Pis'ma v ZhETF, vol. 95, iss. 12, pp. 748 – 750

STM/STS study of $C_{60}F_{36}$ molecules adsorption on 7×7–Si(111) surface

A. I. Oreshkin[+1)], *R. Z. Bakhtizin*[*], *V. N. Mantsevich*[+], *S. I. Oreshkin*[+×], *S. V. Savinov*[+], *V. I. Panov*[+]

[+]*Department of Physics, Lomonosov Moscow State University, 119991 Moscow, Russia*

[*]*Department of Physical Electronics, Bashkir State University, 450074 Ufa, Russia*

[×]*Sternberg Astronomical Institute, Lomonosov Moscow State University, 119991 Moscow, Russia*

Submitted 12 April 2012
Resubmitted 5 May 2012

Spatially resolved images of an individual $C_{60}F_{36}$ fluorofullerene molecules on Si(111)–7×7 surface have been obtained by means of scanning tunneling microscopy/spectroscopy (STM/STS). The presence of isomers with different symmetry (T, C_3, C_1) has been revealed in STM investigation of initial adsorption stage of $C_{60}F_{36}$ on silicon surface Si(111)–(7×7). The adsorbed fluorofullerene molecule can occupy any adsorption site of silicon surface (corner site, faulted half, unfaulted half) that indicates for strong molecule-substrate interaction. The HOMO–LUMO gap of the adsorbed $C_{60}F_{36}$ molecules have been estimated from current image tunneling spectroscopy (CITS) and $z(V)$ with engaged feedback measurements. The value of HOMO–LUMO gap observed experimentally was 3 eV. The $C_{60}F_{36}$ molecules adsorption on Si(111)–(7×7) surface was stable and kept equilibrium configuration during several hours.

Fluorinated fullerenes are promising for the fabrication of electro-active elements in photo-voltaic solar cells and other applications in organic electronics because of their ability to trap and keep hold electrons for a long time [1]. Another property of interest to fluorofullerenes is their high oxidative capacity, which makes them promising for use as electrode materials in lithium batteries. The presence of fluorine atoms attached directly to the fullerene cage, gives the fluorofullerene molecules pronounced electron-acceptor properties, so that they can be used in devices for energy conversion [2]. Besides, the high electron affinity allows fluorofullerenes to act also as p-dopants in the manufacture of light-emitting diodes based on organic semiconductors. However, real application of such devices is still quite far from realization because of many difficulties such as the interaction between the fluorofullerene molecules and silicon-based substrates including the basic principles involved in the growth and crystallization of such thin films. The latter is important for creation of controllable single molecules technologies. Recently the most stable exohedral fullerene fluorides $C_{60}F_{48}$, $C_{60}F_{36}$, $C_{60}F_{18}$ with magic numbers of fluorine atoms have been obtained in high abundance using solid state reactions with transition metal fluorides [3] while the structures of these molecules were reliably established [4]. So far some attempts have been made to study adsorption of fluorofullerene molecules on Si(111)–7×7 surface by means of scanning tunneling microscope (STM). It was shown that adsorbed round-shape symmetrical $C_{60}F_{48}$ molecules can release fluorine atoms either by the rolling movement across the surface or by the oscillatory motion [5] whereas the tortoise-shaped polar $C_{60}F_{18}$ molecules induce strong polarization on the surface [6]. In this paper we present the results of STM measurements of thermodynamically stable fluorofullerene molecules $C_{60}F_{36}$ on clean Si(111) surface. In our study, scanning tunneling spectra (STS) were collected at individual adsorption sites to examine the electronic states as a function of energy and position across the surface. All experiments were carried out in an ultra-high vacuum system with a base pressure $4 \cdot 10^{-11}$ Torr. The samples were n-type Si wafers (P-doped, 1.6 $\Omega \cdot$ cm) that were oriented within 0.5° of (111). Clean Si(111) surfaces were prepared by flashing at 1250 °C during 5 s followed by slow cooling. Such procedure was repeated several times to get the concentration of the initial defects less than 0.2% missing adatoms. These defects consist almost completely of isolated single vacancies. The exper-

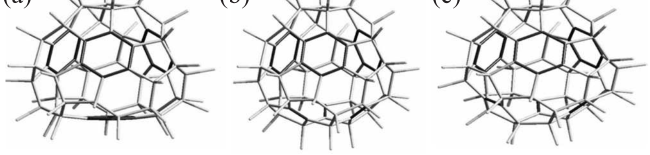

Fig. 1. The structure of $C_{60}F_{36}$ isomers with T (a), C_3 (b), and C_1 (c) symmetry; the benzenoid rings and double bonds are highlighted

[1)]e-mail: oreshkin@spmlab.phys.msu.su

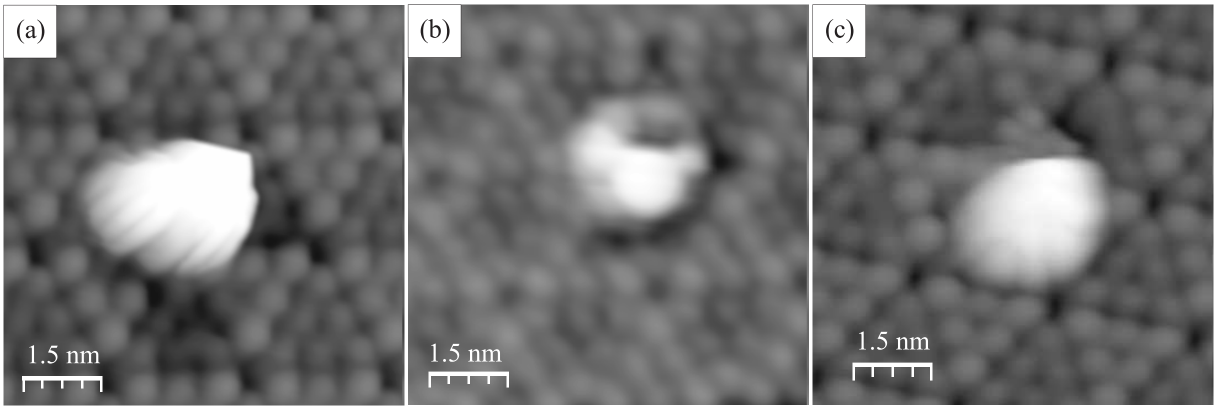

Fig. 2. Three different high resolution STM images of $C_{60}F_{36}$ molecule adsorbed on a Si(111)–7×7 surface; $U_t = -2.0$ V; $I_t = 40$ pA

iments were carried out for several times with different tips. The STM tips were produced from tungsten wires (0.25 mm diameter) that were electrochemically etched in 10% KOH and cleaned by electron bombardment in ultrahigh vacuum. Reproducible scanning of the same area with electrons tunneling from tip to sample verified that there were no structural changes in the surface involving adatom desorption stimulated by tunneling electron irradiation or movement of adsorbates. We used a reaction with MnF_3 under Knudsen cell conditions at 625 K to prepare pure $C_{60}F_{36}$ [3]. This high temperature fluorination of C_{60} yielded three main isomers of $C_{60}F_{36}$: C_3 and C_1 isomers in 2:1 ratio and 2% of T-symmetric structures (Fig. 1) [7, 8]. Due to their thermal stability, fluorofullerenes $C_{60}F_{36}$ can be transferred into the gas phase without decomposition so the deposition of these molecules was performed from Knudsen cell on a clean Si(111)–7×7 surface kept at room temperature. The deposition rate was 0.05–0.1 ML/min. We used Omicron Nanotechnology STM operating at 300 K for topographic imaging and tunneling spectroscopy. We used $z(V)$ spectroscopy and current imaging tunneling spectroscopy (CITS) technique [9, 10] whereby the tunneling current–voltage $(I-V)$ curves were recorded at each pixel of a scanned area while the tunneling gap was fixed by momentarily turning off the feedback loop. To map the surface local density of states (LDOS), we numerically calculated the normalized tunneling conductance, $(dI/dV)/(I/V)$, which is independent from the transmission factor [11]. The basic principle of $z(V)$ spectroscopy is similar to CITS mode. But in this regime the dependence of tunneling gap from bias voltage is fixed with engaged feedback at each pixel of a scanned area. Unlike conventional $I(V)$ spectroscopy, where the strong increase of tunneling current I with bias voltage V exists at higher voltages, $z(V)$ spectroscopy allows to hold the tunneling current fixed at any value by the feedback loop. Figure 2 shows the initial stage of $C_{60}F_{36}$ molecules adsorption on a Si(111)–7×7 surface. We concluded from STM data that the initial nucleation of $C_{60}F_{36}$ molecules can occur on either sites (steps or terraces) of Si(111)–7×7 surface. Moreover, high resolution STM images of $C_{60}F_{36}$ molecules adsorbed on Si(111)–7×7 surface revealed the presence of molecules with different symmetry (Fig. 2). Measurements were performed in constant current mode. Bias voltage and tunneling current were kept constant during measurements. The possibility to obtain STM image presented in Fig. 2c was higher than the possibility to reveal two others. Our previous analysis of low symmetry fullerenes adsorption processes on Si(111)–7×7 surface [6] proved that such molecules interact with substrate being oriented relative to surface in the exatly same manners independently of adsorption site due to strong surface polarization. This statement allowed us to eliminate the explanation that three different STM images observed in our experiments represent only one low symmetry $C_1-C_{60}F_{36}$ fullerene in different projections. Therefore one can conjecture that according to [7] the STM image in Fig.2c demonstrates $C_3-C_{60}F_{36}$ fluorofullerene. The probability to find STM image depicted in Fig. 2a was the least. This fact allows us to conclude that indeed three different types of symmetry for $C_{60}F_{36}$ molecule exist and can be found in STM experiments. The observed symmetry of molecule can be explained by the presence of $C_{60}F_{36}$ isomers of different symmetry (T, C_3, C_1) [7], formed on Si(111)–7×7 surface during deposition. All tunneling spectra obtained in our experiments were measured above the most often observed on Si(111)–7×7 surface $C_3-C_{60}F_{36}$ fluorofullerene molecules. The normalized tunneling conductivity spectrum measured above the surface site containing individual

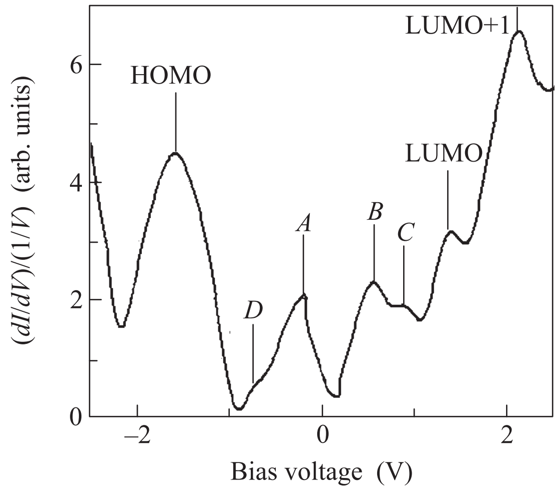

Fig. 3. The normalized tunneling conductivity spectrum measured above $C_{60}F_{36}$ molecule

molecule of $C_{60}F_{36}$ is presented in Fig. 3. Seven distinct peaks are clearly resolved at the wole bias range from -2.5 to $+2.5$ V. There are three maxima at negative sample voltage (-1.6; -0.8; -0.2 V) and four maxima at positive sample voltage (0.55; 0.9; 1.4; 2.1 V). The maxima in $(dI/dV)/(I/V)$ spectrum denoted as A, B, C, D are typical for Si(111)–(7×7) structure and are responsible for adatoms and rest atoms [12]. The remaining three peaks are responsible for HOMO and LUMO orbitals of adsorbed $C_{60}F_{36}$ molecule. It is possible to conclude from our measurements that the HOMO–LUMO gap of adsorbed $C_{60}F_{36}$ molecule is about 3 eV. Obtained data correspond well with measurements obtained with employment of $z(V)$ mode with engaged feedback measurements (Fig. 4) The application of $z(V)$

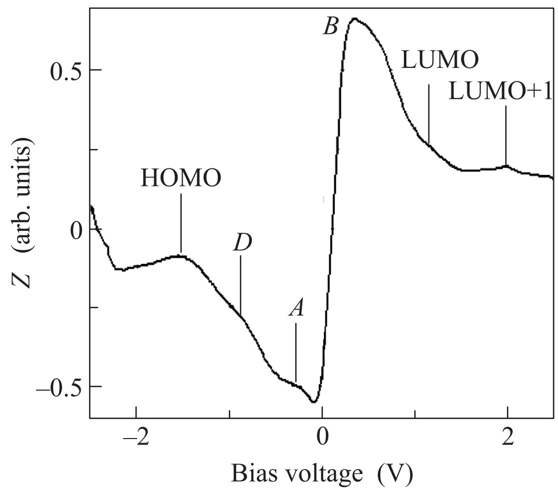

Fig. 4. The spectrum of $z(V)$ measured above $C_{60}F_{36}$ molecule

mode slightly restricts the measurements accuracy but in our case it's employment is reasonable due to negligeable influence for $C_{60}F_{36}$ molecule. The configuration of $C_{60}F_{36}$ molecule remains unchanged. Three central peaks (-0.85; -0.23; 0.4 V) (Fig. 4) are responsible for features of Si(111)–7×7 substrate while three remaining maxima correspond to HOMO, LUMO, LUMO+1 orbitals of adsorbed $C_{60}F_{36}$ molecule on Si(111)–(7×7) surface. The maximum denoted as C in Fig. 3 is not resolved in $z(V)$ mode. Both spectroscopic methods reveal correct energy peaks positions and consequently allow to estimate the HOMO–LUMO orbitals of adsorbed molecule. The comparative peaks' amplitudes differ for both methods due to methodology of measurements described above and don't include an important information.

In conclusion we have performed STM/STS measurements of individual $C_{60}F_{36}$ molecules adsorbed on (7×7)–Si(111) surface. It was shown that $C_{60}F_{36}$ adsorbed molecules can be found as isomers with three types of symmetry (T, C_3, C_1). From the spectroscopic measurement $z(V)$, $(dI/dV)/(I/V)$ we can conclude that HOMO–LUMO gap of adsorbed molecule is approximately 3 eV. The adsorbed fluorofullerene molecule can occupy any adsorption site of silicon surface (corner site, faulted half, unfaulted half). This fact indicates strong molecule-substrate interaction. The adsorbed $C_{60}F_{36}$ molecule on Si(111)–(7×7) surface was stable and kept equilibrium configuration during several hours.

This work was partially supported by RFBR grants # 10-02-00245-a, 12-02-00206a, 10-02-92655-IND-a and the Department of Science and Technology, New Delhi under the Indian-Russian collaboration.

---

1. R. Taylor, J. Fluorine Chem. **125**, 359 (2004).
2. A. A. Gakh and A. A. Tuiman, Tetrahedron Letters **42**, 7133 (2001).
3. O. V. Boltalina, A. Y. Borschevskii, L. N. Sidorov et a., Chem. Commun. **22**, 529 (1996).
4. L. N. Sidorov, Phys. of the Solid State **44**, 413 (2002).
5. J. T. Sadowski, Y. Fujikawa, K. F. Kelly et al., J. Cryst. Growth **229**, 580 (2001).
6. R. Z. Bakhtizin, A. I. Oreshkin, P. Murugan et al., Chem. Phys. Lett. **482**, 307 (2009).
7. A. Popov, V. Senyavin, O. V. Boltalina et al., J. Phys. Chem. A **110**, 8645 (2006).
8. L. G. Bulusheva, A. V. Okotrub, V. V. Shnitov et al., The Journ. Chem. Phys. **130**, 014704 (2009).
9. R. M. Tromp, R. J. Hamers, and J. E. Demuth, Science **234**, 304 (1986).
10. R. M. Tromp, J. Phys.: Condens. Matter **1**, 10211 (1989).
11. R. M. Feenstra, J. Vac. Sci. Technol. B **21**, 2080 (2003).
12. R. M. Feenstra, Surface Science **299/300**, 965 (1994).