

## Molecular-Scale Structure of Pentacene Interfaces with Si (111)

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### ABSTRACT

The morphology and crystal structure of the first few molecular layers of organic semiconductor thin films at organic-inorganic interfaces are important from both electronic and structural perspectives. The first upright layer of pentacene on Si (111) forms on top of a disordered layer of strongly bonded pentacene molecules in a structure similar to the pentacene monolayers formed on insulators. We describe a high-resolution structural study of this crystalline phase of pentacene using low-temperature scanning tunneling microscopy (STM). The arrangement of molecules in these layers observed with STM agrees the results of with structural studies using scattering techniques. The imaging conditions and sample preparation techniques necessary to achieve molecular resolution can be adapted to subsequent STM and scanning tunneling spectroscopy experiments probing individual structural defects including vacancies, dislocations and grain boundaries within and between islands.

### INTRODUCTION

Investigating the structural and electronic properties of organic-inorganic interfaces is important because the electrical characteristics of organic thin films are influenced by the crystal structure of the first few layers between organic molecules and inorganic materials. Charge transport through grain boundaries in polycrystalline thin films can be depends on the arrangement of molecules near the junctions of grains [1].

Structural defects such as vacancies, dislocations and grain boundaries influence the electrical properties of organic thin films. These defects are traps for charge carriers and can degrade charge transport within and between organic islands [1]. Tsiaousis and Munn showed in electronic structure calculations that molecular vacancies in anthracene can trap charges [2]. The electrical effects of grain boundaries on charge transport have been studied both experimentally [3] and theoretically [4]. High angle grain boundaries, for instance, cause reduction in the magnitude of photocurrent in bicrystals [3]. The structures of these defects can be probed using both microscopy and diffraction techniques. Attempts to relate the electrical properties to the microscopic structure of defects have previously used atomic force microscopy (AFM) [5]. X-ray scattering studies have attributed a broadening of Bragg peaks to the presence of dislocations pentacene thin films [6].

STM complements other microscopy techniques in molecular-scale structural studies because it has spatial resolution sufficient to resolve individual molecules. In addition, both morphological and spectroscopic information can be obtained from STM experiments. The structural aspect of STM experiments the orientations (for example, lying-down or upright) and arrangements of molecules and the types and the structure of grain boundaries and other crystal defects.

Pentacene ( $C_{22}H_{14}$ ) is a stable small-molecule organic semiconductor with a long, planar molecular shape that facilitates crystalline packing. Pentacene has been widely used to create organic electronic devices including field-effect transistors (FETs) [7]. The orientation of pentacene molecules at pentacene/inorganic interfaces depends on the molecular interactions between pentacene and the substrate. STM studies of the lying-flat geometry of pentacene molecules on metal and clean Si surfaces are found in the literature [8-10]. The second and higher layers on metal substrates are oriented with their long axes perpendicular to the surface. Defects such as grain boundaries have been imaged in these layers at low temperature in pentacene thin films on metal substrates [9].

On the surfaces of inert solids, such as  $SiO_2$ , which are commonly adopted in FETs as gate dielectric layers [11], pentacene forms a thin film phase in which the long axes of pentacene molecules are oriented almost vertically with respect to the substrate [12]. Due to its non-conductive and rough surface, however, molecular resolution using STM on  $SiO_2$  can not be achieved.

We chose instead to use Si substrates because *in situ* preparation of Si surfaces is straightforward and because Si (111) exhibits a smooth and atomically flat surface over lateral scales of tens to hundreds of nanometers. Clean Si surfaces are highly reactive and inappropriate for organic device applications. By modifying the substrate to reduce the interaction with organic molecules, however, organic crystals in thin films can be formed with many similarities to pentacene films on  $SiO_2$  [13,14]. Pentacene molecules are weakly bonded to each other and to the substrate and are thus highly mobile at room temperature, making high resolution imaging difficult [15]. We have used low temperature STM and AFM to explore the structure and formation of the interface between pentacene molecules and a Si (111) surface.

## EXPERIMENTAL DETAILS

Our experiments were performed in an ultra high vacuum (UHV) environment using an UHV AFM/STM with the capability of cooling samples using a continuous-flow liquid He cryostat. The Si (111) samples ( $0.005 \Omega \text{ cm}$ , As-doped) were degreased in trichloroethylene at  $75 \text{ }^\circ\text{C}$  for 5 minutes and rinsed in room temperature acetone and methanol. The surfaces were cleaned in  $H_2O:NH_4OH:H_2O_2$  (4:1:1) and in  $HCl:NH_4OH$  (3:1) at  $80 \text{ }^\circ\text{C}$  for 5 minutes to remove organic and metal contaminants, respectively. The samples were oxidized in a Shiraki solution and etched in 25 % HF [16]. The oxidizing and etching processes were done twice. After a third oxidation in  $HCl:H_2O:H_2O_2$  (3:1:1) at  $100 \text{ }^\circ\text{C}$  for 10 minutes, the sample was introduced into the UHV chamber and degassed at  $600 \text{ }^\circ\text{C}$  for several hours.

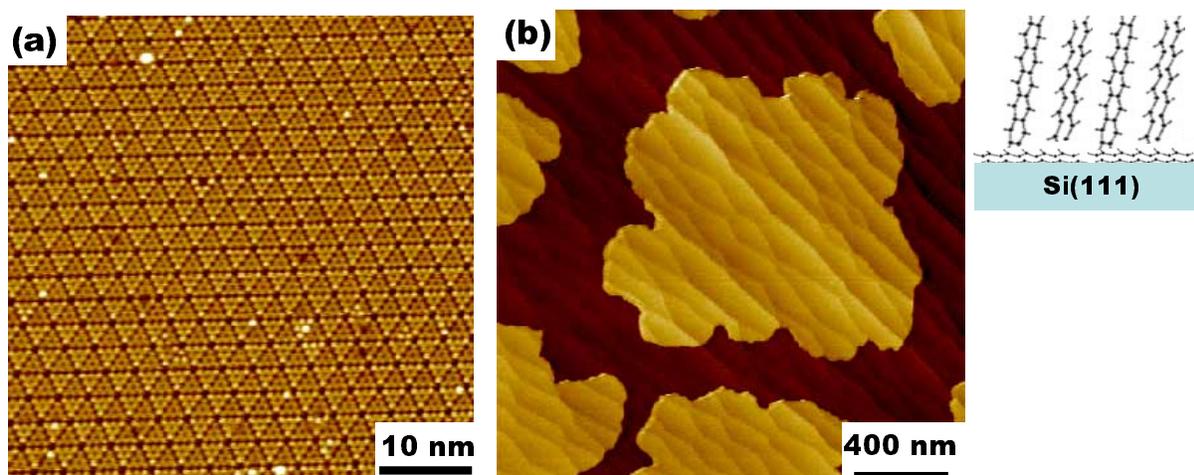
Clean, well ordered Si (111) surfaces exhibiting the  $(7\times 7)$  reconstruction were prepared by heating to  $1250 \text{ }^\circ\text{C}$  for 5 s, quenching at  $950 \text{ }^\circ\text{C}$ , and cooling slowly to room temperature at a rate of  $1 \text{ }^\circ\text{C s}^{-1}$ . STM images of a clean Si (111) surface before the growth of pentacene showed

the  $7\times 7$  reconstruction (Figure 1 (a)). These reproducible surfaces were the starting point for our STM studies of pentacene films.

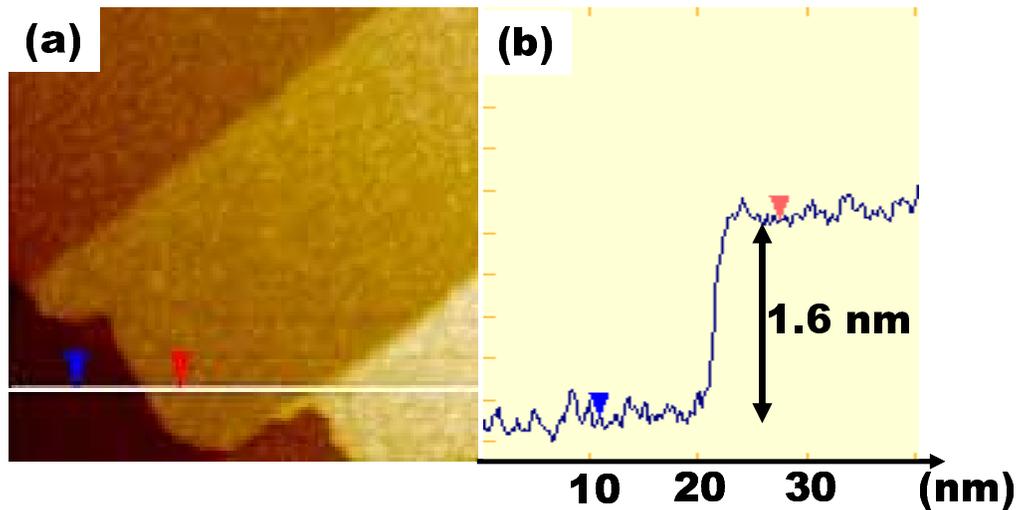
Pentacene was deposited from a thermal evaporator onto the clean Si (111) surface in the UHV chamber. We were able to form images of the pentacene islands, but we were not able to achieve molecular resolution at room temperature. The pentacene molecules on a clean Si (111) surface were observed using a UHV STM at a temperature of  $\sim 57$  K with tunneling currents of 150 to 300 pA and bias voltages between -1.9 V and -2.3 V. The pressure during low temperature scans was below  $1.1 \times 10^{-10}$  Torr. Room temperature STM images of Si (111) were obtained at sample bias voltages between -1.4 and -2.0 V with tunneling currents of 100 to 500 pA. All of our STM studies used a tungsten probe tip.

## DISCUSSION

During the initial stages of thin film growth, pentacene forms strong chemical bonds to the silicon surface, leading to a disordered interfacial layer between the subsequent pentacene film and the Si substrate [17]. In this layer, the long axes of the pentacene molecules are approximately parallel to the surface. When more pentacene is deposited, ordered islands form on top of the disordered layer [18]. The *in situ* non-contact atomic force microscopy (AFM) image obtained at room temperature in Figure 1 (b) shows two dimensional pentacene islands formed on a clean Si (111) surface. The inset in Figure 1(b) is a schematic diagram of lying-flat and upright orientations of pentacene molecules in the disordered and first ordered layer on Si (111). The morphology of the second layers islands in Figure 1(b) is similar to pentacene islands grown on  $\text{SiO}_2$ .

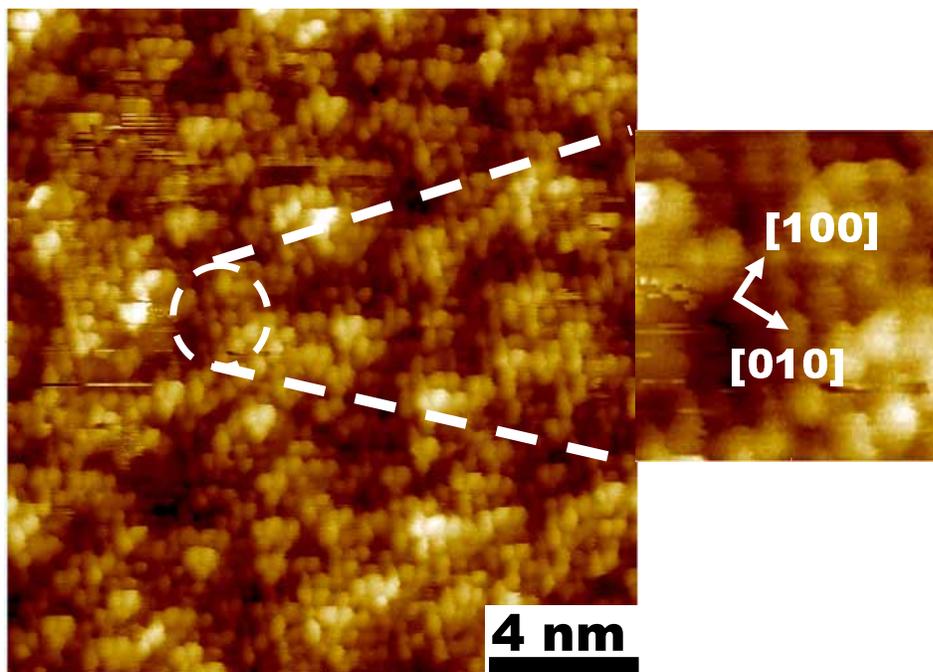


**Figure 1.** (a) STM image of a clean Si (111) surface with a tunneling current of 0.5 nA and the bias voltage of -2.0 V. (b) Non-contact AFM image ( $2 \mu\text{m} \times 2 \mu\text{m}$ ) of pentacene islands formed from the first layer of upright molecules of pentacene on Si (111).



**Figure 2.** (a) Low temperature STM image ( $74 \text{ nm} \times 74 \text{ nm}$ ) of a pentacene island on Si (111) at  $\sim 57 \text{ K}$ . Each substrate step is  $3.1 \text{ \AA}$  high. (b) Cross-sectional profile of the edge of the island.

Figure 2 (a) shows a low temperature STM image of an island in the first ordered layer of pentacene. The Si atomic steps are transmitted from the substrate through the pentacene islands and are visible in both the AFM image in Figure 1(b) and the STM image in Figure 2(a). Each of these steps is  $3.1 \text{ \AA}$  high. The cross-section taken from the line on Figure 2(a) shows a sharp edge of a pentacene island, and a vertical step from the disordered layer to the first ordered layer of  $1.6 \text{ nm}$  (Figure 2(b)). This is approximately the height of one layer of upright pentacene molecules. The variation in height across these pentacene islands is sufficiently small that molecular resolution images can be obtained at low temperatures.



**Figure 3.** (a) Low temperature STM image of the first layer of upright pentacene molecules on Si (111) obtained with a tunneling current of  $0.23 \text{ nA}$  and a bias voltage of  $-1.9 \text{ V}$  at  $\sim 57 \text{ K}$ . (b) An area of this image on which the directions of the  $[100]$  and  $[010]$  lattice directions are indicated.

The low temperature STM image in Figure 3(a) shows the first layer of upright pentacene molecules within an island deposited on clean Si (111). The [100] and [010] basis vectors of the pentacene unit cell are shown in a small area of this image reproduced in Figure 3(b). Each unit cell contains two pentacene molecules. The length of the unit cell vectors estimated from the image are  $0.74 \pm 0.01$  nm and  $0.56 \pm 0.02$  nm in (010) and (100) oriented surfaces, respectively. These lattice parameters are comparable to those in thin film phase reported by Fritz *et al.* [19].

The STM image of pentacene molecules in Figure 3 reveals information about the molecular lattice structure and possible presence of lattice defects within an island. No grain boundaries or stacking faults are immediately apparent in this image. This observation is consistent with the study by Meyer zu Heringdorf *et al.* [13], who reported that much larger islands on Si (001) form as single crystals.

The disorder evident in Figure 3(b) increases after additional exposure of the sample to the residual gas. For this reason, we believe that the disorder arises from contamination of the surface, or of the pentacene/Si (111) interface by reactive molecules. Potential routes for eliminating this disorder and enabling the search for individual structural defects are the use of hydrogen terminated Si surfaces, as in ref. 14, or passivation of the Si surface using organic molecules [20]. It is known from larger-scale imaging experiments, for example, that replacing the reacted layer of pentacene molecules with cyclopentene greatly increases the diffusion length of pentacene molecules on the surface [21].

## CONCLUSIONS

We have used low temperature STM to probe the structure of interfaces between pentacene and Si (111). The STM images show the standing-up orientation of pentacene molecules in the layer on top of the disordered layer initially formed on a clean Si (111) surface. These molecular-resolution STM imaging technique can be extended to gain information about the structural defects including as vacancies, grain boundaries and dislocations within and between islands, glean insight into the connection between structural and electronic properties of organic-inorganic interfaces and a more complex structure of organic devices.

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