

Scanning tunnelling spectroscopy of low pentacene coverage on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S2693

(<http://iopscience.iop.org/0953-8984/15/38/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 15:13

Please note that [terms and conditions apply](#).

Scanning tunnelling spectroscopy of low pentacene coverage on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface

Ph Guaino¹, A A Cafolla, O McDonald, D Carty, G Sheerin and G Hughes

School of Physical Sciences and National Centre for Sensor Research (NCSR),
Dublin City University, Glasnevin, Dublin 9, Republic of Ireland

E-mail: pgu@physics.dcu.ie

Received 10 July 2003

Published 12 September 2003

Online at stacks.iop.org/JPhysCM/15/S2693

Abstract

The low coverage S1 phase of pentacene deposited on Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) has been investigated at room temperature by scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS). Current–voltage data were acquired simultaneously with STM images for this phase. The normalized conductivity reveals two pronounced peaks at -1.10 and $+2.25$ V relative to the Fermi level. These peaks are attributed to resonant tunnelling through the highest occupied molecular orbital and lowest unoccupied molecular orbital molecular levels of the pentacene layer. The electronic properties of this interface are discussed in relation to results obtained for pentacene adsorbed on other metallic surfaces.

1. Introduction

Organic π -conjugated compounds are of increasing interest because of their potential applications in novel molecular scale electronic devices [1, 2]. Scanning tunnelling microscopy (STM) and associated spectroscopies are excellent techniques for investigating the properties of organic films [3, 4]. A detailed knowledge of the structural and electronic properties of organic interfaces is important for a full understanding of device performance. For example, the molecular packing in an organic material can strongly influence the electron and hole mobilities [5].

Deposition of pentacene on the Ag/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface (henceforth referred to as Ag/Si- $\sqrt{3}$) at room temperature (RT) produces three ordered solid phases, S1, S2 and S3, with increasing coverage [6]. In this paper, we report preliminary scanning tunnelling spectroscopy (STS) data acquired simultaneously with STM images of the first solid phase S1.

¹ Author to whom any correspondence should be addressed.

2. Experimental details

The STM and STS experiments were performed at RT in an ultra-high vacuum system with a base pressure of 5×10^{-11} mbar, using an Omicron variable temperature instrument. An electrochemically etched polycrystalline tungsten tip was used.

The Si substrate was p-type boron-doped Si(111) with a resistivity of 0.1–1.0 Ω cm. Atomically clean Si(111)-(7 \times 7) surfaces were prepared in the usual manner by *in situ* direct current heating to 1250 °C after the samples were first degassed at 600 °C for \sim 10 h. The clean Si(111)-(7 \times 7) surface was checked with the STM before preparation of the ($\sqrt{3} \times \sqrt{3}$)-Ag surface. Silver was deposited by e-beam evaporation from a molybdenum crucible onto the Si substrate which was maintained at 500 °C. Pentacene (Aldrich Chemicals) was evaporated from a tantalum crucible in a home-made deposition cell operated at a temperature of \sim 300 °C. Pentacene evaporation was performed in a preparation chamber isolated from the STM chamber. Before evaporation the pentacene was degassed at 250 °C for about 12 h to remove water vapour. The pentacene evaporation rate was approximately 1 ML (monolayer) min^{-1} .

Tunnelling spectra were acquired either in single-point mode or on a grid of specified points within an image. In the latter mode, spectroscopy measurements were performed on a regular subset of the image raster point. At each pixel where an $I(V)$ spectrum is recorded, the scan is interrupted during imaging. The feedback loop is switched off and a voltage ramp is applied after a short delay time in order to allow stabilization of the current preamplifier. In between these pixels the feedback is on and the STM operates in constant current mode. While recording $I(V)$ spectra it was ensured that current measurements did not exceed the dynamic range of the current preamplifier.

3. Results and discussion

3.1. Structural properties

Figure 1 shows an STM image of the solid phase S1, obtained after a coverage of \sim 0.35 ML of pentacene on the Ag/Si- $\sqrt{3}$ surface. This STM image presents an area of 40 nm^2 recorded at a bias voltage of -1.5 V. The molecules adsorb lying flat on the surface, which is often observed for physisorbed planar polyacene molecules [7–10]. Three molecular domains are observed oriented at 120° with respect to each other. Within each domain the molecules are observed to form periodic parallel rows and the individual molecules adopt a head-to-head orientation. The unit cell vectors, b_1 and b_2 , for the S1 phase adlayer are 18.4 and 20.0 Å, respectively, with an angle of $\gamma = 113^\circ$ between these vectors. In order to determine the structure of this phase, we performed an STM study of the initial stages of growth of the S1 phase [11], where it was possible to image both the pentacene molecules and the structure of the Ag/Si- $\sqrt{3}$ substrate. From these results, two adsorption sites were identified: a three-fold hollow site at the centre of a Ag trimer and a six-fold hollow site at the centre of the hexagonal arrangement of silver atoms. We have proposed that this solid phase S1 has a high-order commensurate lattice, Ag/Si(111)-(25 \times 25)-pentacene, containing 75 molecules.

3.2. Current–voltage spectroscopy

Stable STM images could only be recorded at very specific voltages. STS measurements were performed on a grid of 10 \times 10 points during acquisition of the STM image shown in figure 1. The bias voltage was ramped from $V_{\text{sample}} = -2.5$ V to $V_{\text{sample}} = +2.5$ V with a current–voltage set point of 100 pA and -1.5 V. Spectroscopic measurements were limited to

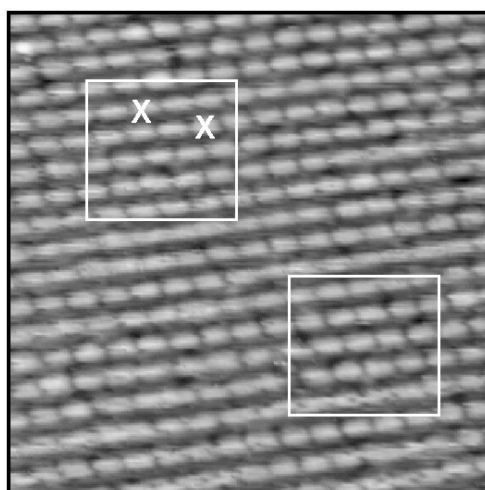


Figure 1. STM image of the S1 phase. Molecules are lying flat on the surface. The unit cell vectors, b_1 and b_2 , for this adlayer are 18.4 and 20.0 Å, respectively, with an angle of $\gamma = 113^\circ$ between these vectors. Crosses indicate points where current–voltage spectra, shown in figures 2(a) and (b), were measured. Boxes show the area of surface where current–voltage spectra were averaged. Image parameters: size = 28×28 nm², $V_{\text{sample}} = -1.5$ V, $I_t = 100$ pA.

this voltage range because, for higher voltages, surface damage occurred. Within this voltage range the molecular adlayer remains intact and unaltered on the surface. This is confirmed by the STM image acquired simultaneously with the spectroscopy measurements. Moreover the condition of the surface was carefully checked by comparing the images taken before and after the spectroscopy measurements. The quality of the STM image recorded during STS acquisition was very sensitive to the current and voltage set point with the best data recorded at the set point given above. For this reason it was not possible to investigate the dependence of features observed in the $I(V)$ spectra on the tunnelling distance.

Examples of $I(V)$ curves, recorded at several points on the surface, are shown in figure 2. The curves (a) and (b) represent $I(V)$ spectra recorded at individual points on the surface while curve (c) shows an $I(V)$ spectrum averaged over several individual measurements acquired in the square region indicated on the STM image. This averaging enhances the signal-to-noise ratio and clearly shows sharp features. Repeated STS measurements on different areas of this surface show that these features are reproducible.

Note that a singularity occurs at zero bias in some $I(V)$ spectra. This is due to an instrumental effect in the data acquisition electronics. This type of singularity has been observed previously [12]. However, this effect has a relatively minor consequence. Effectively, we have performed the same STS measurements by ramping the voltage from a value slightly above or below zero bias to $V_{\text{sample}} = +2.5$ and -2.5 V, respectively. The zero value of the tunnelling current was then adjusted by comparing these two spectra to a single spectrum acquired over the entire voltage range.

In order to interpret the $I(V)$ spectra, we numerically calculated the normalized conductivity given by the normalized derivative $(dI/dV)/(I/V)$ [13]. This normalized conductivity should be related to the local density of states (LDOS) of the surface [14]. Division by the voltage leads to a divergence around zero bias and several methods to eliminate this divergence have been used and discussed [14]. Here we simply add a small constant offset to the I/V curves, without applying any broadening.

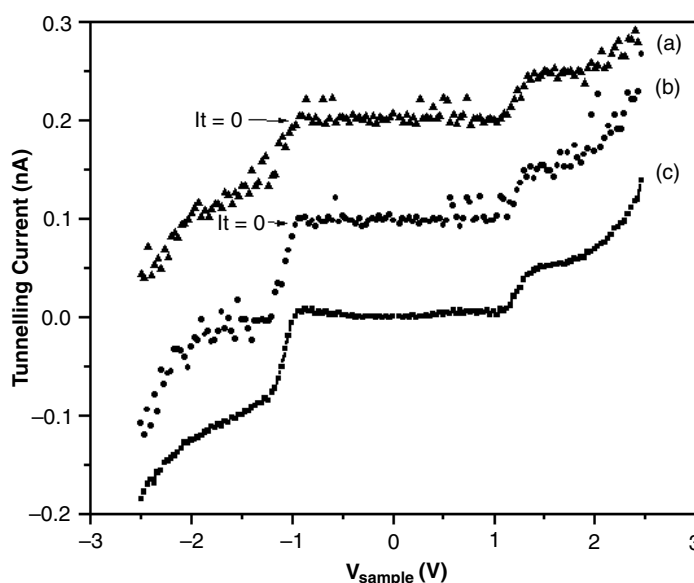


Figure 2. $I(V)$ spectra recorded during STM image acquisition. (a) and (b) spectra recorded at the points indicated by crosses in figure 1, (c) spectra averaged over points in the upper box in figure 1.

Figure 3 shows two normalized conductivity spectra (a) and (b). The spectra reveal two pronounced peaks centred at -1.10 and $+1.25$ V approximately and a broader peak centred at around 0.50 V. These peaks are indicated by the arrows in figure 3. The full width at half-maximum of the narrowest peak is about 0.3 eV, which is typical of the resolution obtained by this spectroscopy technique at room temperature [15].

Tip effects can play a significant role in tunnelling spectroscopy experiments. Measurements on a series of direct-gap III–V semiconductors [13] have shown that the normalized conductance spectrum can vary significantly with different tips. The broader peak at 0.50 V was only seen in one set of STS measurements. We attribute this feature to the electronic properties of the tip.

The two sharp peaks are present in all spectra. We have also performed, with the method described here, STS measurements on the clean $\text{Ag/Si-}\sqrt{3}$ surface. Atomic resolution in the STM image was obtained during these $I(V)$ measurements and both peaks were absent in the normalized conductivity. We can therefore safely associate these reproducible spectral features with the solid phase S1 formed by the pentacene film on the $\text{Ag/Si-}\sqrt{3}$ surface. It is noted that no difference is observed in spectra recorded at different points or in averages over different areas of the surface, except for changes associated with the tip as described above. This may be explained by the relatively low signal-to-noise ratio.

The peaks at 1.10 and 1.25 eV, caused by resonant tunnelling [16] through the molecular levels of the pentacene film, should reflect the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively. Assuming that no band bending occurs at the interface and that changes in the molecular potential with respect to the substrate are negligible [17], the HOMO and LUMO energy levels are at 1.10 and 1.25 eV, respectively, below and above the Fermi level of the film. The width of the gap then has a value of 2.35 eV. This value is almost equal to the charge transport gap of 2.24 eV determined from intrinsic

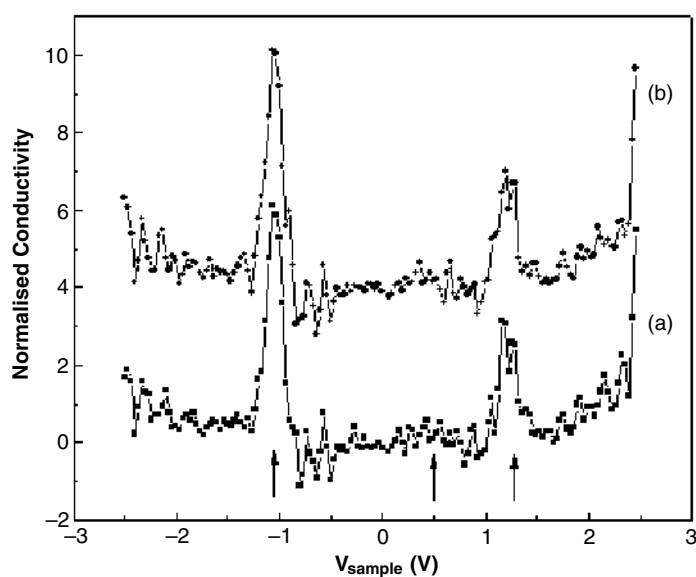


Figure 3. Normalized conductivity spectra ($dI/dV)/(I/V)$ of the pentacene film calculated from the average $I(V)$ spectra measured (a) in the upper box and (b) in the lower box in figure 1. Three peaks appear in the $(dI/dV)/(I/V)$ spectra as indicated by the arrows. The two pronounced peaks at around -1.10 and $+1.25$ V correspond to resonant tunnelling out of and into the HOMO and LUMO levels, respectively. The broader peak at 0.50 V is attributed to a tip effect.

photoconductivity measurements in pentacene [18]. Moreover, the electronic properties of solid pentacene for two different crystalline phases—S (solution-phase crystallized) and V (vapour-phase crystallized)—were recently determined from *ab initio* calculations [19]. In these calculations energy gaps of 2.2 and 1.9 eV were determined for the S and V phases, respectively, which is consistent with our experimentally determined value.

No extra peaks are observed in the $I-V$ spectra within a range of 1.5 eV below the HOMO and above the LUMO peaks. Assuming that the signal-to-noise ratio is sufficiently large, no additional molecular orbitals are present in this energy range. This is consistent with band structure calculations of solid pentacene [19] which show that the energy gap between the first and second occupied (unoccupied) energy bands is greater than 1.0 eV.

Pentacene films deposited on several surfaces have been investigated by ultraviolet photoelectron spectroscopy (UPS). On the samarium surface [20] the Fermi level of the metal is measured at 1.85 eV above the HOMO onset in pentacene. On the Au(111) surface [10] the HOMO–LUMO gap is measured to be 1.85 eV. Our measurement appears reasonable in comparison with values quoted in the literature. However, slight differences occur in the positions of the molecular levels with respect to the Fermi level and in the width of the HOMO–LUMO gap. This is not surprising because charge transfer between the molecules and the substrate depends critically on the nature of the interface [21]. In addition, the molecular packing density may also influence the transport properties of the material. Alvarado *et al* [22] have investigated the charge carrier injection into thin films of CuPc by $z-V$ spectroscopy measurements. They conclude that the effect of stacking results in a reduction of the HOMO–LUMO gap with increasing strength of the intermolecular interaction. Because the pentacene–Ag/Si- $\sqrt{3}$ surface has three different structures, we believe that this system is a good candidate for investigating the contribution of molecular packing to changes in the electronic structure.

3.3. Summary

From simultaneous current–voltage spectroscopy and STM measurements the positions of the HOMO and LUMO with respect to the Fermi level were determined for the S1 phase of the pentacene-Ag/Si- $\sqrt{3}$ surface. Comparison with data for pentacene adsorbed on other substrates shows a difference in the positions of the HOMO and LUMO energy levels with respect to the Fermi level and the energy gap between these two levels. STS measurements on the three different phases should give a better understanding of the influence of the electronic levels involved in charge injection with molecular packing.

Acknowledgments

This work was supported by Enterprise Ireland and the Higher Education Authority through the Programme for Research in Third Level Institutions (PRTL). GS acknowledges support from the Irish Research Council for Science, Engineering and Technology (IRCSET).

References

- [1] Meyer zu Heringdorf F-J, Reuter M C and Tromp R M 2001 *Nature* **412** 517
- [2] Kamma M M, Stranick S J and Weiss P S 1996 *Science* **274** 119
- [3] Proehl H, Toerker M, Sellam F, Fritz T, Leo K, Simpson C and Müllen K 2001 *Phys. Rev. B* **63** 205409
- [4] Alvarado S F, Seidler P F, Lidzey D G and Bradley D D C 1998 *Phys. Rev. Lett.* **81** 1082
- [5] Bredas J L, Calbert J P, da Silva Filho D A and Cornil J 2002 *Proc. Natl Acad. Sci. USA* **99** 5804
- [6] Guaino Ph, Carty D, Hughes G, Moriarty Ph and Cafolla A A 2003 *Appl. Surf. Sci.* **212/213** 537
- [7] Lukas S, Vollmer S, Witte G and Wöll Ch 2001 *J. Chem. Phys. Rev.* **114** 10123
- [8] Lukas S, Witte G and Woll C 2002 *Phys. Rev. Lett.* **88** 028301
- [9] Harada Y, Ozaki H and Ohno K 1984 *Phys. Rev. Lett.* **52** 2269
- [10] Schroeder P G, France C B, Park J B and Parkinson B A 2002 *J. Appl. Phys.* **91** 3010
- [11] Guaino Ph, Cafolla A A, Carty D, Sheerin G and Hughes G 2003 *Surf. Sci.* **540** 107
- [12] Hipps K W, Barlow D E and Mazur U 2000 *J. Phys. Chem. B* **104** 2444
- [13] Feenstra R M 1994 *Phys. Rev. B* **50** 4561
- [14] Stroscio J A and Williams J (ed) 1993 *Scanning Tunnelling Microscopy: Methods of Experimental Physics* vol 27 (Boston, MA: Academic)
- [15] Dekker C, Tans S J, Oberndorff B, Meyer R and Venema L C 1997 *Synth. Met.* **84** 853
- [16] Pomerantz M, Aviram A, McCorkle R A, Li L and Schrott A G 1992 *Science* **255** 1115
- [17] Datta S, Tian W, Hong S, Reifenberger R, Henderson J I and Kubiak C P 1997 *Phys. Rev. Lett.* **79** 2530
- [18] Silinsh E A and Capek V 1994 *Organic Molecular Films* (New York: American Institute of Physics)
- [19] Tiago M L, Northrup J E and Louie S G 2003 *Phys. Rev. B* **67** 115212
- [20] Koch N, Ghijsen J, Johnson R L, Schwartz J, Pireaux J J and Kahn A 2002 *J. Phys. Chem. B* **106** 4192
- [21] Watkins N J, Yan L and Gao Y 2002 *Appl. Phys. Lett.* **80** 4384
- [22] Alvarado S F, Rossi L, Muller P and Reiss W 2001 *Synth. Met.* **122** 73