrates at room temperature the α-CuPc crystal structure arises. XRD data shows that the preferred crystal orientation is one in which the (100) plane is parallel to the substrate surface. This is confirmed by observing lattice fringes in CuPc films grown directly onto TEM grids which have a spacing corresponding to diffraction from the (001) planes. When CuPc is grown on a film of PTCDA, a different crystal orientation arises in which the (11-2) plane is now parallel to the substrate surface, shown by XRD data as a peak occurring at 27.5°. This is again confirmed by observing lattice fringes within grains that correspond to diffraction from the (100) plane, which would occur when the (11-2) plane is parallel to the substrate surface. The (001) as well as the (100) planes can both be imaged by tilting the sample, which brings both these planes into a position where diffraction will occur. This results in lattice fringes that are perpendicular to each other being observed. The results show that XRD data can be confirmed with data obtained in the TEM.

References
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