Study of the initial adsorption state of tetracene on $\mathrm{Ru}(10\bar{1}0)$

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Abstract
Tetracene on the Ru(10̄10) surface has been investigated by ultraviolet
photoemission spectroscopy (UPS). The UPS results show features, from
tetracene, between 2.0 and 10.0 eV below the Fermi level, and their shift in
binding energy with increasing coverage. Angle-resolved UPS (ARUPS) results
indicate that the molecular plane of tetracene near the interface is parallel to
the substrate. Moreover, an *ab initio* calculation has also been carried out to
determine the favourable adsorption structure. Temperature-dependent UPS
measurements show that tetracene is stable on the Ru(10̄10) surface up to
150 °C.

1. Introduction

In recent years, there has been great interest in polyacenes as molecular semiconducting
materials [1–7]. In particular, tetracene ($C_{18}H_{12}$, composed of four benzene rings with
D_{2h} symmetry) and pentacene ($C_{22}H_{14}$, one more benzene ring added to the former, with
the same symmetry) have been extensively investigated, since thin films of these molecules
show promising high charge-carrier mobility in organic devices, such as organic field-effect
transistors (OFETs) [3–5] and organic light-emitting diodes (OLEDs) [6, 7]. It is well
known that charge mobility and injection in organic crystals depend strongly on the molecular
orientation and packing. Therefore, the importance of the interface structures and the quality of
the grown film for organic devices have also motivated a number of surface science experiments
on these materials. Tetracene has been studied on Ag(110) [8], Ag(111) [9], Cu(110) [10],
Si(100)-(2 × 1) [11] and hydrogen-passivated Si(001) [12]. All these studies have shown that,
although different structures are formed, the molecules are adsorbed in a flat-lying geometry
with maximum interactions between molecules and substrates [13]. However, it is noticeable
that few investigations have been carried out on the molecules adsorbed on reactive metal
surfaces, and therefore, our knowledge of the strong interaction between the first molecular
layer and the substrate is still very limited.

Ruthenium is a kind of reactive transition metal. Perylene on the Ru(0001) surface has been studied by Lu *et al* [14]. Ru(10$\bar{1}$0) is a lower symmetry surface comparing with Ru(0001), on which the orientation of an organic molecule can be determined clearly. Scanning tunnelling microscopy (STM) images haves shown that the longer axis of tetracene is along either the [1$\bar{2}$10] or [0001] azimuth [15]. Herein, the electronic structure of tetracene on the Ru(10$\bar{1}$0) surface is elucidated with coverage and surface temperature-dependent UPS measurements, and the possible interaction between molecule and substrate is examined with an *ab initio* calculation.

2. Experimental details

Both sample preparation and investigation were carried out in an ultrahigh-vacuum (UHV) system. The photoemission measurements were taken with an ADES-400 electron energy spectrometer (VG) with an overall resolution of 0.05 eV, as described in detail elsewhere [16–18]. The ultraviolet (UV) light used in the experiments was unpolarized He I, and the photo energy is 21.2 eV. The base pressure of the chambers was better than 2×10^{-10} mbar. The clean Ru(10$\bar{1}$0) surface was obtained after several cycles of argon-ion sputtering (2000 eV for 20 min) followed by an annealing at 800 °C. The surface ordering and cleanliness were checked by both low-energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS) measurements. Tetracene powder (Sigma, 99%) was purified thoroughly by pre-heating in a Ta boat at about 110 °C overnight. The deposition of tetracene was performed when the source temperature was about 140 °C at a deposition rate of 0.5 ML min^{-1}, while the substrate was held at room temperature. The temperature of the sample was detected by a K-type thermocouple attached to the sample stage; the error with respect to the sample temperature is less than 10°. The thickness of the organic adlayer was monitored with a calibrated quartz crystal oscillator.

3. Results and discussion

UPS spectra recorded from the Ru(10$\bar{1}$0) surface with different amounts of organic molecules are shown by solid lines in the left-hand part of figure 1. The spectra were collected along the surface normal direction with a photon incidence angle of 30°. The nominal thickness of the organic film is 0.0, 0.5, 0.7, 1.0, 2.0, 3.0, 4.0, 10.0 and 12.0 ML respectively. As seen in figure 1, with tetracene deposition, the intensity of the emission features of the ruthenium substrate decreased, and the features originating from the tetracene film appear at 2.1, 3.8, 6.5 and 9.4 eV below the Fermi level (labelled as α, β, γ and δ in figure 1). With increasing coverage, peaks β, γ and δ shift towards the lower binding energy range and two new peaks originating from the organic material (labelled as η and ε in figure 1) emerge at 4.8 and 7.1 eV, respectively. When the coverage is about 12.0 ML, the features originating from tetracene are located at 2.1, 3.5, 4.8, 6.0, 7.1 and 9.2 eV in binding energy, respectively. There is less influence from the substrate on tetracene molecules in the case of the multilayer; such a coverage-dependent shift in binding energy can be assigned to the charge redistribution, and indicates that interaction occurs between these molecular orbital and the d band of the ruthenium substrate at the interface.

Based on the variation in the secondary cut off in the UPS, we can obtain the change in workfunction. As shown in the right-hand part of figure 1, the cut-off energies are 17.0, 17.2, 17.4, 17.6, 17.5, 17.5, 17.4, 17.3 and 17.3 eV for the thicknesses of 0.0, 0.5, 0.7, 1.0, 2.0, 3.0, 4.0, 10.0 and 12.0 ML, respectively. The corresponding values of workfunction are 4.2,
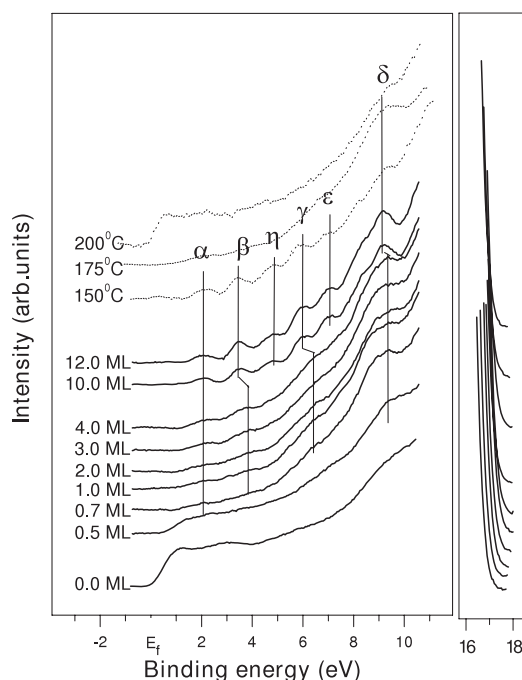
Figure 1. Left: normal emission UPS spectra as a function of surface coverage at room temperature (solid lines) and temperature-dependent UPS spectra of multilayer tetracene on the Ru(10$\bar{1}$0) surface (dashed lines). Right: the coverage-dependent cut-off energies.

4.0, 3.8, 3.6, 3.7, 3.7, 3.8, 3.9 and 3.9 eV. The decrease in workfunction can be attributed to the formation of a small polaron, which is caused by polarization of the organic molecules at the beginning of deposition. The minimum work function of 3.6 eV represents the coverage of 1.0 ML. The work function increases slightly with further deposition, and the value 3.9 eV represents the workfunction of the organic film. The change in workfunction is typical on an interface between organic semiconductors and metals.

A high-accuracy theoretical calculation, including algebraic diagrammatic construction [ADC (3)] schemes with shake-up ionization energy, has been carried out for an individual tetracene molecule. The work can not only determine the symmetry of both π and σ orbitals with accurate binding energies but also reconstruct the full photoemission spectrum with reasonable relative intensities. Table 1 shows the molecular orbitals of tetracene with binding energy less than 14.0 eV. The normal direction of the molecular plane is defined as the z axis. The theoretical results together with the symmetry of the orbital are also summarized in table 1, and the photoemission data from a monolayer and a multilayer on the Ru(10$\bar{1}$0) surface are corrected with the workfunctions 3.6 and 3.9 eV respectively.

Gas-phase tetracene [19] has photoemission peaks at 6.9, 8.3, 8.6, 9.6, 9.7, 9.9, 10.2, 11.2, 12.0, 13.3 and 14.2 eV, in which the peaks at 8.3, 9.6, 10.2, 11.2 12.0, 13.3 and 14.2 eV have the strongest intensities, due to the superposition of unresolved states. Compared with the presence of the solid surface, the UPS spectra of tetracene on the Ru(10$\bar{1}$0) surface are relatively broad. Therefore the peaks can be assigned only to the bands arising from several electronic states; they are also corrected with the workfunction. The peak α, corresponding to the highest occupied molecular orbital (HOMO), originates from the same orbital of tetracene in the gas phase at 6.9 eV. It is well resolved, since there are no other states close to this energy.

Table 1. The molecular orbitals of tetracene with binding energy less than 14.0 eV.

Level	ADC(3)	Type	Symmetry	Monolayer		Multilayer		Gas phase
1	−5.122 03	π	b_{1g}	2.1	5.7	2.1	6.0	6.9
2	−6.6077	π	b_{1g}					
3	−6.704 26	π	b_{1u}					
4	−7.778 11	π	b_{1g}	3.8	7.4	3.5	7.4	8.3
5	−8.0463	π	b_{2g}					
6	−8.536 45	π	b_{1g}			4.8	8.7	8.6
7	−9.059 23	σ	a_{g}					
8	−9.398 96	σ	b_{1g}					9.6
9	−9.403 58	σ	b_{3u}					
10	−9.451 73	π	b_{1u}					
11	−10.1519	σ	a_{g}	6.5	10.1	6.0	9.9	10.2
12	−10.2114	σ	b_{2u}					
13	−10.5416	π	b_{2g}					10.8
14	−11.149	σ	b_{3u}			7.1	11.0	11.0
15	−11.245	π	b_{1u}					11.2
16	−11.4017	σ	b_{3u}					
17	−11.5304	σ	b_{1g}					11.5
18	−11.6122	σ	b_{1g}					
19	−11.8121	σ	b_{2u}					12.0
20	−12.3167	σ	a_{g}					
21	−12.4992	σ	b_{1g}					
22	−12.6026	σ	b_{2u}					12.5
23	−12.617	σ	a_{g}	9.4	13.0	9.2	13.1	13.1–13.6
24	−13.7248	σ	b_{2u}					
25	−13.73	σ	b_{3u}					14.0

The peaks β, η, γ, ε and δ originate from the orbitals of tetracene in the gas phase at 8.3, 8.6, 10.2 11.0 and 13.3 eV respectively.

In table 1, the symmetry labels providing the ionized states of the molecule are consistent with the standard molecular orientation. A clear understanding of the symmetry of the individual electronic state is essential for determining the molecular orientation from UPS under restricted collection geometry. On the Ru(10$\bar{1}$0) surface, to identify the adsorption geometry, we combine a molecular orbital symmetry analysis with the angular-dependent UPS measurements. In the ARUPS measurements, the spectra were taken from a saturated monolayer of tetracene on Ru(10$\bar{1}$0) with different photon-incidence angle. A change in the intensities of the peaks can be observed, as shown in figure 2(a). The intensities of peaks α and β decrease, but those of peaks γ and δ increase with increasing incidence angle. The emissions of α, β, γ and δ are corresponding to the orbitals of 6.9, 8.3, 10.2 and 13.3 eV featuring in the gas phase. The emissions of α and β, with π character located at C–C bands, are dominated by the states with b_{1g} symmetry. On the other hand, the emissions of γ and δ with σ character located at C–H and C–C bands are dominated by the states with a_{g} and b_{1u} symmetries, as seen in figure 2(b). The calculation is different from that of previous publications [15], but the orbital looks similar. At normal incidence with a collection angle of 30° off the direction normal to the surface, if the molecule is lying flat on the surface, the orbital of α and β should have the larger photoemission cross section, and the orbital of γ and δ should have a relatively small photoemission cross section. With the incidence angle increased, the photoemission cross section of the α and β orbital decreases, while that of the γ and δ orbital increases. The intensity variation of the orbital from ARUPS measurements suggests that the molecular plane is parallel to the substrate.
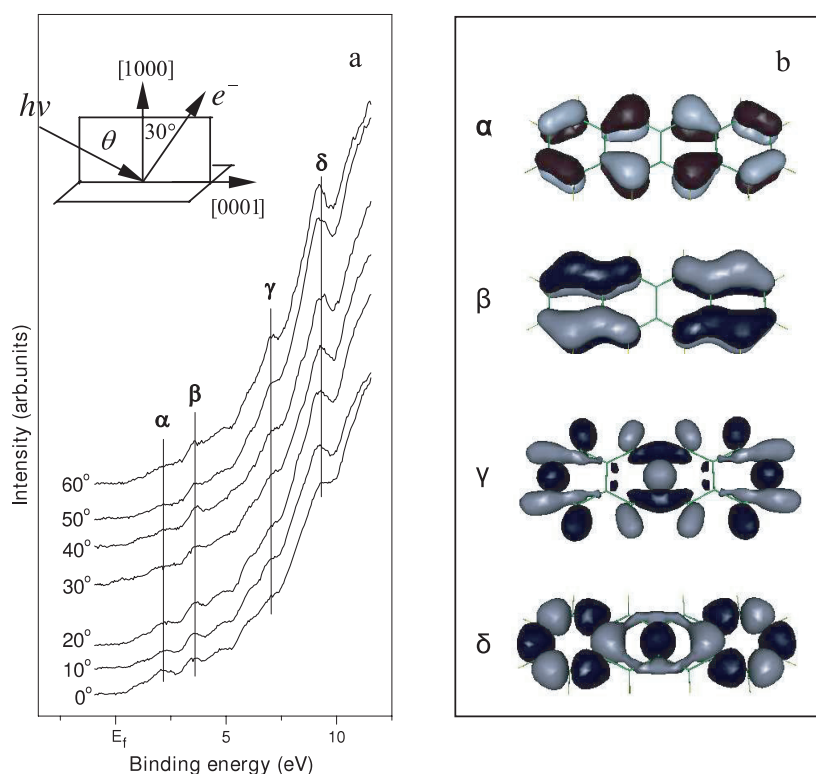
Figure 2. (a) ARUPS measurement with different photon incidence angle, θ, relative to the surface normal direction from a monolayer of tetracene adsorbed on the Ru(10$\bar{1}$0) surface. (b) Charge density of the main orbital of peaks α, β, γ and δ.

ARUPS measurements, as shown in figure 2(a), were carried out with the incidence plane in the [0001] azimuth. No difference can be observed when we changed the incidence plane from the [0001] to the [1$\bar{2}$10] azimuth. This suggests that the molecular orientation is not identical, and this has been confirmed by STM measurements [15]. Figure 3(a) is an STM image of sub-monolayer tetracene on the Ru(10$\bar{1}$0) surface. The long axis of tetracene is along either the [1$\bar{2}$10] or the [0001] azimuth on the Ru(10$\bar{1}$0) surface. A statistic analysis of the distribution of these two orientations from hundreds of molecules shows a ratio close to 1:1. Only less than 1% molecules do not lie along either of these two directions.

To determine the favourable adsorption site of tetracene on Ru(10$\bar{1}$0), *ab initio* calculations were performed with the *Gaussian* 03 package [20] using the LanL2mb basis set [21, 22] and B3LYP density functional theory [23]. Individual tetracene molecules prefer the lying-flat adsorption mode with their long axes either along the [0001] or [1$\bar{2}$10] azimuth. The symmetry will reduce from D_{2h} for isolated tetracene to C_{2v} for tetracene on the substrate. For tetracene molecules aligning along each azimuth, there are four possible adsorption geometries with the highest symmetry: C_{2v}. Accordingly, there are eight typical adsorption configurations with different adsorption sites, as shown in figure 3(b).

The energy of an isolated molecule together with the substrate supercell was calculated. The adsorption structure was optimized with minimum energy. The results indicate that, for all eight configurations, the molecular plane is not completely parallel to the ruthenium surface, but there is a slight bend due to the different interaction between the carbon atom of tetracene
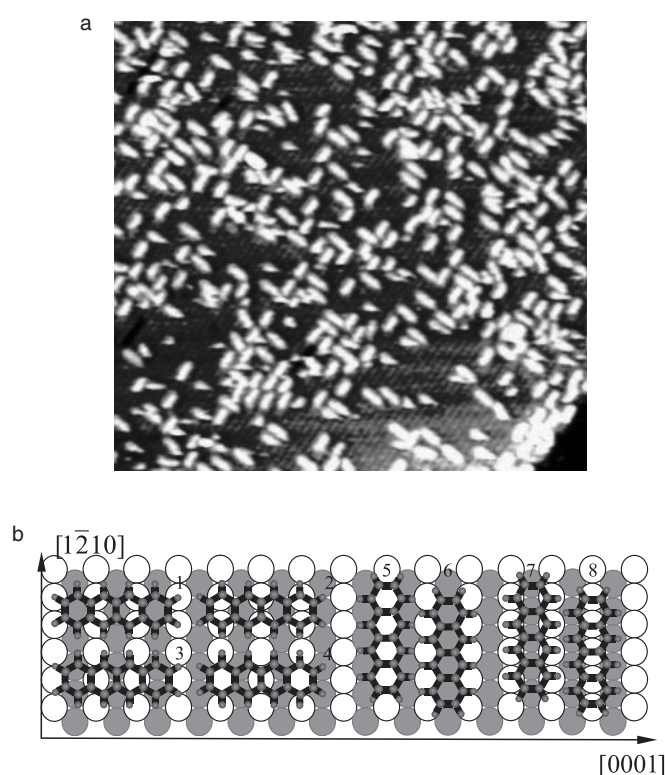
Figure 3. (a) STM image (35 nm ×35 nm) from a Ru(10$\bar{1}$0) substrate covered with sub-monolayer tetracene. The tip bias voltage is 0.358 V relative to the sample and the tunnel current is 0.535 nA. (b) Supposed adsorption configurations of a single tetracene molecule in the 'lying-flat' mode.

and the ruthenium atom in different positions. The energy on site 2 is 1.5–3.5 eV lower than that on sites 1, 3 and 4, and the energy on site 7 is 0.9–1.0 eV lower than that on sites 5, 6 and 8. The energy on sites 2 and 7 is the lowest compared with that on other sites, which suggests that sites 2 and 7 are favourable according to the first-principle calculation, and this agree well with the previous calculations [15]. The centre of the tetracene molecule is either on the short bridge site with the long molecular axis in the [0001] azimuth or on the hollow site with the long molecular axis in the [1$\bar{2}$10] azimuth. When tetracene is adsorbed on the ruthenium surface, the separation between the molecule and the substrate, i.e. the difference between the height of the tetracene molecular mass centre and that of the ruthenium atoms in the first layer, is from 2.2 to 3.0 Å for each site. The separations for sites 2 and 7 are 2.2 and 2.5 Å respectively, which is smaller than that for others. The smaller separation implies that stronger interaction occurs between the molecule and the substrate. The separation is also smaller than a typical value of 3.3 Å for a flat-lying aromatic molecule on silver [18], which implies that ruthenium is more active than silver. The stronger interaction between molecule and substrate suggests that more charge transfers from the substrate to the molecule. As mentioned above, the change in the work function at the initial adsorption state is attributed to the charge transfer.

With pre-optimized molecule–substrate separation, a potential energy surface (PES) as a function of the angle between the long axis of molecule and the azimuth was calculated. Figures 4(a) and (b) present the angle-dependence of the PES for the two kinds of favourable
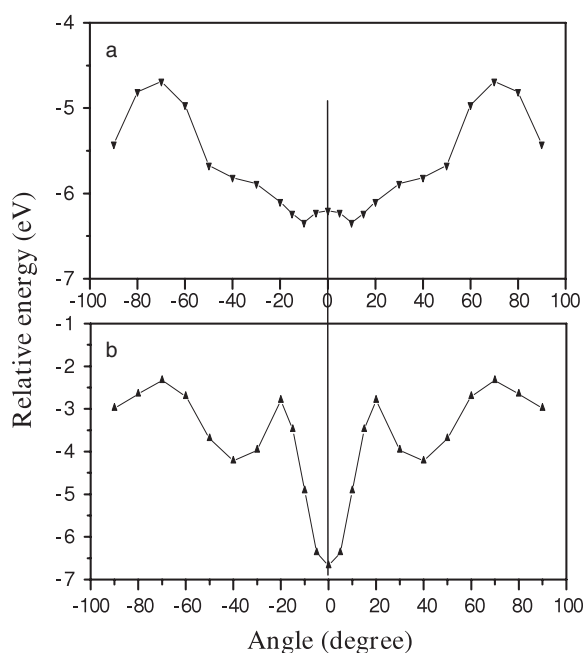
Figure 4. (a) Calculated PES as a function of the angle between the molecular long axis and the [1$\bar{2}$10] azimuth, when the tetracene is on the hollow site (site 7 in figure 3(b)). (b) Calculated PES as a function of the angle between the molecular long axis and the [0001] azimuth, when the tetracene is on the short-bridge site (site 2 in figure 3(b)).

site, site 7 and 2, respectively. The angle is zero when the long molecular axis is aligned along the [1$\bar{2}$10] or [0001] azimuth in figures 4(a) and (b). The curves show that the angular position for the minimum PES is close to 0°. The PES increases quickly when the molecule rotates away from the [0001] azimuth. The curve away from [1$\bar{2}$10] is rather broad and the true minimum PES is ±10° away from the [1$\bar{2}$10] azimuth. A possible reason could be that the supercell for calculation is not large enough. From the STM image only less than 1% of the molecules do not lie along either of these two directions.

For the clean Ru surface, the LEED shows sharp integral spots. With increasing coverage of the molecular film, the sharp diffraction spots fade. Up to a monolayer, no diffraction spots could be observed, which suggests that no long-range ordered structure is formed at the initial adsorption state of tetracene on the Ru surface. The interaction between the tetracene molecule and the ruthenium substrate is rather strong and it plays an important role in forming the adsorbed layer. In contrast to perylene on the Ru(0001) surface [14], no long-range ordered structure of tetracene on the Ru surface is formed, since tetracene molecules are adsorbed on the Ru surface in two orientations.

To understand the thermal behaviour of tetracene thin film on the Ru surface, normal emission UPS spectra have been recorded as a function of annealing temperature, as shown by the dashed line in the left-hand part of figure 1. Typical multilayer emissions were found at a surface temperature below 150 °C. From 25 to 125 °C, the UPS intensities are almost constant. However, when the temperature was more than 150 °C, a decrease in intensity of the features from tetracene was observed due to the desorption of the tetracene films. When the temperature was above 200 °C, all emissions from tetracene molecules disappeared completely and the valence band of the ruthenium substrate was somehow recovered. Some small signal

in the UPS could be related to residual hydrocarbon as a result of thermal decomposition of the adsorbed molecules.

4. Conclusions

In summary, the interaction between tetracene molecules and an active metal surface, e.g. the Ru(10$\bar{1}$0) surface, is rather strong. The molecule is adsorbed with the molecular plane parallel to the Ru(10$\bar{1}$0) surface with its long axis along either the [1$\bar{2}$10] or [0001] azimuth. The short-bridge site and the hollow site are two most favourable sites for tetracene on the Ru(10$\bar{1}$0) surface. The smaller separations between the molecules and the substrate on these sites in comparison with other sites suggest stronger interactions. Tetracene on the Ru(10$\bar{1}$0) surface is stable and no desorption of molecules takes place below 150 °C.

Acknowledgments

References

[1] Bartels L, Rao B V and Liu A 2004 *Chem. Phys. Lett.* **385** 36
[2] Florio G M *et al* 2005 *J. Phys. Chem.* B **109** 4520
[3] Schon J H, Kloc C and Batlogg B 2000 *Nature* **406** 702
[4] Schon J H and Kloc C 2001 *Appl. Phys. Lett.* **78** 3821
[5] Gundlach D J *et al* 2002 *Appl. Phys. Lett.* **80** 2925
[6] Barth J V, Costantini G and Kern K 2005 *Nature* **437** 671
[7] Stroscio J A and Celotta R J 2004 *Science* **306** 242
[8] Lu B *et al* 2005 *Appl. Surf. Sci.* **245** 208
[9] Langner A, Hauschild A, Fahrenholz S and Sokolowski M 2005 *Surf. Sci.* **574** 153
[10] Chen Q, McDowall A J and Richardson N V 2003 *Langmuir* **19** 10164
[11] Rada T, Chen Q and Richardson N V 2003 *J. Phys: Condens. Matter* **15** S2749
　　 Rada T, Chen Q and Richardson N V 2004 *Phys. Status Solidi* b **241** 2353
[12] Tersigni A, Shi J, Jiang D T and Qin X R 2006 *Phys. Rev.* B **74** 205326
[13] Choudhary D, Clancy P and Bowler D R 2005 *Surf. Sci.* **578** 20
[14] Lu B *et al* 2005 *Appl. Phys. Lett.* **86** 061915
[15] Lu Y H *et al* 2006 *Appl. Surf. Sci.* **253** 2025
[16] Mao H Y *et al* 2004 *J. Chem. Phys.* **121** 6972
[17] Huang H *et al* 2004 *Physica* B **352** 36
[18] Huang H *et al* 2006 *J. Chem. Phys.* **124** 054716
[19] Coropceanu V *et al* 2002 *Phys. Rev. Lett.* **89** 275503
[20] Frisch M J *et al* 2003 *Gaussian 03, Revision B.03* (Pittsburgh, PA: Gaussian, Inc.)
[21] Hehre W J, Stewart R F and Pople J A 1969 *J. Chem. Phys.* **51** 2657
[22] Collins J B, Binkley J S and Pople J A 1976 *J. Chem. Phys.* **64** 5142
[23] Becke A D 1993 *J. Chem. Phys.* **98** 5648