# Film formation of non-planar phthalocyanines on copper(I) iodide†

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Structural templating is frequently used in organic photovoltaic devices to control the properties of the functional layers and therefore improve efficiencies. Modification of the substrate temperatures has also been shown to impact the structure and morphology of phthalocyanine thin films. Here we combine templating by copper iodide and high substrate temperature growth and study its effect on the structure and morphology of two different non-planar phthalocyanines, chloroaluminium (ClAlPc) and vanadyl (VOPc) phthalocyanine. X-ray diffraction, atomic force microscopy and low energy ion scattering show that both the morphology and the structure of the films are starkly different in every case, highlighting the versatility of phthalocyanine film growth.

## Introduction

Structural templating layers are widely employed in organic electronic devices as a method to alter the structure and morphology of organic semiconductor films.[1–4] Many structural templating layers, both organic and inorganic, have been shown to provide improvements in device parameters.[5–9] Copper(I) iodide has attracted particular attention for its templating effects in small molecule photovoltaic devices.[1,2,10] Of particular interest is the difference in the effect of CuI on phthalocyanine thin films depending on their planarity and the chemical identity of the central metal atom/moiety. Additionally there is little understanding of the film formation processes of structurally templated phthalocyanine layers.[11]

Our previous work has shown that growth onto templating surfaces held at elevated temperatures produces films which have structures and morphologies that are vastly different to their room temperature counterparts.[12] In this paper we present the growth behaviour of chloroaluminium phthalocyanine (ClAlPc) on CuI (111) thin films at elevated surface temperatures. We investigate ClAlPc film formation on CuI, with increasing thickness using atomic force microscopy (AFM) and low energy ion scattering (LEIS) and compare it to another non-planar phthalocyanine, vanadyl phthalocyanine (VOPc). The structural templating effect of CuI on ClAlPc is starkly different

from that reported for VOPc and this is reflected in the structure and morphology of each.

## Experimental details

Copper iodide 98% (Sigma Aldrich, UK) was used as received and evaporated from a home built evaporator at 310 °C at a rate of 0.3 Å s$^{-1}$ as measured by a calibrated quartz crystal microbalance. VOPc 80% (Acros Organics, BE) and ClAlPc 85% (Sigma Aldrich, UK) were both triply purified by thermal gradient sublimation and the resulting crystals were used for growth from a home built evaporator at 370 °C and 390 °C, respectively, and at a rate of 0.3 Å s$^{-1}$. All films were grown in a custom built ultra-high vacuum (UHV) chamber with a base pressure of 3 × 10$^{-9}$ mbar in which inorganic and organic materials were sublimed onto elevated temperature substrates. A K-type thermocouple mounted close to the sample and calibrated using an optical pyrometer was used to measure the substrate temperature. The substrates used were 10 × 10 mm pieces of thermally oxidized silicon (100) single crystal (IDB technologies, UK) cleaned *via* sonication in Decon-90/de-ionised water mix, acetone and isopropanol. These were dried in a stream of dry nitrogen and cleaned in UV-ozone before being loaded into vacuum. Thin film X-ray diffraction (XRD) patterns were measured using a PANalytical X'Pert Pro MRD diffractometer with monochromatic Cu Kα$_1$ radiation. Atomic Force Microscopy (AFM) images were recorded using an MFP-3D AFM (Oxford Instruments Asylum Research, Santa Barbara, USA) in AC mode (tapping mode) using Olympus AC240-TS silicon tips. Low Energy Ion Scattering (LEIS) was carried out using an IONTOF Qtac$^{100}$ LEIS instrument. A 3 keV He primary ion beam was rastered over a 500 μm$^2$ area, with an ion beam current of 4400 nA. Total scan time was 100 s and the ion beam dose delivered to the sample surface was 2.76 × 10$^{12}$ ions. The

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scattered primary ions were collected over an energy range of 500 to 3000 eV, in order to identify the scattering peaks of the Cu and I at 2379 and 2674 eV, respectively.

## Results and discussion

### Structure and morphology of ClAlPc on CuI (111)

Thin films of ClAlPc (50 nm), CuI (111) (30 nm) and bilayers of ClAlPc (50 nm)/CuI (30 nm) were prepared at elevated substrate temperatures in accordance with the methodology reported previously and in the experimental section.[13] Our previous work has shown that the (111) orientation of CuI is responsible for the structural templating interaction and therefore the focus of our investigations has been on (111) oriented films.[13–15]

X-ray diffractograms (Fig. 1) of 50 nm ClAlPc films grown on SiO$_2$ at $T_{sub} = 155$ °C show two peaks, at $2\theta = 6.8°$ and 27.1°. According to the crystal structure of ClAlPc reported by Wynne (CCDC No. 1134071) these peaks correspond to the (001) and (004) orientations respectively.[16] These peaks suggest the molecules of ClAlPc adopt a "lying down" orientation with the plane of the molecule parallel to the surface. AFM topography images of these films (Fig. 1) show small faceted grains and exhibit a root mean square roughness ($R_q$) of 26.8 nm. For comparison the equivalent film grown at ambient substrate temperature exhibits no peaks in its X-ray diffractogram (Fig. S1†). Morphologically the film has a low $R_q$ (3.2 nm) and is comprised of small spherical grains (Fig. S1†).

Equivalent ClAlPc films grown sequentially on to 30 nm (111) oriented films of CuI are structurally distinct. At $T_{sub} = 25$ °C diffraction measurements show a peak at $2\theta = 25.9°$ which can be assigned to the $(04\bar{1})$ plane (Fig. S2†). The presence of this peak suggests that the ClAlPc molecules are adopting a "standing up" orientation with their ligand molecular planes perpendicular to the substrate. The morphology of the ClAlPc film is similar to that on SiO$_2$ in identical conditions. The film is comprised of small spherical grains and has a low $R_q$ of 3.5 nm (Fig. S2†). In contrast 50 nm ClAlPc thin films grown on a 30 nm (111) oriented CuI films at $T_{sub} = 155$ °C exhibit three diffraction peaks in corresponding X-ray diffractograms (Fig. 2).

These peaks are observed at $2\theta = 13.4°$, 27.0° and 55.8° and can be assigned to the (111), (222) and (444) orientations of ClAlPc. The {111} Miller planes imply the ClAlPc molecules adopt an orientation in-between "lying down" and "standing up" relative to the substrate. In addition to the change in structure
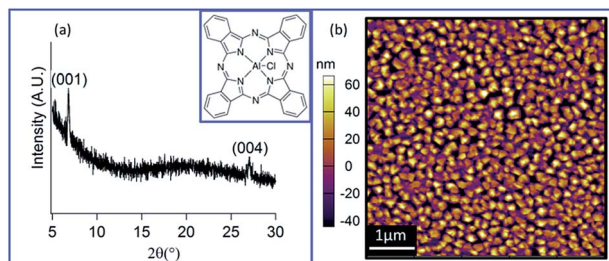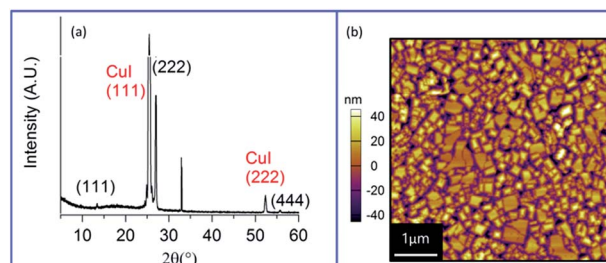


Fig. 2 (a) XRD pattern and (b) AFM topography image of 50 nm ClAlPc/ 30 nm CuI/SiO$_2$ both layers grown at $T_{sub} = 155$ °C.

caused by growth at an elevated substrate temperature, the morphology of the ClAlPc film exhibits a change (Fig. 2) with larger, more rectangular grains present and an $R_q$ of 27.4 nm.

The change in morphology and structure on increasing growth temperature of structurally templated ClAlPc films is similar to the behaviour observed in thin films of VOPc on CuI.[17] Although templating at an elevated substrate temperature results in both phthalocyanine molecules exhibiting a change in structure, the resulting structures of both thin films are significantly different. XRD measurements of templated VOPc films show an adoption of two distinct molecular orientations, one perpendicular to the plane of the substrate the other parallel. In addition to the differences in structure between the two molecules the growth mechanisms for both molecules are different as will be seen below.

### Film formation of ClAlPc on CuI (111)

Thin films of ClAlPc were grown ($T_{sub} = 155$ °C) at a range of thicknesses (1, 2.5, 5, 10, 25 nm) onto 30 nm (111) oriented CuI films. AFM was used to probe the growth mode of the phthalocyanine film by examining the morphological evolution at these intermediate points. At the lowest thickness of ClAlPc (1 nm ($R_q = 6.76$ nm)) there are few discernible features which can be attributed to the phthalocyanine layer (Fig. 3) and the morphology is characteristic of the CuI first layer.[15] At ClAlPc thickness of 2.5 nm the onset of film formation can be observed as additional grain boundaries appearing on grains of CuI. This becomes more pronounced at 5 nm, where CuI grains appear bisected by dark grain boundary features with seemingly random orientation with respect to the grain edges. At 2.5 nm there is a large increase in the roughness of the films to 15.3 nm and at 5 nm the $R_q$ remains similar at 14.5 nm. At greater thicknesses (10 nm/25 nm ($R_q = 16.9$ and 14.5 nm respectively)) there is a reduction in the size of the visible ClAlPc grains, or at least the size of areas defined by the darker features. These observations lead to the conclusion that ClAlPc films forms as islands on top of the existing ClAlPc layers suggesting a Stranski–Krastanov growth mode.[18]

### Film formation of VOPc on CuI (111)

As with ClAlPc, thin films of VOPc were grown ($T_{sub} = 155$ °C) at a range of thicknesses (1, 2.5, 5, 10, 25 nm) on to 30 nm (111) oriented CuI films. The difference in growth modes between
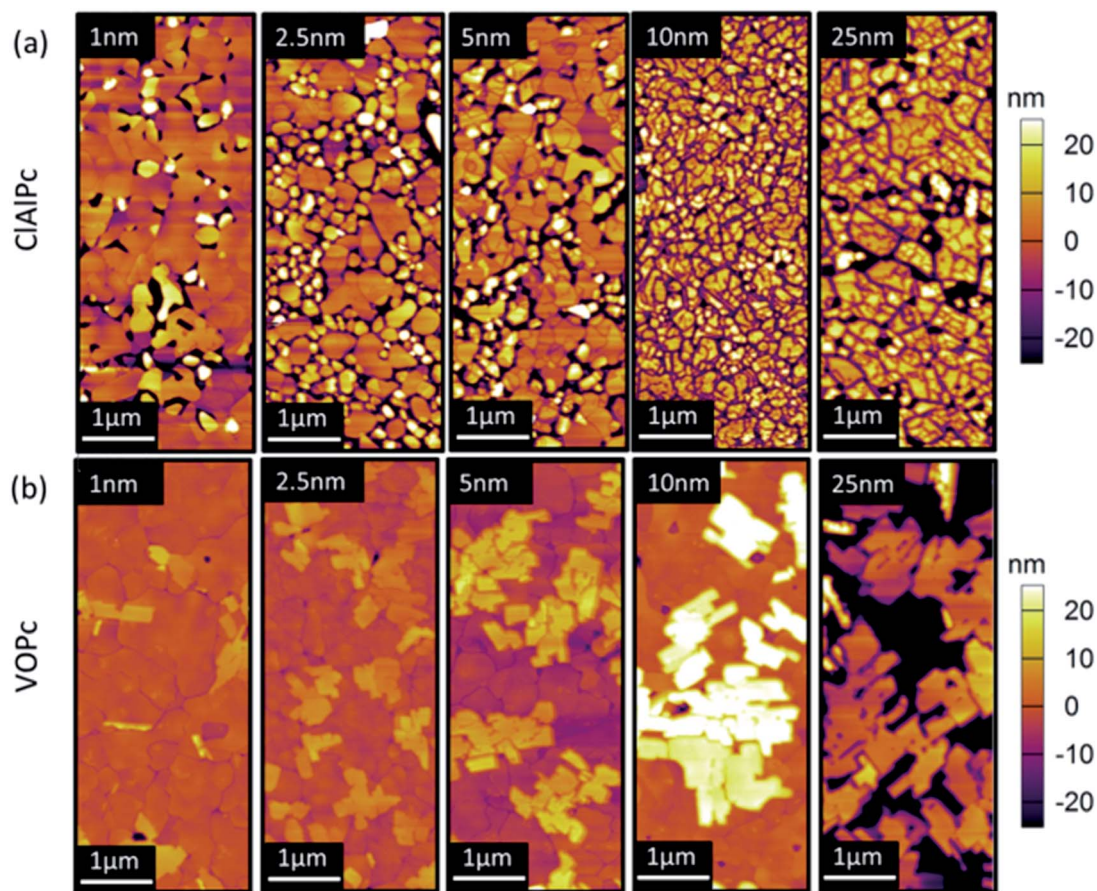


Fig. 1 (a) XRD pattern and (b) AFM topography image of 50 nm ClAlPc/ SiO$_2$ grown at $T_{sub} = 155$ °C. Inset shows chemical structure of ClAlPc.

**Fig. 3**  (a) AFM topography images of increasing thicknesses of ClAlPc, as indicated in image, on 30 nm CuI/SiO$_2$ and (b) AFM topography images of increasing thicknesses of VOPc, as indicated in image, on 30 nm CuI/SiO$_2$ all samples grown at a $T_{sub}$ = 155 °C.

ClAlPc and VOPc on CuI is stark even at 1 nm VOPc thickness (Fig. 3). Small islands of VOPc form at random points on the CuI film at a thickness of 1 nm ($R_q$ = 3.42 nm). These islands are mostly rectangular, appear to grow across CuI grain boundaries and are separated by bare grains of CuI. At 2.5 nm the number of islands increases resulting in a similar $R_q$ of 3.9 nm. With increasing thickness the aspect ratio of the islands of VOPc decreases. Above 5 nm thickness there is a significant increase in the roughness of the films and the size and height of the islands whilst the number of islands does not significantly increase. For 5 nm, 10 nm and 25 nm VOPc films the $R_q$ values are 6.6, 11.0 and 18.2 nm respectively. At 25 nm there are still areas of the CuI film which appear bare as the islands of the VOPc have not yet coalesced. Although it is possible that continuous layers of VOPc form over the CuI film the visibility of VOPc islands at thicknesses as low as 1 nm suggests that a Volmer–Weber growth mode is dominant in the formation of VOPc films on CuI.

Despite the similarities in molecular structure between the non-planar phthalocyanines there are significant differences between their structural and morphological behaviours which are highlighted here in their different growth modes and morphologies on thin film CuI. The film formation behaviour of the non-planar metal phthalocyanines studied here is distinct

from that of planar metal-centred and metal-free phthalocyanines. When iron(II) phthalocyanine is grown using identical procedures on CuI templating layers a single molecular orientation is inferred from XRD and a single crystallite morphology is observed in AFM.[15] In the case of metal-free phthalocyanine (H$_2$Pc) polymorphism is observed and multiple crystallite morphologies are evident within thin films.[12] These comparisons clearly demonstrate the differences between film formation processes in molecules including the same phthalocyanine ligand, but with different atoms or chemical moieties in the central four-fold imidazole cavity.

**Low energy ion scattering**

Low energy ion scattering measurements were carried out on 50 nm films of both phthalocyanines on 30 nm films of CuI and the results shown in Fig. 4. Although attempts were made to minimise surface contamination there is evidence of fluorine present on the surface of both films. Both films also show a peak corresponding to the presence of carbon on the surface of the sample. The phthalocyanine ligand contains 32 carbon atoms and is likely the origin of this carbon peak. The influence of small amounts of adventitious carbon from exposure to ambient environments cannot be deconvoluted from the inherent molecular signal.
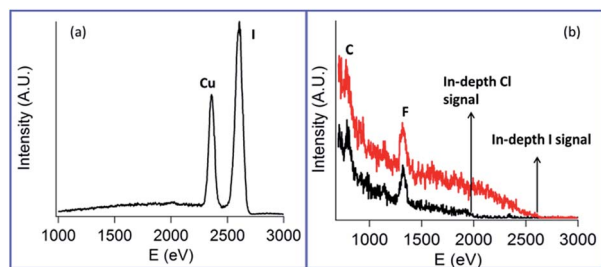
**Fig. 4** (a) LEIS data of 30 nm (111) oriented CuI thin film on SiO$_2$ and (b) LEIS data of 50 nm ClAlPc (black trace) and 50 nm VOPc both films as bilayers on 30 nm CuI/SiO$_2$ (red trace).

Both LEIS traces exhibit high-energy tails after the fluorine peaks. As there is no high-energy tail for fluorine the tail must be caused by other elements present. In the case of the VOPc films this is due to an in-depth signal resulting from the presence of iodine.[19] The high-energy tail for the ClAlPc films is a result of an in-depth signal relating to the presence of Cl at the surface of the films and iodine cannot be detected.

LEIS is incredibly sensitive to the atoms present in the topmost surface layers.[20] The presence of iodine in the scattering measured from the VOPc/CuI bilayers suggests that there are areas of CuI which are not covered by a phthalocyanine layer. This is reflected in the corresponding AFM image of the bilayers. This confirms that the VOPc layer adopts a Volmer–Weber growth mode. As islands of VOPc have formed on top of the CuI layer there are areas of the CuI film uncovered by VOPc islands even at higher VOPc film coverages. Therefore ion scattering from iodine atoms present in the topmost few layers of the CuI film is possible. If the VOPc film formation was occurring by a growth mode which involved layer by layer growth we would not observe the signal for iodine in the scattering measurements.

In contrast scattering for the ClAlPc films shows an in-depth signal relating to the presence of Cl at the surface. As the phthalocyanine molecules have chlorine as part of their central moiety this is unsurprising, however the lack of an in-depth signal relating to iodine, which was observed for the VOPc films, suggests that there are no exposed areas of CuI visible to the ions at the surface. This demonstrates that the ClAlPc growth onto the CuI film involves a continuous layer of the ClAlPc molecules forming over the surface of the CuI layer. The scattering measurements in combination with the AFM measurements suggest that the ClAlPc layer forms *via* a Stranski–Krastinov growth mode.

## Conclusions

The structure and morphology of ClAlPc thin films templated by CuI at ambient and elevated substrate temperatures are reported. It is observed that growth at an elevated substrate temperature results in ClAlPc thin film morphology and structure that is vastly different from ambient substrate temperature growth. Furthermore, at high temperatures, templating changes the molecular orientation of ClAlPc on the CuI substrate.

By examining the evolution of ClAlPc film morphology for thicknesses between 1 to 25 nm, and combining with the detailed chemical composition using LEIS, a Stranski–Krastanov growth can be identified on high temperature CuI. This is in contrast to the behaviour of VOPc, which grows *via* a Volmer–Weber mode. These observations highlight the need for caution when comparing phthalocyanine molecules with similar chemical structures but different central moieties, especially when out of plane groups are present. Although the phthalocyanines in this work are both non-planar molecules, with perpendicular moieties in their central cavity, their structures, morphologies and growth modes are very different.

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