

## Research Paper

# Effect of Dodecane on the Surface Structure and the Electronic Properties of Pentacene on Modified Si (001)

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**Abstract** The structural and the electronic properties of pentacene on modified Si (001) were investigated using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and ultraviolet photoelectron spectroscopy (UPS). Dodecane was used to modify Si (001) substrates and then pentacene was deposited on dodecane/Si (001). Our STM results show a uniform distribution of aggregated dodecane molecules all over the clean Si (001). The surface structure of pentacene on dodecane/Si (001) examined by AFM is analogous to that of pentacene on SiO<sub>2</sub>. The UPS data showed that the work function of pentacene on clean Si (001) and pentacene on modified Si (001) with dodecane was 6.41 and 5.57 eV, respectively. Our results prove that dodecane results in the work function difference between pentacene on clean Si (001) and pentacene on dodecane/Si (001).

**Keywords:** Organic semiconductor, Organic-inorganic interface, Organic thin films

## I. Introduction

Organic-inorganic interfaces play an important role in organic electronic devices such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs) [1-3]. The properties of organic thin-film transistors depend on the charge transport at the interface between the semiconductor and the electrodes or the inorganic gate insulator. More flexibility in fabricating and controlling devices can be obtained by modifying electrodes, which can lead to tuning the molecular energy levels of an organic semiconductor and thus changing the energy barriers for charge transfer [4-7]. One way to control the alignment of molecular energy levels is to modify the electrodes using self-assembled monolayers (SAMs) [6,7,8]. SAMs can change the electrostatic potentials at the metal-organic semiconductor interface, which control the injection barrier to the organic semiconductors [8]. In addition, SAMs attached to inorganic insulator in OFETs can modulate the charge carrier density in organic semiconductors [9,10].

We created organic-inorganic interfaces using pentacene on modified Si (001) with organic molecules. Pentacene (C<sub>22</sub>H<sub>14</sub>) is an organic semiconductor with a long, planar molecular shape consisting of five benzene rings that facilitates crystalline packing. Pentacene has been widely

used to create organic electronic devices including OFETs, OLEDs and photovoltaics. Pentacene forms a triclinic crystal in bulk with lattice constants of  $a=7.90$  Å,  $b=6.06$  Å and  $c=16.01$  Å [11,12]. Pentacene is easy to work with in ultrahigh vacuum (UHV).

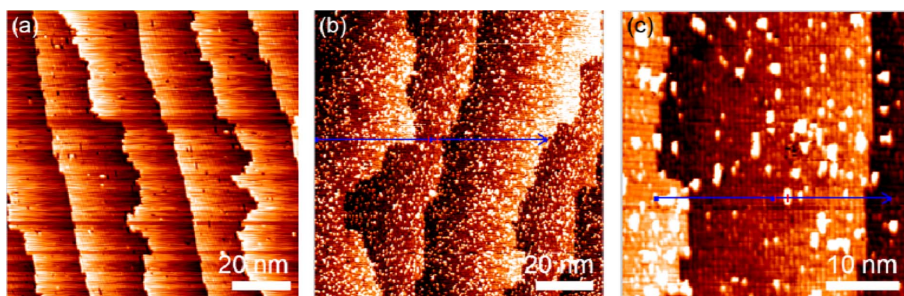
Dodecane was used as a SAM to modify the Si (001) substrates. Dodecane is liquid alkane hydrocarbon with the chemical formula of C<sub>12</sub>H<sub>26</sub>. The *in situ* thin film deposition and the surface characterization using scanning tunneling microscopy (STM) can be done in UHV. Our understanding of the interface properties of organic semiconductors can be improved by describing a molecular-scale structure of the relevant organic-inorganic interfaces using STM. The work function measurements were performed to examine the electronic properties of pentacene on modified Si (001).

In this study, we investigated the effect of dodecane on the surface structure and the electronic properties of pentacene deposited on modified Si (001). We found that the shift in the work function between pentacene on clean Si (001) and pentacene on modified Si (001) is attributed to a change in the electronic property of pentacene due to dodecane.

## II. Experimental

The substrates preparation, dodecane deposition, and STM characterization were carried out in UHV. For STM studies, we used Si (001) wafer as substrates since clean Si (001) is atomically flat, structurally uniform, and highly

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**Figure 1.** STM images of (a) clean Si (001) and (b) dodecane on clean Si (001). (c) The enlarged view of dodecane on clean Si (001). The image sizes are (a) 100 nm×100 nm, (b) 100 nm×100 nm, and (c) 40 nm×40 nm.

conductive. The Si wafer (antimony-doped, *n*-type,  $\rho = 0.02 \text{ W} \cdot \text{cm}$ ) was cleaned by the IMEC procedure [13]. After the IMEC procedure, the sample was degassed at 600°C overnight in the UHV chamber. Clean Si (001) surfaces exhibiting the (2×1) reconstruction were prepared by flashing the sample to 1200°C for 5 s, quenching at 1000°C, and then cooling slowly at a rate of 1°C s<sup>-1</sup>.

Dodecane liquid (Sigma Aldrich, Inc) was deposited on clean Si (001) by introducing 20 Langmuir (1 Langmuir =  $1 \times 10^{-6}$  Torr/s) into the UHV chamber using a leak valve. Pentacene was deposited on dodecane/Si (001) by thermal evaporation in the preparation chamber at the pressure of  $\sim 3 \times 10^{-6}$  Torr. The deposition rate was varied from 0.17 ML/min to 0.25 ML/min with the deposition time ranging between 8 min. and 20 min. Pentacene was deposited at two different source temperatures of 193°C and 200°C and the substrate was kept at room temperature.

The STM measurements were performed using a commercial Omicron UHV STM apparatus with the base pressure below  $1 \times 10^{-10}$  Torr. Clean Si (001) was imaged at  $V = -1.5 \text{ V}$  and  $I = 500 \text{ pA}$  before deposition of organic molecules to make sure the substrate is clean. The measured step height in the sectional profile was approximately 120 pm, which is close to the theoretical value of 138 pm. After the Si (001) exposure to dodecane in the UHV chamber, the STM images of dodecane/Si (001) were obtained at negative tip biases at  $V = -2.0 \text{ V}$  and  $I = 200 \text{ pA}$ . The AFM analysis of pentacene on dodecane/Si (001) was performed in ambient condition using tapping mode (Digital Instruments Multimode IV, USA).

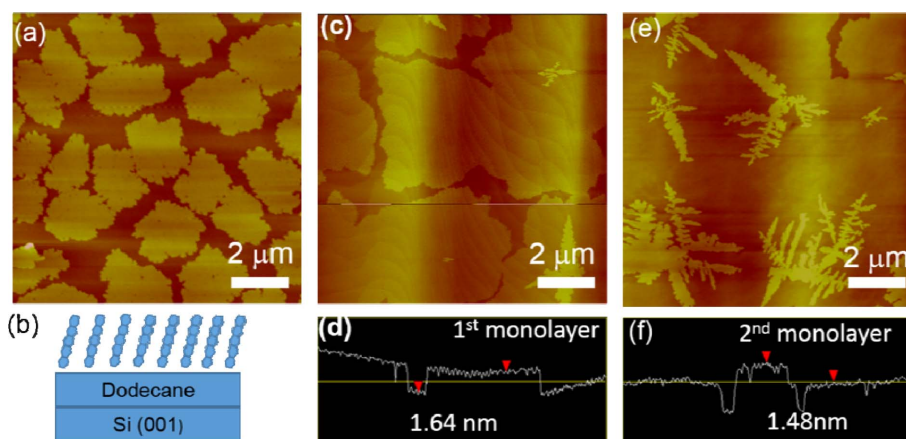
### III. Results and Discussions

The STM images of clean Si (001) before and after the exposure of dodecane are shown in Fig. 1. The STM image in Fig. 1(a) shows the (2×1) reconstructed surface of clean Si (001) without dodecane. The (1×2) and (2×1) domains alternate in each atomic layer with dimer rows rotated by 90°, giving rise to (2×1) periodicity. The dimer rows and vacancies are clearly visible, which confirms that no dodecane is exhibited. On the contrary, there is a drastic change in the STM image of dodecane on clean Si (001) after the exposure of dodecane as shown in Fig. 1(b). The

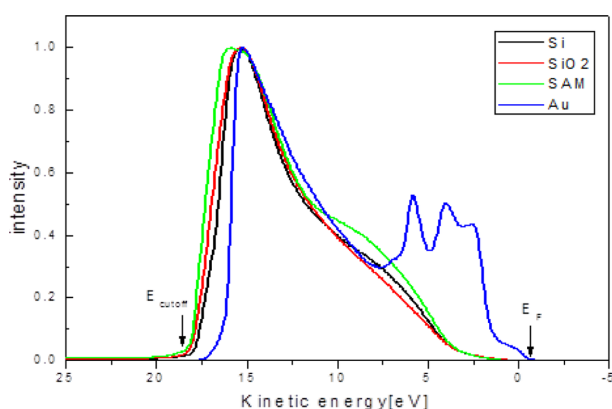
STM image shows dodecane molecules distributed all over the Si surface after dodecane exposure. The dodecane molecules appear as bright features in the image and the height of the bright feature indicated by a blue line is approximately 162 pm. The enlarged STM image of dodecane on Si (001) in Fig. 1(c) shows that each bright feature is not a single molecule, but aggregated dodecane molecules. The height of the aggregated dodecane molecules represented as a blue line is about 144 pm. A series of repeatable height measurements revealed that the average height of the aggregated dodecane molecules is  $157 \pm 50 \text{ pm}$ . Taking into account that the fully extended chain length of dodecane is 180 pm [14], the smaller height measured in the STM images implies that the dodecane molecules are not completely standing up. Even though some fraction of the Si (001) dimers is exposed, the coverage of dodecane on clean Si (001) measured from a set of samples ranges between 37% and 46%.

Theoretical calculations predicted that the reactive sites of Si (001) dimers are covered by physical adsorption of dodecane molecules [15]. Single dodecane molecule prefers lying down on clean Si (001) along the [110] direction to reduce instability; on the other hand, dodecane molecules in a film partially stand up due to the lack of space to fully seat all of the molecules [15]. In connection with the STM image of dodecane/Si (001), as the concentration of dodecane increases, impinging dodecane molecules seem to adsorb around the molecules already situated on the substrate.

Fig. 2 shows the AFM images of pentacene deposited on dodecane/Si (001), which exhibits a typical pentacene thin film growth on SiO<sub>2</sub> with standing-up molecular orientation. This means the structure of pentacene on dodecane/Si (001) is similar to that of pentacene on SiO<sub>2</sub>. Fig. 2(a) shows the first molecular layer of pentacene at the initial stage of pentacene thin film growth with random-shaped islands. The schematic diagram in Fig. (b) illustrates the upright geometry of pentacene molecules on dodecane/Si (001). The larger view of pentacene on dodecane/Si (001) in Fig. (b) shows that the pentacene film is so smooth that the Si atomic steps are visible through the dodecane layer. This means a high-quality pentacene thin films can be designed using a modified Si (001) substrate



**Figure 2.** (a) AFM image of the first molecular layer of pentacene on dodecane/Si (001). (b) Schematic of pentacene on dodecane/Si (001). (c) Enlarged AFM image of the first molecular layer of pentacene on dodecane/Si (001). (d) Sectional profile corresponding to (c). (e) AFM image of the first and the second molecular layer of pentacene on dodecane/Si (001).



**Fig. 3.** UPS spectra of pentacene deposited on clean Si (001), SiO<sub>2</sub>, dodecane (SAM), and gold represented as black, red, green and blue lines.

with dodecane. The sectional profile of the first molecular layer of pentacene in Fig. 2(d) confirms that the pentacene island is one-molecule high.

As the pentacene deposition increases, the second molecular layer of pentacene starts forming on top of the first molecular layer of pentacene as shown in Fig. 2(e). The measured height of a second molecular layer of pentacene in Fig. 2(f) is one-molecule thick.

The electronic property of pentacene on dodecane/Si (001) was investigated using UPS. Pentacene was deposited on various substrates to compare the work function of the pentacene samples. Fig. 3 shows the UPS spectra of pentacene deposited on clean Si (001), SiO<sub>2</sub>, dodecane, and gold indicated as black, red, green, and blue lines, respectively. Gold (Au) was used as a standard spectrum to measure the work function of pentacene.

The work function of pentacene can be obtained with the binding energy of the electrons at the secondary edge ( $E_{\text{cutoff}}$ ) as the following equation:

$$\Phi_{\text{pentacene}} = h\nu - |E_{\text{cutoff}} - E_F|$$

Here,  $\Phi$  is the work function of pentacene and  $E_F$  is the

Fermi energy. The UV photons energy is 21.21 eV for He I radiation. The work function of pentacene from the UPS spectra was 6.51, 5.73, and 5.57 eV for pentacene on Si (001), SiO<sub>2</sub>, and dodecane/Si (001), respectively. Our data indicate that the work function of pentacene on SiO<sub>2</sub> is close to pentacene on dodecane/Si (001). The difference in the work function between pentacene on clean Si (001) and pentacene on dodecane/Si (001) was only 0.16 eV. However, the work function of pentacene on dodecane/Si (001) differs from that of pentacene on clean Si (001) by 0.94 eV, which means dodecane results in a shift in the work function of pentacene on clean Si (001) and pentacene on modified Si (001). This result implies that the presence of dodecane caused a change in the electronic property of pentacene.

### III. Conclusions

The surface structure and the work function of pentacene on modified Si (001) with dodecane molecules were examined to elucidate the effect of dodecane on the electronic property of pentacene on a modified substrate. The STM data show that aggregated dodecane molecules are all over the clean Si (001) surface. Our results show that the structure of pentacene on dodecane/Si (001) is analogous to that of pentacene on SiO<sub>2</sub>. The UPS results demonstrate that dodecane is attributed to a change in the work function of pentacene on dodecane/Si (001) in comparison to that of pentacene on clean Si (001), which suggests that dodecane has influence on the energy levels of pentacene.

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