

Initial stage of fluorofullerene molecules adsorption on Si surface

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Spatially resolved images of an individual $C_{60}F_{18}$ fluorofullerene molecule on $Si(100) - 2 \times 1$ surface have been obtained using scanning tunneling microscopy (STM). STM results and *ab initio* calculations show that the fluorofullerene molecules interact with the $Si(100) - 2 \times 1$ surface with *F* atoms pointing down towards the surface. The adsorption energy of a $C_{60}F_{18}$ molecule on $Si(100) - 2 \times 1$ surface is ~ 12.1 eV, which is much higher than the adsorption energy of the same molecule on $Si(111) - 7 \times 7$ surface (6.65 eV). $C_{60}F_{18}$ molecules are located in the troughs in-between the dimer rows occupying the four-dimer site on $Si(100) - 2 \times 1$ surface.

The continuous shrinking size of Si based devices and associated physical limitations have led to great interest in molecular electronics which is being studied as a successor to conventional Si-based electronics technology. One of its perspectives is the fabrication of devices whose function is governed by single molecules so that an important step in single molecule technologies is the linking of individual molecules at specific locations on Si surfaces. Fullerenes are promising candidates for the fabrication of electro-active elements in nano-science applications and can be considered as their building blocks. Therefore, electronics based on individual molecules demands active control of the combined electronic properties of molecule and substrate [1]. An essential peculiarity of fullerenes and their derivatives used in molecular electronics is their ability to trap electrons and to keep holding them for a long time. Fullerenes can also serve as temporal electron acceptors effectively splitting excitons and generating charge carriers—free electrons and holes. Fluorinated fullerenes have been considered as attractive objects for novel material applications due to the possibility of the creation of new wide band gap semiconductors and dielectric materials [2]. In this work we present results of the scanning tunneling microscope (STM) imaging of individual $C_{60}F_{18}$ molecules deposited on $Si(100) - 2 \times 1$ surface. To prepare pure $C_{60}F_{18}$, a new method of fluorination

of C_{60} in solid-state reactions with transition metal fluorides (MnF_3 or K_2PtF_6) was employed [3, 4]. Fluorination was conducted under Knudsen cell conditions with mass spectrometric identification of gaseous products. As a rule, the mass spectrum contained two main peaks which were attributed to C_{60} and $C_{60}F_{18}$, and a few additional peaks which were attributed to the fragments of $C_{60}F_{18}$ molecules that arose from the loss of some fluorine atoms under electron ionization.

The deposition of $C_{60}F_{18}$ molecules has been performed from Knudsen cell on a $Si(100) - 2 \times 1$ surface kept at room temperature. The deposition rate was in the range of 0.05–0.1 ML/min. All experiments were carried out at room temperature using a home-built ultra high vacuum field ion-scanning tunneling microscope (base pressure $2 \cdot 10^{-11}$ Torr) equipped with standard surface preparation facilities [5]. Phosphorus doped $Si(100)$ wafers with resistivity of $8 \div 15 \Omega \cdot cm$ were cut into pieces of $20 \times 7 \times 0.5 mm^3$ and then ultrasonically washed in acetone and distilled water. Samples were mounted on a tantalum sample holder using “Ni-free” tools and the surface was cleaned by outgassing overnight at $650^\circ C$ and then flashing at $1250^\circ C$ for 20 s followed by slow cooling at rates of $< 2^\circ C/s$ from $950^\circ C$ to room temperature [6]. In situ STM measurements were carried out at room temperature by using commercial Pt–Ir tips. The tortoise-shaped polar $C_{60}F_{18}$ molecule is very asymmetrical [7] with all the eighteen fluorine atoms bound to only one hemisphere of C_{60}

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(see Fig.2). It results in to a large electric dipole moment (> 9 Debye). The carbon atoms interacting with F atoms have four nearest neighbors and the local bonding character changes from predominantly sp^2 in pure C_{60} to sp^3 type. The associated C–C bonds elongate in the range of 1.5–1.6 Å. There is a 6-membered ring of sp^2 bonded carbon atoms (alternate bond lengths 1.372 and 1.376 Å) which is isolated from the residual molecular system by a belt of sp^3 -hybridized C-atoms, each having an F atom. Thus the F atoms flatten C_{60} molecule and reduce its I_h symmetry to a 3-fold rotational symmetry (C_{3v}) in $C_{60}F_{18}$. The calculated C–C bondlengths in $C_{60}F_{18}$ lie in the range of 1.37 to 1.68 Å and agree well with the experimental values [7]. The shortest bonds correspond to sp^2 bonded carbon atoms while the longest bonds to C–C bonds in pentagons having F atoms. The binding energy of F atoms on C_{60} is calculated [8] to be 3.6 eV per F atom which is large and therefore the $C_{60}F_{18}$ molecule is very stable.

When $C_{60}F_{18}$ molecules are deposited on Si(111) – 7×7 surface, our STM data show that the initial deposition occurs on the unfaulted half, the faulted half, and the corner hole in the unit cell. We have studied in detail [8] adsorption on a corner hole of the surface unit cell because its symmetry allows us to analyze the interaction between $C_{60}F_{18}$ molecule and Si adatoms on the Si(111) – 7×7 surface. It was found that generally at room temperature the adsorbed fluorofullerene molecules did not react with Si(111) – 7×7 surface initially and there was no movement of $C_{60}F_{18}$ on the surface except for the occasional tendency to move from a corner hole to a faulted half position during the measurements. The optimized geometries showed that the orientation in which most of the F atoms directly interact with the surface, has the lowest energy. The adsorption energy of the molecule in the lowest energy configuration has been calculated to be 6.65 eV [8]. Fig.1 shows the initial stage of the adsorption of $C_{60}F_{18}$ molecules on a Si(100) – 2×1 surface. From STM data we conclude that the initial nucleation of deposited $C_{60}F_{18}$ molecules can occur on either sites (steps or terraces) of Si(100) – 2×1 surface. Moreover, two additional features are clearly distinguished from the STM images: (1) We observe a zigzag buckling of dimers which form $c(4 \times 2)$ reconstruction in the vicinity of the adsorbed $C_{60}F_{18}$ molecules. Similar pattern was observed [9] when the influence of defects on a clean Si surface was studied and also in the case [10] where the authors studied C_{60} adsorption on Si(100) – 2×1 surface. (2) We also noted that almost all $C_{60}F_{18}$ molecules deposited at room temperature are located in the troughs in-between the dimer rows and randomly distributed across the surface. For

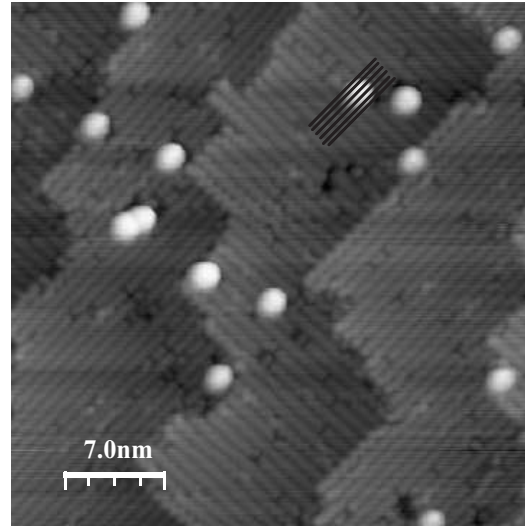


Fig.1. The initial stage of $C_{60}F_{18}$ molecules adsorption on the Si(100) – 2×1 surface. Filled states STM image. $U = -2.0$ V; $I = 20$ pA Several lines have been drawn along the (011) direction above the Si–Si dimers in the range of adsorbed individual $C_{60}F_{18}$ molecule to estimate the adsorption site

C_{60} adsorption on Si(100) – 2×1 surface this feature has been originally highlighted in [11] and confirmed in [10]. Four-dimer or two-dimer sites in the trough have been considered. To estimate which adsorption site is preferable in our case we used high resolution STM image, which shows clear dimer structures of Si(100) – 2×1 surface and adsorbed $C_{60}F_{18}$ molecules that appear as billiard-ball-like protrusions on the surface. We drew several lines along the (011) direction (parallel to the Si–Si dimer axis) in the range of adsorbed individual $C_{60}F_{18}$ molecule. From this scheme it is clearly seen that the center of molecule is located exactly in the trough between two dimer rows. The lateral size of the $C_{60}F_{18}$ molecules observed by STM is 20 Å. It is easy to calculate because the distance between the adjacent dimers in a row is well known to be 3.84 Å. The experimental value of the lateral size of the molecule is larger than the real one due to the fact that the STM image is convolution of the electronic density of states of the sample and the tip. The corresponding optimized atomic structure with buckled dimers is shown in Fig.2. In this case the Si(100) surface was modelled with a six layer slab with hydrogen on one side of the slab and computational details were adopted from our earlier works [8]. The bottom three layers were kept frozen and the upper layers were fully optimized using the projector augmented wave pseudopotential method as implemented in VASP code [12, 13] and generalized gradient approxi-

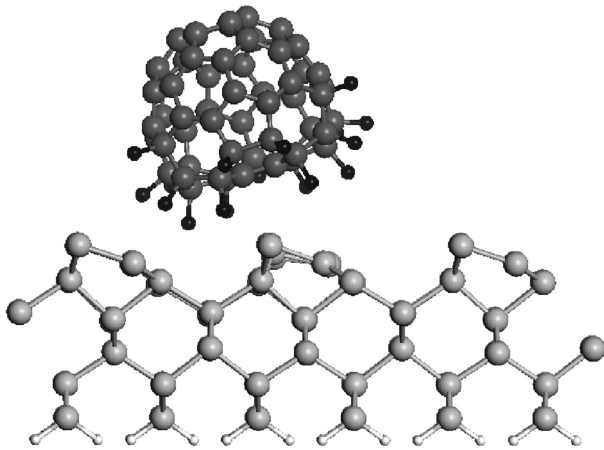


Fig.2. The ball and stick model of $C_{60}F_{18}$ molecule adsorbed on a $Si(100) - 2 \times 1$ surface. The surface is modelled by a slab of six layers with H terminating the dangling bonds on one side. Large dark, small dark, large light-grey, and small light-grey balls correspond to C, F, Si, and H atoms, respectively

mation for the exchange-correlation energy. The buckled dimers can be seen in Fig.2. The $C_{60}F_{18}$ molecule was placed on a dimer row to begin with and the optimized structure shows some tilting in the trough between the dimer rows. The molecule covers approximately the area of a 2×2 unit cell of dimers. The adsorption energy of $C_{60}F_{18}$ molecule has the maximum value of ~ 12.1 eV for the orientation with F atoms pointing towards the surface. The adsorption energy is higher than the value on $Si(111) - 7 \times 7$ surface (6.65 eV) due to the larger number of dangling bonds on $Si(100)$ surface. Therefore, as on $Si(111) - 7 \times 7$ surface, we would expect the $C_{60}F_{18}$ molecule to adsorb on $Si(100)$ surface with F atoms pointing towards the surface.

The spectrum of the normalized tunneling conductivity measured above the surface sites with monolayer coverage is presented in Fig.3. Six distinct peaks are clearly distinguished at bias range from -4.0 to $+4.0$ V. There are three maxima at negative sample voltage (-3.6 ; -1.6 ; -0.6 V) and three maxima at positive sample voltage (0.5 , 1.8 , 2.8 V). In order to understand this, we have shown in Fig.4a the calculated density of states (DOS) of $Si(100) - 2 \times 1$ surface as well as the spectrum of $C_{60}F_{18}$ while in Fig.4b, the total and partial DOS of $C_{60}F_{18}$ adsorbed on $Si(100) - 2 \times 1$ surface are shown. From the results of DOS in Fig.4b, the maximum at -0.6 V in the tunneling conductivity is responsible for the π -bonded state of (2×1) - $Si(100)$ electronic structure [14] (see a peak below the E_F). The presence of π^* -antibonding state (see a peak above the E_F) is masked by the LUMO

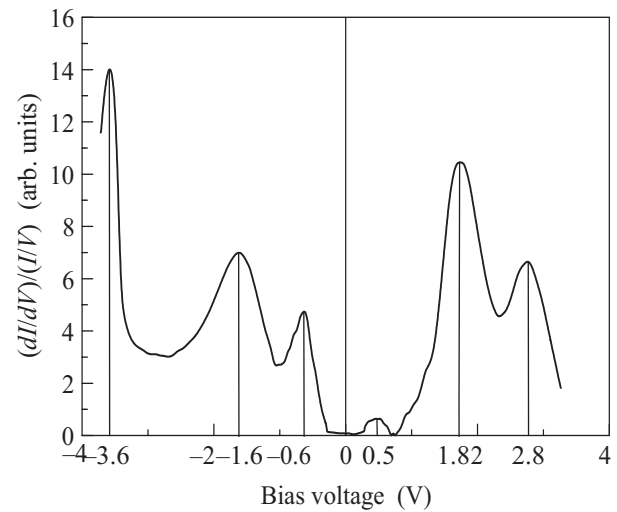


Fig.3. Normalized tunneling conductivity measured above 1 ML of $C_{60}F_{18}$ on $(2 \times 1) - Si(100)$ surface

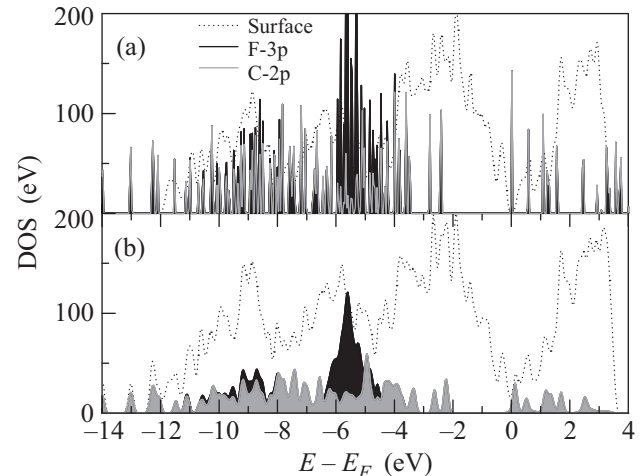


Fig.4. The calculated density of states for (a) a clean $Si(100) - 2 \times 1$ surface (dotted line) and the spectrum of isolated $C_{60}F_{18}$ molecule, and (b) total DOS of adsorbed $C_{60}F_{18}$ molecule on $Si(100) - 2 \times 1$ surface and the partial DOS of adsorbed $C_{60}F_{18}$ molecule. Light grey and dark grey shaded states depict to C-2p and F-3p states, respectively. C-2p and F-3p states are multiplied by factor of 3

state of adsorbed $C_{60}F_{18}$ molecule (see a peak around the same energy for the adsorbed $C_{60}F_{18}$ molecule). In this case the surface state band gap for (2×1) - $Si(100)$ is nearly 1 eV in accordance to [15]. The relative intensity of these peaks is generally consistent between measurements and always has a smaller value than the intensity of other observed maxima. Two other peaks at negative sample bias at -1.6 and at -3.6 V we ascribe to the $C_{60}F_{18}$ states (see peaks at around -2.1 and -3.7 eV in the partial DOS of $C_{60}F_{18}$ in Fig.4b). The small dif-

ferences are likely to be due to the approximation of exchange-correlation functional. Our values of peak positions agree with the experimental data of [16], where the values of 1.8 eV and 3.2 eV for HOMO and HOMO-1 levels respectively have been obtained by means of photoelectron spectroscopy. The small differences in the observed values are due to the substrate influence. The authors in [16] used thin SiO₂ interlayer to prevent both chemical interaction of fullerenes with Si substrate and the contribution of substrate signal into the top of valence band spectra. The peaks at 1.8 eV and at 2.8 eV are apparently responsible for the unoccupied levels of C₆₀F₁₈, as one can see states around these energies in the partial DOS of C₆₀F₁₈ in Fig.4b. From these results we can also conclude that the HOMO-LUMO gap of the adsorbed molecule is reduced as compared to the value for an isolated molecule (compare Fig.4a and b). From the observed STS spectra and the calculated results we can say that the electronic structure of the fluorofullerenes is sensitive to substrate influence.

In conclusion we have performed STM measurements and *ab initio* calculations of individual polar C₆₀F₁₈ molecules adsorbed on (2 × 1) – Si(100) surface. It has been shown that C₆₀F₁₈ molecules are located in the troughs in-between dimer rows. The calculations of the adsorption energy show that the orientation of C₆₀F₁₈ molecule with F atoms pointing towards the surface is preferable for the case of adsorption on (2 × 1) – Si(100) surface. The calculated adsorption energy is ~ 12.1 eV. From the observed STS spectra and calculated DOS results we can conclude that HOMO-LUMO gap of adsorbed molecule is reduced as compared to the isolated molecule. This work was partially supported by RFBR

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1. C. Schull, N. Neel, M. Becker et al., *New Journal of Physics* **10**, 065012 (2008).
2. N. Liu, H. Touhara, F. Okino et al., *J. Electrochem. Soc.* **143**, 2265 (1996).
3. O. V. Boltalina, V. Yu. Markov, R. Taylor, and M. P. Waugh, *Chem. Commun.* **22**, 2549 (1996).
4. O. V. Boltalina, *J. Fluorine Chem.* **101**, 273 (2000).
5. T. Sakurai, T. Hashizume, I. Kamia et al., *Prog. Surf. Sci.* **33**, 3 (1990).
6. B. S. Swartzentruber, Y.-W. Mo, M. B Webb, and M. G. Lagally, *J. Vac. Sci. Technol. A* **7**, 2901 (1989).
7. I. S. Neretin, K. A. Lyssenko, M. Y. Antipin et al., *Angew. Chem. Int. Ed.* **39**, 3273 (2000).
8. R. Z. Bakhtizin, A. I. Oreshkin, P. Murugan et al., *Chemical Physics Letters* **482**, 307 (2009).
9. R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
10. D. Chen and D. Sarid, *Surf. Sci.* **329**, 206 (1995).
11. X.-D. Wang, T. Hashizume, H. Shinohara et al., *Jpn. J. Appl. Phys.* **31**, L983 (1992).
12. P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
13. G. Kresse and J. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
14. R. J. Hamers, Ph. Avouris, and F. Bozso, *Phys. Rev. Lett.* **59**, 18, 2071 (1987).
15. R. Wiesendanger, *Scanning probe microscopy and spectroscopy*, Cambridge University Press, 1994.
16. V. M. Mikoushkin et al., *J. Electron Spectroscopy and Related Phenomena* **168**, 25 (2008).