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Copper phthalocyanine thin films on Cu(111): Sub-monolayer to multi-layer

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ABSTRACT

Scanning tunneling microscopy (STM) has been used to observe the growth mode and crystal structure of sub-monolayer (ML) to multilayer thin films of copper phthalocyanine (CuPc) molecules on the Cu(111) surface at room temperature (RT). At sub-ML coverage the molecules are mobile on the surface. At approximately one ML coverage the molecules become sterically confined and lying flat on the Cu substrate form an ordered, multi-domained, 2D oblique lattice. As coverage is increased beyond 1 ML the molecule–substrate interaction diminishes in strength while the intermolecular interaction begins to dominate, causing the layer separation to increase, and the crystal domain size and lattice constants to shrink as the crystal structure begins to more closely resemble the bulk α-phase CuPc molecular solid. This trend continues for the layer-by-layer growth of 3 complete ML, eventually giving way to the emergence of large 3D islands at a coverage equivalent to 4 ML.

1. Introduction

Copper phthalocyanine is an industrially important synthetic pigment. In recent years this material has attracted considerable attention as an important small molecule organic semiconductor. CuPc is the most widely used member of a large class of molecules known as metal phthalocyanines (MePc). These molecules are of interest for use in organic electronics, both in existing and future device applications including gas sensors, organic thin film transistors (OTFT), organic photovoltaics (OPV), and organic light emitting diodes (OLED) [1–4].

CuPc has molecular formula $C_{32}H_{16}CuN_8$, and is a planar, cross-shaped molecule composed of four isoindole units connected by nitrogen atoms forming a 4-fold rotationally symmetric macrocycle. At the center of the macrocycle is a Cu^{2+} ion. In the solid phase, CuPc forms a number of organic molecular crystal polymorphs including the thermodynamically stable β-phase and at least eight additional meta-stable phases [5]. When grown from vapor deposition in vacuum, CuPc generally forms the meta-stable α-phase at room temperature and the β-phase at temperatures exceeding 210 °C (the α-phase can be converted to the β-phase by heating above 210 °C) [6,7]. Of the many polymorphs, the α- and β-phases are the most widely studied, and see the widest industrial use. These two polymorphs both feature columns of co-facially stacked molecules. These columns, when viewed end on, are arranged in 2D oblique lattices, having lattice parameters a = 12.886 Å, c = 12.061 Å and β = 90.62°, and a = 19.407 Å, c = 14.628 Å and β = 120.56°, and 1 and 2 molecules per unit cell in the α- and β-phase respectively. In the α-phase, the normal to the molecular plane forms an angle of 24.9° with the column axis, in the β-phase this angle is 45°. The face-on, intermolecular separation along the column axis has been measured at 3.769 Å in the α-phase, and 4.78 Å in the β-phase, resulting in a molecular spacing, perpendicular to the molecular faces, of 3.42 Å and 3.37 Å respectively [8,9]. The α-phase structure is detailed below in Fig. 1.

In the α-phase the orientation of the molecular plane with respect to the column axis is currently believed to be identical in neighboring columns, producing the brick stone type packing shown in Fig. 1 [9]. In the β-phase, the molecular plane orientation instead alternates in neighboring columns, resulting in a herringbone type structure [8]. This herringbone structure is also found in the α-phase crystals of a number of other phthalocyanines, such as H_2Pc and PtPc, and until recently the α-phase of CuPc was believed to also always exhibit this herringbone structure. This apparent misapprehension is thought to stem from an early interpretation of diffraction results from 1966, which was then propagated through a number of subsequent studies [10]. The α-phase structure of CuPc was however reinterpreted in 2003 by Hoshino et al. who studied CuPc films grown on a KCl substrate using transmission electron microscopy (TEM), leading to the current brick stone model [9]. As a survey of recent literature will confirm however, there is still some confusion concerning the correct structure [11].

In organic electronic devices the interfaces formed between organic molecules and metal electrodes have a strong influence on a variety of important performance characteristics. These metal-organic interfaces are thus of importance to the field of organic electronics [13]. Furthermore, the interfacial layers formed between organic molecular solids and the substrates on which they are grown can exhibit a very strong influence on the molecular packing structure and, in turn, on important

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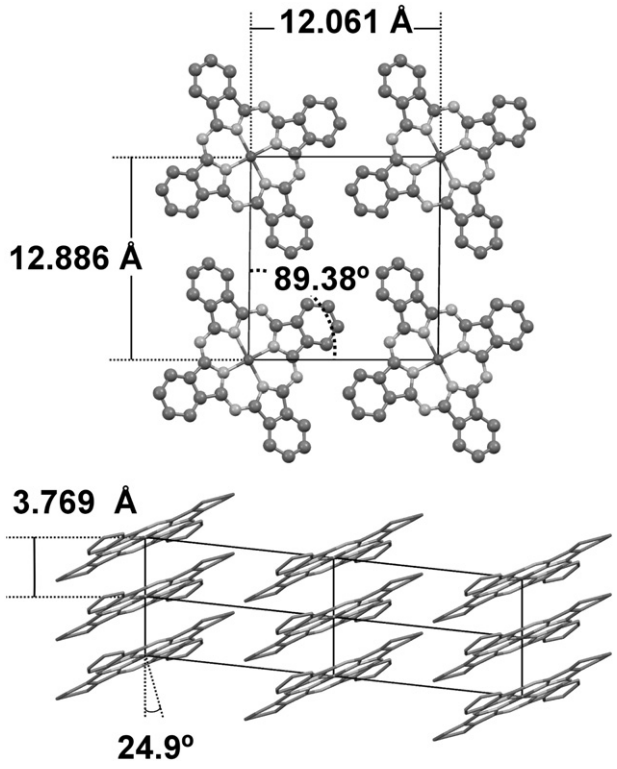

Fig. 1. Structure of the CuPc molecule and the α-phase molecular solid: The CuPc molecule has chemical formula $C_{32}H_{16}CuN_8$, and is a 4-fold rotationally symmetric, planar macrocycle composed of 4 isoindole units, connected by 4 nitrogen atoms and a central Cu^{2+} metal ion. The upper diagram shows four molecules in the 2D oblique lattice formed when the α-phase columns are observed end-on. The lower diagram shows a side view of the α-phase molecular columns. Crystal structure from Hoshino [9], plotted using Mercury program [12].

opto-electronic properties of the organic molecular solid [14]. Thus understanding the metal/organic interface and its influence on organic molecular crystal structure are of significant interest to the development of organic electronic devices. In light of this significance, MePc film growth has been intensively studied on a variety of technologically important substrates [15,16].

Phthalocyanine molecules deposited on substrates presenting a strong interaction with the molecules, such as single crystal noble metals, are typically observed to adsorb in a flat lying configuration, forming an ordered 2D molecular monolayer [17–19]. Molecular column growth on these surfaces tends to proceed in a direction outwards from the surface. The structure of the initial, flat lying molecular monolayer can have a strong templating effect on the crystal growth, producing a complicated interfacial region before the film structure resembles that of the bulk crystal. In order to gain further insight into the structures of MePc thin films and MePc-metal interfaces, we have used STM to study the adsorption of CuPc on the Cu(111) surface from sub-ML up to several ML thicknesses at RT. This study has revealed a complex interplay of evolving molecule–molecule and molecule–substrate interactions producing a variety of molecular packing structures. Initially, at low sub-ML coverages the molecules form a diffuse mobile layer, with immobilized molecules decorating the monatomic step edges. As concentration is increased and the mobile molecules become sterically confined the molecular layer undergoes a concentration dependent phase change and, at a coverage of approximately 1 ML, transitions to a 2D crystal phase. As further layers are added, the interaction with the Cu(111) substrate is diminished and the film exhibits structural changes indicative of a transition from the 2D ML structure to the bulk α-phase 3D molecular crystal. We have made detailed structural measurements on these crystal phases providing insight into the growth of CuPc crystals and the influence of the Cu(111) substrate.

2. Material and methods

All samples were prepared and analyzed in a single UHV–STM chamber with a base pressure of 5.0×10^{-11} Torr. The Cu(111) crystal substrate was purchased from Princeton Scientific Corp. and atomically clean surfaces were prepared in vacuum, using cycles of Ar^+ ion sputtering at 0.75 keV and annealing at 820 K. CuPc molecules where deposited at a rate of 0.5 ML/min at normal incidence from a fused quartz Knudsen cell containing sublimation purified CuPc powder purchased from TCI Chemicals. Deposition rates were monitored using an in situ quartz crystal microbalance (QCM). All CuPc coverages reported are referenced to 1 CuPc ML equivalent which we define as 0.053×10^{15} molecules/cm^2, which is the previously reported planar packing density of CuPc molecules lying flat on the Cu(111) surface [20], and is considerably below the planar density of Cu atoms on this surface (1.76×10^{15} molecules/cm^2). Samples were annealed via a ceramic radiative heating element mounted at the back of the sample plate within the sample manipulator head; temperatures were monitored with a Raytek optical pyrometer. Room temperature STM measurements were made using the Omicron UHV–STM-1, and mechanically cut Pt–Ir tips (90:10%). Tips were cleaned in situ using Ar^+ ion sputtering. All STM images have been leveled via polynomial background subtraction. Where noted, images have been calibrated and corrected for drift using the well-known Cu(111)–C_{60}-p(4 × 4) structure as a calibration standard and the multi-image linear lateral drift correction algorithm described by Rahe et al. [21].

3. Results and discussion

3.1. Sub-monolayer adsorption

As previously reported, sub-ML coverages of CuPc on the Cu (111) surface at RT, are thought to be mobile [20]. STM reveals molecules immobilized at step edges and impurity defects, but the majority of the sub-ML molecules are not individually resolved using STM. The presence of the mobile sub-ML molecules can be confirmed by exposure to a high, positive tunneling voltage which pins the initially mobile molecules to the surface [20]. Similar mobile, sub-ML adsorption states are known to occur for a number of different combinations of small organic molecules and metal surfaces, at a variety of temperatures, and are often described as 2D molecular gases owing to the absence of both long and short range ordering [18,22–24].

Fig. 2 below shows a typical RT–STM image of a sub-ML CuPc film on Cu(111). Monatomic steps running horizontally across the image are decorated with chains of immobilized molecules. Within the step edge chains, the molecules exhibit a nearly uniform adsorption geometry. Each molecule is adsorbed with single isoindole lobes on both the upper and lower terraces and the second lobe axis parallel to the step edge. Similar step edge adsorption geometries are reported for F_{16}CuPc on Cu(111) [25]. The step edge immobilized CuPc are loosely ordered and there is variability found in the precise adsorption geometry of each molecule. Variations in the angle formed between the lobe axis and the step edge allows the chains to conform to kinks and directional changes of the step edges. Occasionally, at step edge kink sites, a very small number of molecules are observed to adsorb with two lobes on both the upper and lower terraces, that is rotated approximately 45° from the dominant orientation. An example of such an adsorption is indicated in Fig. 2b by an arrow. A similar geometry has been reported for sub-ML coverages of FePc molecules on the Au(111) surface [26]. In the case of FePc on Au(111) the conformation of the step-edge adsorbed molecules with two lobes on each terrace is observed with near uniformity, but a very small number of molecules are also detected with one lobe on each terrace. The situation is thus the reverse of that observed