

Adsorption of PTCDA on Si(100) and Si(100)-H

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ABSTRACT

Submonolayer coverages of perylene-tetracarboxylic-dianhydride (PTCDA) molecules deposited on Si(100) and Si(100)-H surfaces have been investigated with scanning tunneling microscopy (STM) and monolayer coverages by X-ray photoelectron spectroscopy (XPS). At monolayer coverage, X-ray measurements indicate that both on Si(100) and Si(100)-H surfaces, most of the molecules do not react with the surface. At lower coverage, the STM images show that the molecules adsorb mostly in a planar configuration with its axis parallel to the Si dimers. Only a few molecules appear to be chemisorbed. Finally, we compare one ML deposition on both surfaces. A complete coverage is observed on Si(100), associated with a low mobility of the molecules, whereas islands are formed on Si(100)-H, associated with a high mobility of the molecules.

Keywords : Silicon surface, PTCDA, STM, XPS

1 INTRODUCTION

In the general development of the molecular electronic devices, the growth of two dimensional molecular films on inorganics substrates is of major interest because of possible application as organic LEDs [1], organic field effect transistors [2], non-linear optical devices [3], ...Thin layers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) deposited on metals (Cu(110) [4,5], Au(111) [6], Au(100) [7], Ag(111) [8] and semiconductors surfaces (GaAs(100) [9] and InAs(001) [10] have been mainly studied by means of scanning tunnelling microscopy (STM) or low energy electron diffraction (LEED). PTCDA is generally found to grow in a herringbone fashion [7].

In this paper, we investigate, using both STM and X photoemission spectroscopy (XPS) the interaction of the PTCDA molecules with Si(100)-2x1 and hydrogenated Si(100)-2x1 surfaces. The XPS technique allows to analyse the chemical nature of the molecule-surface

bounding and the STM gives structural and conformational details of the molecules on the surfaces.

2 EXPERIMENTAL and DISCUSSION

Experiments were performed in an UHV system containing different chambers with base pressure less than 10^{-10} Torr. The Si(100) surfaces, doped with P in the range of 0.004 to 0.006 Ωcm , were prepared by standard procedures [11]. To prepare hydrogen-terminated Si(100)-2x1 surface, the surface is exposed to atomic hydrogen obtained by cracking molecular hydrogen with a 1500°C W filament placed 5 cm away from the sample surface. The UHV chamber is backfilled with 2×10^{-6} T of H_2 during 3 min which corresponds approximatively to 360 L. During the hydrogen exposure, the sample is heated at 350-370°C to prevent dihydride formation and subsequent etching of the Si surface [12]. The PTCDA molecule (see figure 1) were deposited from a *home made* Knudsen cell held at 380 °C, at a rate of about ??? molayer per second. Prior to the STM experiments, the W tips were electrochemically etched, cleaned in UHV and their radius of curvature was checked in field emission. All STM images were taken in constant current mode. For XPS measurements, the samples were transferred to a XPS chamber using a clean box, under overpressure of dry nitrogen.

The chemical structure of PTCDA molecule is shown in Figure 1.

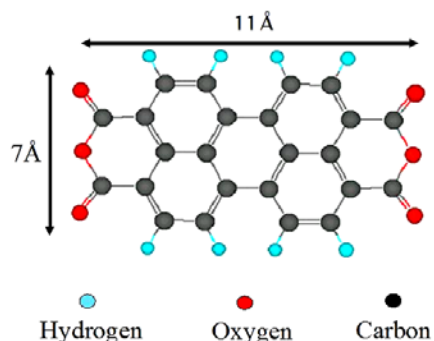


Figure 1 : Chemical representation of the PTCDA molecule

The XPS technique was first used in order to determine the chemical interaction between the molecules and the silicon surfaces (Si or Si-H). Figure 2 gives XPS spectra of the C1s levels for a monolayer coverage.

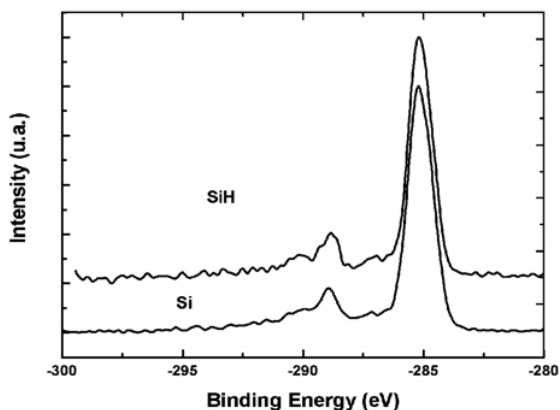


Figure 2 : XPS spectra of the C1s level associated with PTCDA deposited on Si and Si-H surfaces.

The main peak, located at 285.1 eV is associated with the carbon atoms of perylene group. The peak positioned at 289 eV is associated with the carbon atoms of the anhydride group. The main results are : i) the XPS spectra are similar, for both surfaces, ii) no Si-C peak is observed, showing that whatever the silicon surfaces, the molecules are mainly physisorbed, i.e. in low interaction with the surface.

In order to characterize individual molecules with the STM, sub-monolayer of PTCDA were sublimated on Si(100)-2x1 surfaces. Figure 3 is a typical STM image ($V=-3.5$ volts, $I = 40$ pA, 200 nm x 200 nm). The rows of silicon dimers are clearly apparent and the bright hillock are associated with the molecules. Taking the silicon surface as a reference for the dimension, the observed adsorbates have the size of the PTCDA molecules (typically $11 \text{ \AA} \times 7 \text{ \AA}$). Figure 4 and 5 are high resolution STM image (size 6.8 nm x 6.8 nm and 5.2 nm x 5.2 nm respectively) of individual molecule on Si(100)-2x1 surface. In Figure 4, the molecule is perpendicular to the silicon dimer rows (as illustrated on the schematic representation associated with the STM image) and is located over two adjacent dimers. Two bright lobes are observed, associated with the two perylene groups. At the corners of the adsorbate, four spots are observed, with a lower contrast than the main part of the hillock. These spots can be associated with the carboxylic groups. The chemical structure of the molecule seems to be unperturbed and we propose that this molecule is in low

interaction with the surface, i.e. is physisorbed, in agreement with the XPS results.

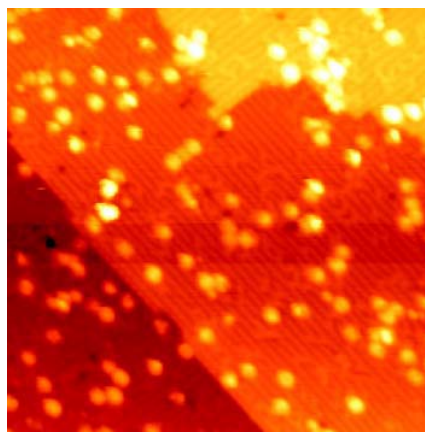


Figure 3 : STM image ($V=-3.5$ volts, $I = 40$ pA, 200 nm x 200 nm) of individual PTCDA molecules on Si(100)-2x1 surface

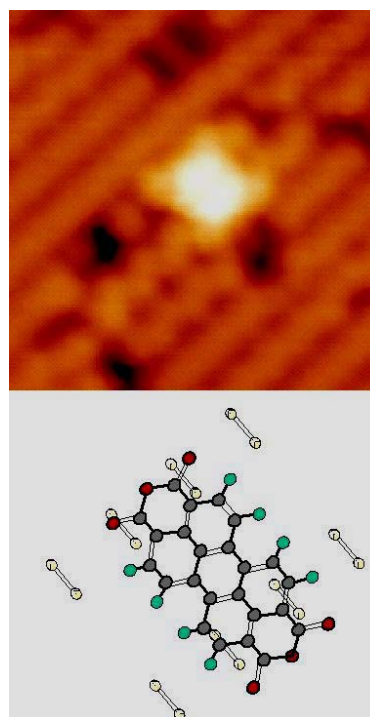


Figure 4 : High resolution STM image (6.8 nm x 6.8 nm, $V = -2.5$ volts, $I = 40$ pA) of individual PTCDA molecule

For a few percent of the molecules, the STM image is completely different, as shown in Figure 5.

In such case, four bright lobes are clearly observed. The spots aligned on a silicon dimer row are separated by a distance of typically 1 nm, whereas the distance between two lobes perpendicular to a silicon dimer row is typically 7 Å. The center of the molecule exhibits a low contrast.

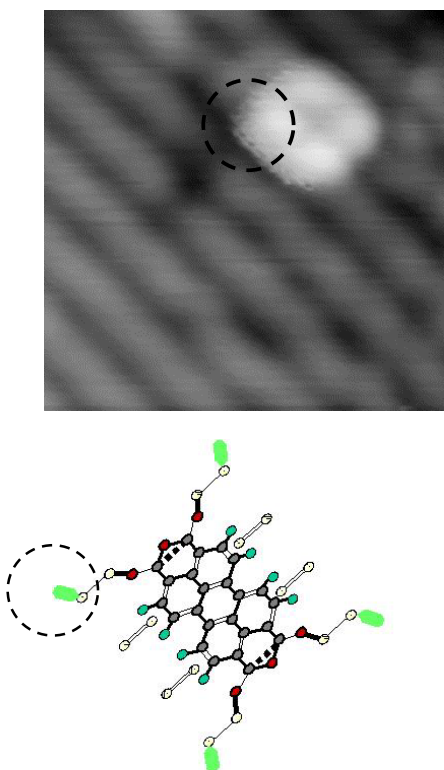


Figure 5 : High resolution STM image (5.2 nm x 5.2 nm, V = -3.5 volts, I = 80 pA) of individual PTCDA molecule

As shown in the schematic representation in Figure 5, below the STM image, we propose that the molecule is parallel to the silicon dimer rows and located between two adjacent rows. The molecule is chemisorbed (cycloaddition reaction [14]) on the surface *via* the atomic binding of the oxygen atom of the anhydride groups and silicon surface atom (creation of a Si-O bond). Consequently, there is a modification of the chemical structure of the molecule (the π C=O bonds of the anhydride groups are broken and a new C=C is formed between the two carbon atoms of the anhydride group). The four associated silicon dimmers are also modified.

The π Si=S bond is broken. One silicon atom is bonded to an oxygen atom and a dangling bond is associated with the second silicon atom (dotted circles in Figure 5). As the energy level of the dangling bond (sp^3 level) is near the Fermi level of the surface [13], the dangling bond appears bright in the STM image.

Finally, we first achieve the deposition of one monolayer PTCDA films, on Si(100)-2x1 surfaces. Figure 6 is an STM image (85 nm x 85 nm, V = -3.5 volts, I = 40 pA) of a Si(100)-2x1 surface.

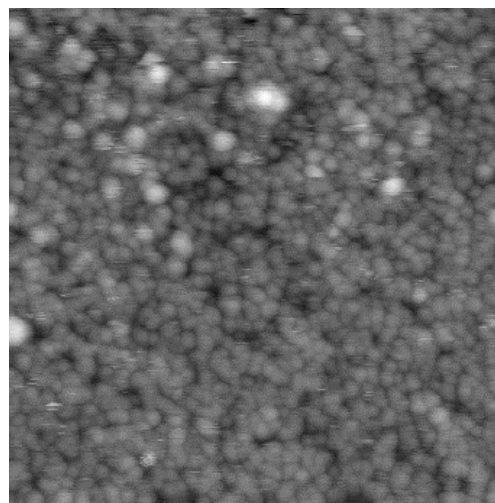


Figure 6 : STM image of Si(100)-2x1 surface after the deposition of one ML of PTCDA (V= -3.5 volts, I = 40 pA)

There is a uniform coverage of the surface, without any islands. Only few small clusters of molecules are observed. We deduce that the physisorbed molecules have a low diffusion behaviour on the silicon surface. As demonstrated by XPS results, there is no strong molecule-surface interaction, but the interaction is high enough to prevent any diffusion of the molecules. After the deposition of a 2 ML of molecules, there is the formation of islands, with a crystal - like structure as shown in Figure 7 where the top surface of an island exhibits a regular structure.

On the contrary, the deposition of one ML of PTCDA molecules on a hydrogenated Si(100) - 2x1 exhibits a complete different behaviour, as shown in Figure 8. In such a case, we observe the spontaneous formation of islands, associated with the two main bright features. They have an average lateral size of 12 nm and a height of 1.2 nm. The small features (a few nm size) are small clusters of molecules. We thus deduce that on such a surface, the mobility of the molecules is high. A detailed

study of the kinetics of formation of the islands is under study.

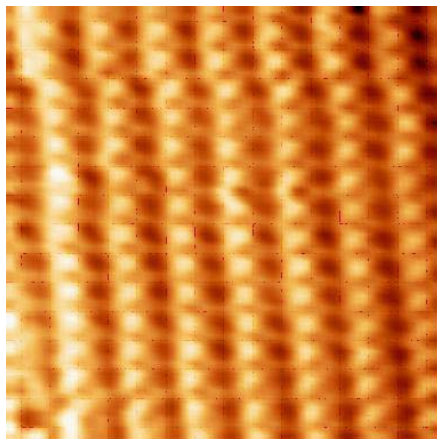


Figure 7 : STM image (15 nm x 15 nm, V = -3.8 volts, I = 35 pA) of the top face of a PTCDA island after a 2 ML deposition on a Si(100)-2x1 surface.

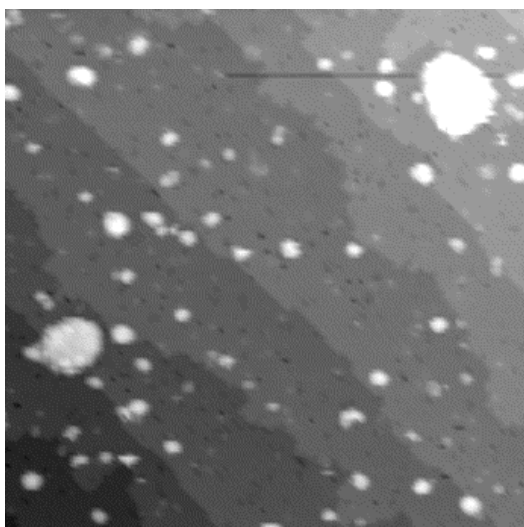


Figure 8 : STM image (85 nm x 85 nm, V = -3.5 volts, I = 40 pA) of a H-Si(100)-2x1 surface after the deposition of one monolayer of PTCDA molecules.

3 CONCLUSION

Using both XPS and STM techniques, we have shown that PTCDA molecules are mainly physisorbed on Si(100)-2x1 or H-Si(100)-2x1 surfaces. However, the mobility of the molecules is higher on H-Si surface compare to Si surface, leading to the creation of islands on H-Si surface even for one monolayer PTCDA deposition. The kinetics of formation of these islands is under study.

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