

Adsorption of cobalt phthalocyanine on Ag terminated Si(111)

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Abstract

We have investigated the adsorption of cobalt phthalocyanine on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface using scanning tunnelling microscopy. The molecules are found to diffuse freely on the surface and form a highly ordered close-packed array as the coverage approaches a monolayer. A model for the ordering of the molecules on this surface is proposed based on images acquired for sample biases in the range $-1.5 \text{ V} \rightarrow -1.6 \text{ V}$ for which it is possible to image the surface through the molecular layer. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phthalocyanine (Pc) molecules [1] are of interest in a wide variety of fields including chemical sensors, optoelectronic devices and solar cells and are closely related to biological molecules such as porphyrins. Metal phthalocyanine (MPc) molecules, shown in Fig. 1, have been synthesised using elements from every group of the periodic table. Molecular layers of Pcs have previously been studied using techniques such as low energy electron diffraction, reflection high energy electron diffraction (RHEED), photoemission and scanning tunnelling microscopy (STM) [1–15]. Pc molecules deposited on many different surfaces, including Cu [3], Au [4], Si [5,6], GaAs [7] and graphite [8], have been investigated using STM.

In this paper we present the results of a STM investigation of cobalt phthalocyanine (CoPc)

molecules adsorbed on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° (henceforth Ag/Si- $\sqrt{3}$) surface. This surface was chosen since the substrate–adsorbate interaction is expected to be intermediate in strength between the Si surfaces for which Pc adsorption has been previously studied. On reactive surfaces such as Si(100)-(2 × 1) and Si(111)-(7 × 7) Pc molecules are adsorbed parallel to the surface and are unable to diffuse at room temperature [5,12], while for unreactive Si surfaces (passivated by H) molecules may diffuse and form islands [15]. Pc multilayers on H terminated Si may be ordered with the molecular plane either parallel or perpendicular to the substrate. We find that the CoPc molecules are free to diffuse on the Ag/Si surface. At coverages close to a monolayer the molecules appear as an array of bright features, forming domains with three different orientations with respect to the underlying surface. A notable difference with previous work on Pc adsorption on Si surfaces is the clear identification of an ordered monolayer which is completed prior to

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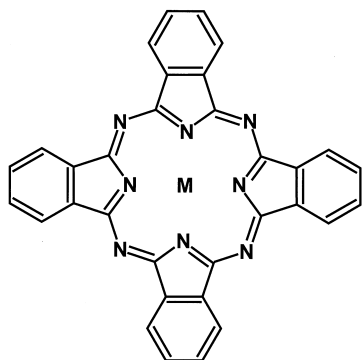


Fig. 1. Molecular structure of a typical metal (II) phthalocyanine.

the growth of higher layers. Over a range of sample biases the CoPc molecules are ‘transparent’ in the STM images and the underlying surface features are imaged. This bias dependent imaging has been used to determine a model for the ordering of the CoPc molecules on this surface.

2. Experimental

All of the experiments described below were performed using a commercially supplied ultra-high vacuum (UHV) STM system (Oxford Instruments SPM Group). Clean Ag/Si- $\sqrt{3}$ surfaces were prepared using (7 × 3) nm² pieces of Si cut from a p-type (111) wafer. Samples were loaded into the UHV system and outgassed at ~800°C overnight. After flash annealing at ~1200°C for ~120 s and cooling to room temperature the samples exhibit a clean (7 × 7) reconstruction with a low defect density. The Ag/Si- $\sqrt{3}$ surface reconstruction was prepared by depositing Ag onto a Si sample which was heated to ~500–600°C. High-purity CoPc was prepared from a commercially supplied source by sublimation purification under vacuum. After three cycles of purification the CoPc had an estimated purity >99% and was subsequently deposited by sublimation from a Knudsen cell held at 350°C, giving a deposition rate of ~0.3 monolayers min⁻¹ (background pressure 3 × 10⁻¹⁰ Torr). The silicon was held at room temperature during deposition. All STM images were acquired in constant current

mode using an instrument operating at room temperature.

3. Results

For low coverages of CoPc (~0.1 monolayer) deposited on the Ag/Si- $\sqrt{3}$ surface it was difficult to confirm the presence of adsorbed molecules in the STM images (due, we believe to the rapid diffusion of molecules across the surface, as discussed below). However as the coverage was increased to almost a monolayer the molecules appeared as a close-packed array of bright features, as shown in Fig. 2. The intermolecular separation of this ordering along both principal axes is measured to be 1.30(±0.05) nm, and the height of the molecules above the surface is typically 0.1–0.2 nm, suggesting that the molecules adsorb parallel to the surface. The presence of a highly ordered array of molecules indicates that the CoPc molecules are free to diffuse on the Ag/Si- $\sqrt{3}$ surface at room temperature. A comparison of many images reveals that three domain orientations of

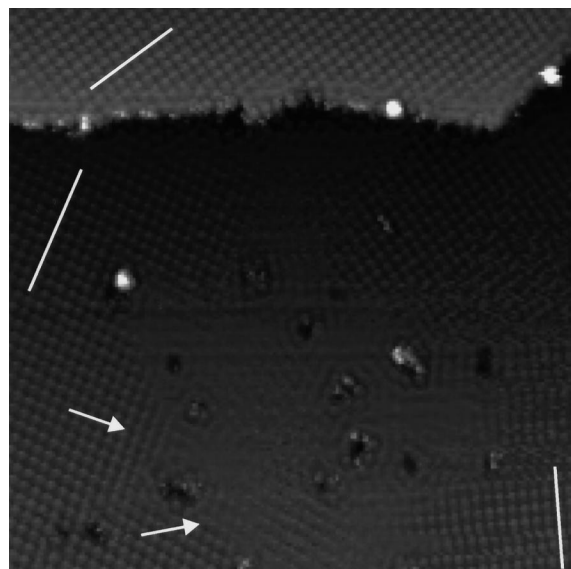


Fig. 2. STM image of a single layer coverage of CoPc molecules of the Ag/Si- $\sqrt{3}$ surface. Three domains of ordering (lines) and regions of ‘fading’ molecules (arrows) are highlighted. Image parameters: 60 × 60 nm², sample voltage 1.5 V, tunnel current 0.6 nA.

this ordering exist on the Ag/Si- $\sqrt{3}$ surface, all of which are present in Fig. 2. The defects in the ordering observed in Fig. 2 are associated with defects of the underlying Ag/Si- $\sqrt{3}$ surface.

Higher resolution images show that the edges of the ordered domains seem to slowly fade into the surface over the length comparable to the width of three to five molecules, so that there is not a sharp transition between the island and the surface. Areas where this effect can be observed are highlighted by arrows in Fig. 2. It was not possible to resolve any surface features within the regions between domains. We account for this observation in terms of molecules which are weakly bound to the edge of an island and continuously detach from one site, diffuse across the surface and become re-attached to another island where they are temporarily bound before continuing the process of detachment and diffusion. Molecular diffusion may also account for the apparent absence of molecules at low coverage-diffusing molecules do not remain under the STM tip for a long enough period of time to be imaged.

To determine a model for the ordering of CoPc molecules we have exploited an interesting bias dependent imaging of the surface (see below) which enables the Ag/Si- $\sqrt{3}$ surface directly below the molecules to be imaged. Under certain bias conditions, typically in the range $-1.5 > V_s > -1.6$ V, Ag/Si- $\sqrt{3}$ surface features were imaged. However with positive sample biases the molecular layer was imaged. Fig. 3 shows an STM image in which the sample bias polarity has been reversed from -1.5 V in the upper half to $+1.5$ V in the lower half. The upper half of the image shows features typical of filled states images of the Ag/Si- $\sqrt{3}$ surface, and the lower half is a square arrangement of bright features associated with CoPc molecules. By repeatedly imaging the same region with different biases it was determined that the molecular layer is not pushed aside to image the surface. The Ag/Si- $\sqrt{3}$ surface is imaged *through* the layer of molecules. It has been difficult to determine the precise bias range over which this effect is observed, since for $|V_s| < 1.5$ V sequential imaging in $-ve$ and $+ve$ biases was not possible due to tip instability. The maximum sample bias at which this effect has been observed is $|V_s| = 1.6$ V.

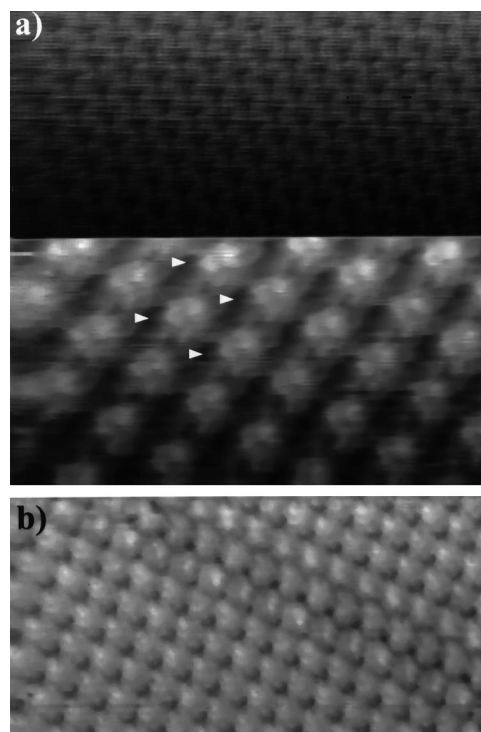


Fig. 3. (a) STM image (11×11 nm²) showing bias dependent imaging. The lower half (sample voltage 1.5 V, tunnel current 0.5 nA) shows the molecular layer and the upper half (sample voltage -1.5 V, tunnel current 0.5 nA) shows the Ag/Si- $\sqrt{3}$ surface. The dark holes between molecules are arrowed. (b) STM image (22×11 nm², sample voltage 1.4 V, tunnel current 0.3 nA) showing an out of phase boundary between two different phases of the same domain orientation.

The registry of the molecules to the surface was determined using the dark holes present between molecules (arrowed in Fig. 3a). Fig. 4 shows one unit cell of the model for one of the domains of ordering. The hexagonal lattice in the background represents the Ag/Si- $\sqrt{3}$ surface. There is a trimer of Si atoms at the centre of each hexagon and a trimer of Ag atoms centred above each vertex of the lattice [16,17]. If the dark holes between the molecules are joined with straight lines the lattice of dark lines shown in Fig. 4 is produced. These dark lines are aligned along the principal axes of the ordering. Each rhombic unit of the lattice contains a single molecule and is 1.38 nm along each side. The unit cell is not quite square since the angles at the corners are 92.2 and 87.8°. The

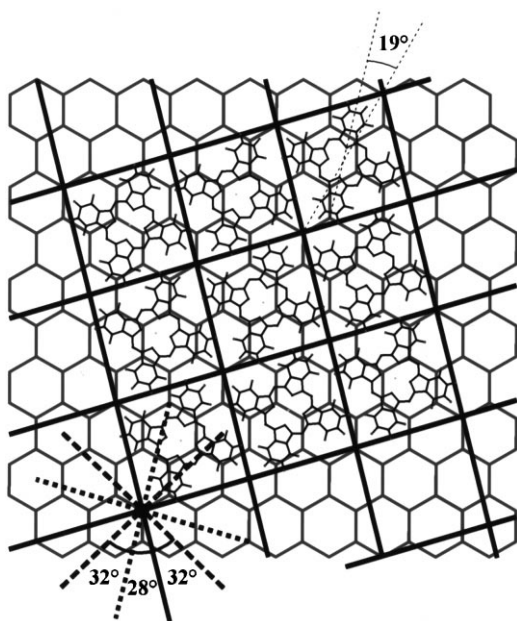


Fig. 4. This figure shows one unit cell of the arrangement of CoPc on the Ag/Si- $\sqrt{3}$ surface. The thick dark lines are the principal axes of the ordering and the honeycomb network represents the Ag/Si- $\sqrt{3}$ surface (there is a Ag trimer at each vertex and Si trimer at the centre of each hexagon [13]). The other two domain orientations are shown as dotted and dashed lines in the lower left hand corner.

direction of the principal axes of the lattice for the other two domains of the ordering are illustrated in Fig. 4. The angles between the different domains are predicted to be 27.8 and 32.2°, this compares well with the angles between domains measured from the images, which are on average $31.8(\pm 0.5)^\circ$. The corners of the lattice occupy two different surface sites, above Si and Ag trimers. This means that one unit cell of the ordering contains 3×3 molecules. When the registry of the lattice with respect to the underlying surface is considered there are found to be 15 different registries of each domain, several of which are illustrated in Fig. 4. When two different registries of the same domain meet they form an out of phase boundary. One such boundary is shown in Fig. 3b.

The orientation of the molecule within each rhombic unit has also been determined. The angle (see Fig. 4) between the lattice and the axes of the

molecule in high-resolution images is measured to be $19(\pm 1)^\circ$. However molecules may be rotated either clockwise or anticlockwise by this amount. Therefore with three domain orientations and two molecular orientations there are a total of six different domains of this ordering.

Imaging surface features beneath a layer of adsorbed molecules has been reported previously. Kanai et al. [5] observed that when imaging CuPc molecules adsorbed on a Si(111)- (7×7) surface at +1.6 V *some* of the molecules were 'transparent' to the STM. Mizutani et al. [18] observed that it was possible to image a graphite surface through a layer of liquid crystal molecules. To explain this observation Mizutani et al. proposed a resonant tunnelling model. At the higher bias the predominant tunnelling process is resonant tunnelling through the molecular orbital of the molecule. At lower bias direct tunnelling occurs between tip and surface. Dekker et al. [19] have investigated CuPc adsorbed on graphite using low temperature (35 K) scanning tunnelling spectroscopy (STS). They observe a peak in STS 0.4 eV below the Fermi level that they attribute to resonant tunnelling through the highest occupied molecular orbital (HOMO) of the CuPc molecule.

Our observations suggests that at +1.5 V the images result from resonant tunnelling through the lowest unoccupied molecular orbitals (LUMO) of the CoPc molecule. At -1.5 V tunnelling occurs within the HOMO-LUMO gap resulting in the appearance in STM images of features corresponding to the underlying surface. This implies that the HOMO lies >1.5 eV below the Fermi level. A similar value has been reported by Ottaviano et al. for NiPc adsorbed on Si(111)- (7×7) [12].

4. Conclusion

In conclusion we have found that CoPc diffuses freely on the Ag terminated Si(111) surface. At coverages close to a monolayer the molecules order in a close-packed arrangement. Under certain bias conditions the underlying surface may be imaged through a layer of adsorbed molecules and it has been possible to determine a model for the ordering.

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