Growth of PTCDA crystals on H:Si(111) surfaces

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Abstract

The room temperature deposition of PTCDA on hydrogen passivated Si(111), as a function of evaporation temperature and dosing time, has been studied by STM. At low evaporation temperature, 200 °C, clusters with an average size of 3.5 nm are formed on the surface. The mobility of the small clusters is so high, even at room temperature, that most of the clusters are trapped at surface defects. By increasing the evaporation temperature to 230 °C, larger clusters are formed which have lower mobility. The growth process is identified as a Volmer-Weber mechanism. On increasing the evaporation temperature further to 250 °C, crystals with dendritic shape are formed with an average size of 150 nm. The terraces of the crystal are formed with the (102) basal plane of the α-phase. Molecular resolution on the terrace also allows us to identify the molecular mechanism involved in the growth of the dendritic crystals.

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1. Introduction

The possibility of including organic semiconductors as the active component in various devices, such as, the light-emitting diodes, transistors and optical switches, has increased the interest in these materials during the last decade [1–5]. Such organic devices certainly have the advantages of cheap processing, tunability and flexibility. However, it has also been realised for some time, that the electronic conductivity of these organic materials may restrict the development of commercial devices with long lifetime and low power consumption [6]. The low conductivity or the mobility of the charge carrier and the quantum efficiency of organic devices are directly related to the quality of the organic thin film, in other words, the density of impurities and particularly of structural defects [7,8]. Only recently [1,9–13], it has been suggested that the use of high quality organic single crystals provides the possibility to increase the conductivity or the mobility of the charge carriers substantially.

For the development of commercial devices, efforts have been focused on controlling the structures of ordered thin films of the organic semiconductors, using molecular beam methods [1,14–22]. The thermodynamic equilibrium structures of the thin films are determined by the balance between surface energy, interfacial energy and the strain energy within the thin films. In
general there are three different growth modes namely the Frank-van der Merwe (FM) mode (layer-by-layer growth), the Stranski-Krastanov (SK) mode (the first layer or layers remain smooth with two-dimensional growth and 3D clusters then form on top) and the Volmer-Weber (VW) mode in which 3D growth is initiated from the outset [23]. When the adsorbate strongly interacts with the substrate with minimum misfit of the lattice, the interfacial energy is much larger than the cost of strain energy, therefore an FM growth mode is expected. However, when the adsorbate weakly interacts with the substrate with strong strain in the film, the 2D growth is not thermodynamically favourable and instead the growth will be in a VW mode. If the adsorbate–substrate interaction is strong and the lattice strain within the layer is not too great, then it is likely to grow into a SK mode, so the first several layers act as a wetting layer to passivate the substrate, while the clusters on top of the 2D growth region can release the stress initiated by the templating effects of substrate.

For molecules containing functional groups, such as the anhydride groups in 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecule, the intermolecular potential energy surfaces become much deeper and narrower than their un-functionalised analogues. This tends to ensure the multilayer structure is the same as the thermodynamically stable bulk structure(s) [24–28], which, of course, is then most likely incommensurate with the inactive substrates, such as H passivated Si(1 1 1).

Previous low energy electron diffraction (LEED) intensity, Raman peak shape and atomic force microscopy (AFM) studies have shown some evidence of PTCDA clusters formed on H:Si(1 1 1) surfaces [10,19,20], while a scanning tunnelling microscopy (STM) study at limited resolution [29] suggested an almost completely covered surface. These apparently contradictory results may be related to different growth conditions. Organic molecular beam deposition of PTCDA on alkali halide single crystal surfaces has shown the formation of dendritic crystals [26–28]. Recent studies of PTCDA multilayer growth on Cu(1 1 0) [30] and Ag(1 1 1) [31] have revealed that annealing is necessary for the transition of the multilayer into clusters with a Stranski-Krastanov mechanism.

X-ray [28] and electron diffraction [26] have been used to study the 3D structures of both α- and β-phases of PTCDA on alkali-halide crystal substrates. It has been suggested that the (1 0 2) basal plane of the PTCDA crystal is aligned parallel to the substrate. The structures of this (1 0 2) plane in the α- and β-phases are shown in Fig. 1A and B respectively. The angle between the longer molecular axes of the two molecules within the unit cell is different for the two phases: 96° for the α-phase and 104° for the β-phase. Of course, diffraction techniques are not sensitive to the details of defects, domain boundaries, steps and shape of the crystals. Although AFM [27] and TEM [26,28] studies have revealed some of the shape and size

![Fig. 1. Structures of α-phase (A) and β-phase (B) of bulk PTCDA crystals. The dashed lines indicate the shift of the second layer unit cell.](image-url)
properties of PTCDA crystals, there is, to date, no molecularly resolved, real space study to demonstrate the molecular arrangement within that (102) basal plane of the PTCDA crystal and how the crystal morphology is determined by the intermolecular interactions within that unit cell.

In this paper, we present the crystalline structure formed by PTCDA deposited on hydrogen passivated Si(111) surfaces with a Volmer-Weber mechanism. We demonstrate STM of PTCDA nano-crystals at molecular resolution. The size of the clusters is correlated with the evaporation temperature, while the density of clusters is determined by the dosing time. High resolution STM images allow the identification of the crystal orientation and the molecular mechanism for the formation of the observed dendritic shapes.

2. Experimental

The experiments were carried out in three interlinked UHV chambers equipped with LEED, vt-STM (Omicron) and reflection absorption infrared spectroscopy (Nicolet). The Si(111) substrate was hydrogen-passivated with a wet chemical etching method, involving two oxidation steps in a solution of HCl and H$_2$O$_2$ (H$_2$O$_2$:H$_2$O:HCl = 1:1:4 by volume, 5 min at 80 °C) followed by etching in buffered HF (pH 5, 5 min). The final etching was finished with buffered NH$_4$F solution (pH 7.8, 6.5 min) to achieve an atomically flat surface. The sample is transferred through a dried N$_2$ environment into the UHV chamber through a fast entry lock, followed by a mild annealing (100 mA through the sample) up to 150 °C. The cleanliness of the surface was characterised by sharp (1×1) LEED patterns and large flat terraces in STM. PTCDA was dosed onto the surface by vacuum deposition. The PTCDA sample was mounted in the vacuum chamber before the chambers were baked, since the vapour pressure of the PTCDA is sufficiently low, even at the baking temperature of 125 °C. The doser consists of a glass tube with heating wire and thermocouple sensor, so the dosing temperature is well controlled and the reproducibility is ensured. Prior to dosing the PTCDA, the H:Si(111) sample is isolated in the STM chamber to maintain the cleanliness of the surface, while the doser is gradually heated to 200 °C and maintained at that temperature for 30 min. The PTCDA is then dosed by direct line of sight onto the sample at a temperature between 200 and 250 °C, while the sample was kept at room temperature. The background pressure during dosing was about $5 \times 10^{-10}$ mbar. All STM images were recorded at room temperature.

3. Results and discussion

We first present STM images of PTCDA thin films grown at low surface coverage and low evaporation temperature (200 °C). Fig. 2 shows both the clean H:Si(111) surface and the surface after dosing with PTCDA for 5 min at 200 °C with the sample at room temperature. At this temperature, the deposition rate is about 0.2 Å/min. On the clean surface, shown in Fig. 2A, defects and step edges can be clearly identified. The defects are the etch pits with one atomic step height which were created by the oxygen in HF solution during the etching process. After exposure to PTCDA for 5 min, clusters, in a narrow size range of 3.5 ± 1.5 nm diameter, can be identified on the surface, shown in Fig. 2B.

The species adsorbed at room temperature are highly mobile, which allows them to diffuse and be trapped by surface defects. Similar size clusters have also been observed by depositing the PTCDA on glass surface [32]. A variation in the mobility of clusters, as a function of average size, has been proposed from in situ photoluminescence measurements of PTCDA growth on alkali halide surface [27]. In our experiments, increasing the evaporation temperature to 230 °C leads to higher flux (2 Å/min) and thereby larger, but less mobile, clusters are formed on the surface. Fig. 3 shows a sequence of STM images at increasing dosing times, while the doser temperature was maintained at 230 °C. It is clear that, while the number of clusters increases with the exposure time, the average size of the clusters (65 nm diameter and 4 nm thickness) increases only very slightly until the
surface is densely covered by the dendritic clusters. The slow increase of the average size is contributed by the incorporation of the few small (3.5 nm), mobile cluster species. Submonolayer of small clusters with a dimension of 3.5 nm, trapped on the defects and domain boundaries, can also be found, shown in Fig. 3D. The limited growth of these small clusters suggests that either the clusters form the diffusion unit or the small clusters do not have the right crystal orientation for further epitaxial growth with (102) plane parallel to the substrate.

By further increasing the PTCDA dosing temperature to 250 °C, with the sample held at room temperature, larger dendritic clusters are formed after 7 min exposure, shown in Fig. 4. At this temperature, the deposition is about 10 Å/min. Typically, the crystal has a dimension of 150 nm along the longer side of the cluster with an average height of 7.5 nm. The insert in Fig. 4 shows a enlarged large area (40 nm×40 nm) in between large clusters. The small clusters (3.5 nm) can also be found decorating the region between the large clusters, which is similar to that observed in the dosage dependent STM observation (230 °C), shown in Fig. 3. Meanwhile, the size distribution is still as narrow as that found after dosing at 230 °C. Different from those clusters on a Cu(110) surface [30], here, some of the clusters are overlayed on top of the others.

Under the higher evaporation temperature conditions, individual crystallites show a clearer dendritic structure, which is due to the preferential growth of the crystal along specific directions. Along these crystal growth directions, the intermolecular interactions must be more strongly attractive compared with other directions. When the unit cell has two or more directions with similar attractive interactions, varying growth of the crystal between these directions can lead to dendritic structures. Similar dendritic crystal shapes have also been observed for PTCDA growth on alkali halide surfaces with AFM [27] and pentacene on Si(001) and SiO₂ surfaces [33].

In the bulk PTCDA crystal, the unit cell of the (102) plane has a rectangular shape, with a short vector of 11.96 Å ([0 1 0] direction of the α-phase) and 12.45 Å ([2 0 1] direction of the β-phase). Along these directions, molecules are closely packed. The obtuse angle between the diagonal and the shorter unit cell vector is 121.0° (122.8°) in the α-phase (β-phase), while between the diagonal and the longer unit cell vector is 149.0° (147.2°). Meanwhile, the angle between diagonals is 118.0° (114.4°). The angles defining the macroscopic crystal edges as measured in our STM images are about 120°, which are close to the angle between two diagonal directions or that between the shorter unit cell side and the diagonal direction. However, an image with molecular resolution can,
in principle, distinguish which of these alternatives defines the crystal morphology and in turn therefore is able to give direct evidence for the driving force responsible for the formation of particular dendritic structures. We note that calibration of the STM image is not sufficiently precise to distinguish between \( \alpha \) - and \( \beta \) - phases, on the basis of the macroscopic crystal angles.

Fig. 5A shows the STM image of a single cluster with lateral dimensions greater than 120 nm. Angles at the edge of the cluster are characteristic of the bulk PTCDA structure. The cluster is terminated with a flat terrace. Interestingly, on the upper right side of the cluster, a hole with a dimension of 20 nm \( \times \) 10 nm can be identified as a large 3D defect. Since the large terrace is flat and the crystallite shows good conductivity, we are able to achieve molecular resolution within this

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**Fig. 3.** STM images as a function of dosing time (A) 2 min, (B) 5 min, (C) 15 min. All images have the same size 1 \( \mu \)m \( \times \) 1 \( \mu \)m and tunnelling condition (bias = 2.7 V, tunnelling current = 0.06 nA). (D) A small area image (100 nm \( \times \) 100 nm, 5 min dose) shows 3.5 nm clusters apart from the large clusters.

**Fig. 4.** STM image of PTCDA crystals deposited at 250 \( ^\circ \)C (1 \( \mu \)m \( \times \) 1 \( \mu \)m, bias = 2.32 V, tunnelling current = 0.07 nA). The insert shows an enlarged small area (40 nm \( \times \) 40 nm) with low density of 3.5 nm clusters.
terrace. Fig. 5B and C shows the high resolution STM images in two different areas of the cluster. The herringbone structure can be clearly identified, with a typical unit cell of $12.0 \times 19.5 \text{ Å}$ containing two molecules per unit cell. The bright STM features are elongated consistent with the rectangular shape of the molecule. The longer axis of the molecule can be easily identified. The measured enclosed angle between the long axis of the two molecules in the unit cell is about $98^\circ \pm 1^\circ$. This angle suggests that it is the $\alpha$-phase ($96^\circ$) rather than the $\beta$-phase ($104^\circ$) is formed at room temperature.

The crystal structure of PTCDA has already been examined with X-ray [28] and electron diffraction [26] techniques. Both techniques extract the structural information from the reciprocal space. With molecular resolution, one can easily identify the termination of the step edges. It is clear that only two types of step edges occur to define the macroscopic $\alpha$-phase crystal shape, either along [010] vector, the short axis, or [211] vector, the diagonal axis, of the PTCDA bulk crystal unit cell. Of course, these two directions are important in the bulk PTCDA crystal. Only the strongest attractive interactions define the orientation and structure of individual step edge when the local thermodynamic equilibrium is achieved. This idea was established by Hartman and Perdok [34–36], which requires that the morphology of crystals is governed by chains of strong bonds with a period defined as periodic bond chain vectors (the PBC vectors). Along the short unit cell vector, molecules are densely packed which could be a
result of local attractive coulombic interactions between the negatively charged oxygen of the anhydride group and the positively charged hydrogen atoms on the adjacent CH bonds. The nearest distance between the hydrogen atoms and the oxygen atoms is about 1.9 Å and the O⋯H–C distance is about 3.0 Å. For a typical H-bonding, the X-H–Y distance is about 2.8 to 3.4 Å. Therefore, it is likely that the H-bonding also contributes to the stabilisation of in-plane structures.

Along the close-packed direction, molecules achieve maximum attractive interactions between these two oppositely charged groups (atoms). Meanwhile, along the diagonal direction, similar coulombic interactions are also satisfied, forming an H-bonding matrix. To quantify these attractive intermolecular interactions, we have carried out ab initio calculations on clusters of PTCDA molecules resembling part of the unit cell in the bulk (102) plane. Fig. 6A shows the charge distributions of an isolated molecule calculated using the Gaussian 98 package [37] within the B3LYP density functional method [38] and an STO-3g basis set. In Fig. 6B and C, we indicate the interaction energy of two different PTCDA dimers using their relative positions within the unit cell. Since we do not aim to distinguish α- and β-phase, to simplify the calculation, we use the average dimension between α- and β-phases, that is 12.2 Å × 19.6 Å with an angle of 40 between the long molecular axis and the short axis. The arrangement shown in Fig. 6B corresponds to a pairwise attractive interaction of 22.3 kJ/mol between the translationally inequivalent molecules of the unit cell, which define the herringbone structure, while the parallel aligned model of Fig. 6C relates to an attractive interaction of 21.5 kJ/mol between translationally equivalent molecules along the shorter unit cell vector. To confirm that these attractive interactions are the dominating forces responsible for the formation of the molecular arrangement equivalent to that within the (102) plane of the PTCDA crystal, a cluster of five PTCDA molecules representing an extended unit cell was also calculated. The total attractive interaction was found to be 133.9 kJ/mol. As there are four T-type interactions...
and two parallel interactions along the short axes in this cluster, the total interaction based on the sum of molecular pairwise interactions should be 132.3 kJ/mol. The small difference (1.6 kJ/mol) between these estimates suggests that indeed these are the strongest intermolecular interactions within the structure found in the (102) plane. Meanwhile, because the interactions in these two different arrangements are very similar, the boundaries of the crystal edges are dominated by alignment along both the short axis and the diagonal axis of the unit cell. Therefore, the crystal shape is determined by the growth short axis and the diagonal which, in turn, contributes to the form of the dendritic crystal with enclosed angles of 120°.

4. Growth mechanism

Typically, the growth of metal thin films on insulator substrates proceeds by 3D cluster formation in the VW mode, because the surface energy of the metal film is much higher than that of the substrate, while semiconductor films are often in the SK mode, because the interaction with the substrate is strong. However, the growth of organic thin films on inorganic solid surfaces has not been systematically studied, since the system is relatively complicated in terms of lattice matching and adsorbate–substrate interactions. Organic crystalline clusters can be formed by releasing the interlayer strain through either the SK or VW growth mechanism. Previous studies of multilayer PTCDA on InAs(001) [39], Cu(110) [30] and Ag(111) [31] suggest a SK growth mode for the transition from layer by layer into clusters. The remaining two layers of PTCDA on the InAs(001) surface act as wetting layer. In our experiment, no such a wetting layer is observed on the H:Si(111), instead, only a low density of trapped small clusters can be found. Therefore, unlike that on a InAs(001) surface [39], the growth of PTCDA on a H:Si(111) surface is by a VW growth mode, which is consistent with previous LEED, Raman and AFM studies [10,19,20].

Epitaxial growth of clusters is a non-equilibrium kinetic phenomena. Therefore the clusters size, shape and density depend not only on the surface temperature, but also on the deposition rate. Normally, with less diffusion time, the density of clusters increases with deposition rate. However, for the PTCDA on H:Si(111) surface, the mobility of the surface species is so high that the deposition rate cannot affect the density of clusters efficiently. On the other side, our experiment also shows the growth process as a function of surface coverage. The images shown in Fig. 3 indicate the nucleation regime with low cluster density, where the possibility for the additional deposited molecules diffuse to meet the existed clusters is smaller than the possibility of nucleation. Increase the surface coverage, Fig. 4, the density of the clusters increases to a critical value which leads to a transition form nucleation to growth.

For PTCDA growth on a hydrogen passivated Si(111) surface, the interaction between adsorbate and the substrate is expected to be very weak. The strain imposed by a layered structure cannot, in this case, be compensated by a sufficient molecular/substrate interaction so 3D clusters are preferred. The exclusive orientation of the clusters with their (102) plane parallel to the substrate reflects the preferential π interaction at the interface.

When the adsorbate–substrate interaction is weak, the aspect ratio (height against lateral size) of clusters is determined by the surface energy ratio of corresponding faces. Therefore, the aspect ratio is volume independent. Our experiments have confirmed that the average aspect ratio of the clusters with different sizes is similar. For the clusters with a size of 65 nm, the aspect ratio is about 0.06, while for the cluster with a size of 150 nm, the aspect ratio is about 0.05. Thus, we can estimate that the surface energy of the (102) plane is about 20 times smaller than the side planes and the adsorbate–substrate interaction is very weak.

5. Summary

In this work, we present an STM study of molecular deposition of PTCDA on a passivated, hydrogen terminated Si(111) surface. At low evaporation temperature, 200 °C, small clusters,
with a diameter of 3.5 nm, are formed on the surface, which are able to diffuse and trapped at surface defects. Larger clusters are formed on the surface at higher evaporation temperatures in a 3D growth mechanism. The diffusion of clusters with a size larger than 30 nm is limited at room temperature. For the larger clusters, dendritic crystal shapes are observed. STM images with molecular resolution have been analysed which suggests that the \( \alpha \)-phase is formed at room temperature. The molecular mechanism for the formation of the dendritic crystals has also been discussed.

References